# Diffusion Monte Carlo simulations of crystalline FeO under pressure

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Why?

## FeO

- magnesiowüstite, $Mg_xFe_{1-x}O$, is (believed to be?) one of the most abundant minerals in the lower Earth mantle
- FeO is a subset of $Mg_xFe_{1-x}O$

## quantum Monte Carlo

- conventional band-structure methods unreliable for materials with $3d$ electrons

# The method

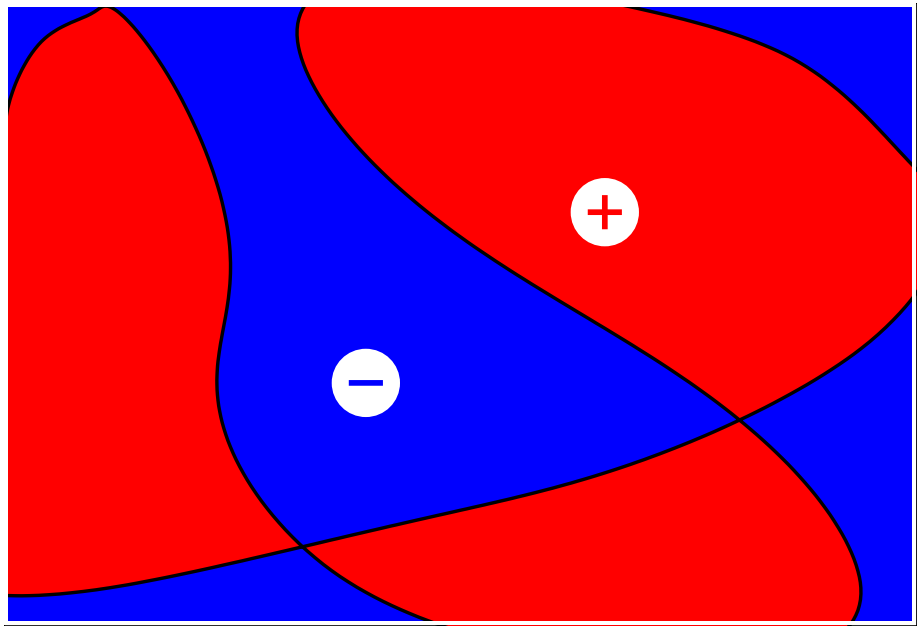
# Diffusion quantum Monte Carlo (DMC)

- stochastic implementation of **projector on the ground state**

$$e^{-\hat{H}\tau}|\Psi_T\rangle \xrightarrow{\tau\to\infty} e^{-E_0\tau}|\Psi_0\rangle\,,$$

  modified diffusion in $3N$-dim space, $\Psi(1,\ldots,N)$ acts as a probability distribution

- fermionic $\Psi$ changes sign (antisymmetry w.r.t. particle exchanges) $\longrightarrow$ **fixed-node approximation**




$$\operatorname{sign}\Psi(1,\ldots,N) = \operatorname{sign}\Psi_T(1,\ldots,N)$$

# DMC and DFT

diffusive projection

$$e^{-\hat{H}\tau}|\Psi_T\rangle \xrightarrow{\tau\to\infty} e^{-E_0\tau}|\Psi_0\rangle$$

Hohenberg-Kohn theorem
&
Kohn-Sham equations

give exact answers if we know

nodes of the wave function

the exchange-correlation functional

**nodal quality for solids:** even the simplest ansatz for nodes is seen to provide considerably better results than DFT based methods

# Trial wave function

- "trial" wave function
  - sampling efficiency
  - nodal structure
  - initial guess

$$\Psi_T(1,\ldots,N) = \underbrace{\det\left[\psi_i(j)\right]}_{\text{Slater determinant of 1-body orbitals}} \times \underbrace{\exp\left[J(1,\ldots,N)\right]}_{\text{Jastrow many-body correlation factor}}$$

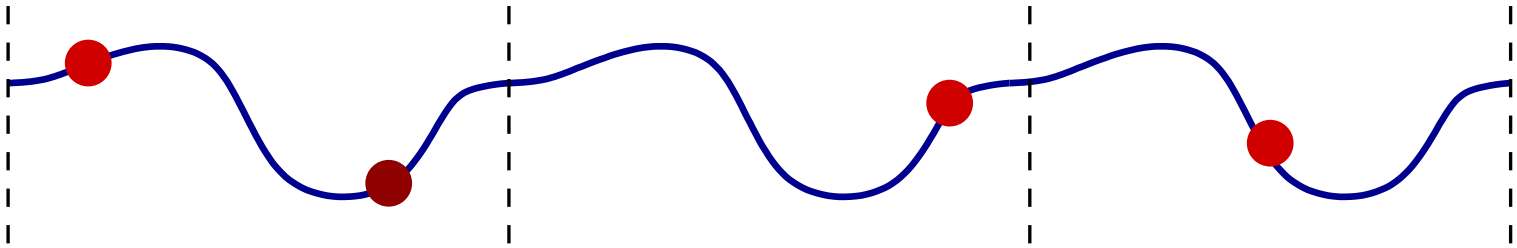
- 1-body orbitals = variational "parameters"
  - Hartree-Fock approximation
  - PBE0$_x$ — PBE-GGA mixed with $x$ % of exact exchange

- Jastrow factor

$$J(1,\ldots,N) = \sum_{ij} f_{ee}(\mathbf{r}_i - \mathbf{r}_j) + \sum_{i,\alpha} f_{eI}(\mathbf{r}_i - \mathbf{R}_\alpha)$$

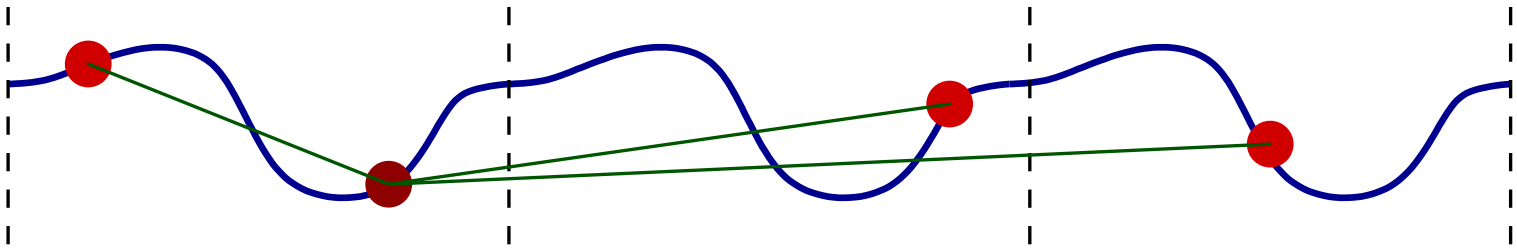
# Reduction to the primitive cell?

## non-interacting particles in a periodic potential



$$E[\text{config}_1] = E[\text{config}_2]$$

## interacting particles in a periodic potential



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No 1-electron Bloch theorem $\longrightarrow$ **large simulation cell** needed

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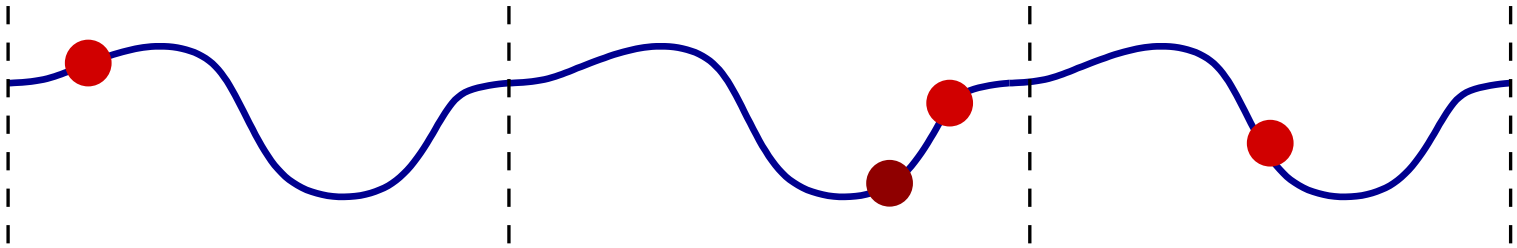

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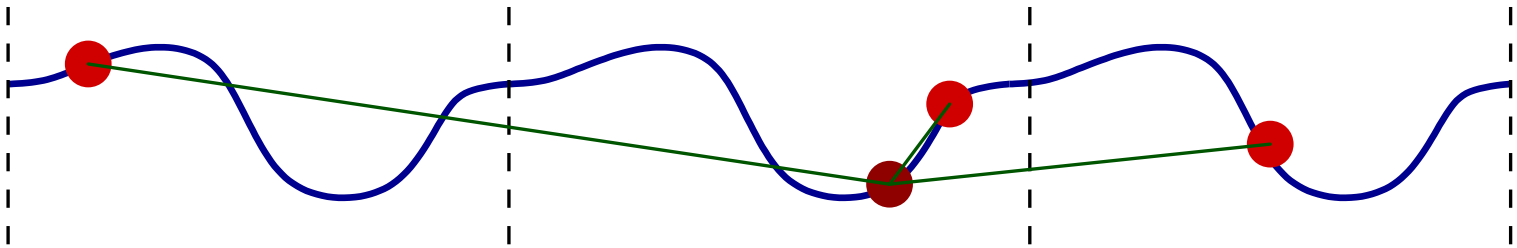

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# Periodic Coulomb interaction

Periodically repeated supercell ($\mathbf{k} = 0 \ldots$ homogeneous background)

$$v_{ee}(\mathbf{r}) = \sum_{\mathbf{R}_S} \frac{1}{|\mathbf{r} - \mathbf{R}_S|} \simeq \frac{4\pi}{\Omega} \sum_{\mathbf{k}\neq 0} \frac{1}{k^2} e^{i\mathbf{k}\cdot\mathbf{r}}$$

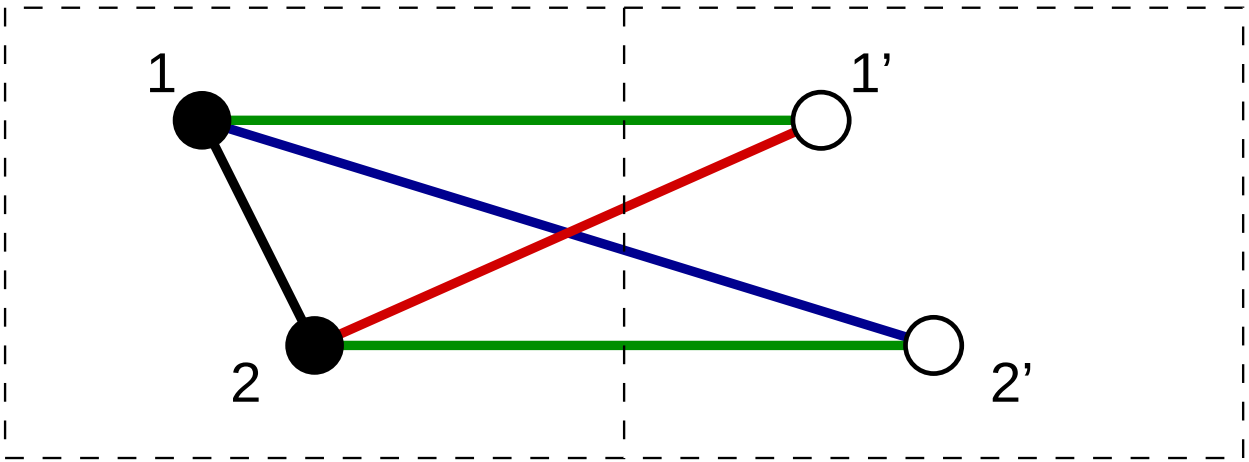
Both sums converge slowly $\longrightarrow$ **cure:** combine them into one

$$\sum_{\mathbf{k}\neq 0} \frac{1}{k^2} e^{i\mathbf{k}\cdot\mathbf{r}} = \sum_{\mathbf{k}\neq 0} \frac{1}{k^2} e^{-k^2/(4\alpha^2)} e^{i\mathbf{k}\cdot\mathbf{r}} - \lim_{\mathbf{k}\to 0} \frac{1}{k^2} \left(1 - e^{-k^2/(4\alpha^2)}\right) + \sum_{\mathbf{k}} \frac{1}{k^2} \left(1 - e^{-k^2/(4\alpha^2)}\right) e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$= \sum_{\mathbf{k}\neq 0} \frac{1}{k^2} e^{-k^2/(4\alpha^2)} e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{4\alpha^2} + \frac{\Omega}{4\pi} \sum_{\mathbf{R}_S} \frac{1}{|\mathbf{r} - \mathbf{R}_S|} \operatorname{erfc}(\alpha|\mathbf{r} - \mathbf{R}_S|)$$

# Total interaction energy (Ewald)

Total $e$–$e$ interaction energy per simulation cell.




$$V_{ee} = \frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}} + \frac{1}{2}\sum_{i}\left[v_{ee}(\mathbf{r}_{ii}) - \frac{1}{r_{ii}}\right] + \frac{1}{2}\sum_{i<j}\left[v_{ee}(\mathbf{r}_{ij}) - \frac{1}{r_{ij}}\right] + \frac{1}{2}\sum_{j<i}\left[v_{ee}(\mathbf{r}_{ij}) - \frac{1}{r_{ij}}\right]$$

# Total interaction energy (Ewald), cont.

The same formula once more in B&W.

$$V_{ee} = \underbrace{\frac{1}{2}\sum_{i\neq j} v_{ee}(\mathbf{r}_{ij})}_{\substack{\text{interaction of } i \text{ with } j \\ \text{and with images of } j}} + \underbrace{\frac{1}{2}\sum_{i} \lim_{\mathbf{r}_{ii}\to 0}\left[v_{ee}(\mathbf{r}_{ii}) - \frac{1}{r_{ii}}\right]}_{\substack{\text{interaction of } i \text{ with} \\ \text{its periodic images}}}$$

$$= \frac{1}{2}\sum_{i\neq j}\sum_{\mathbf{R}_S} \frac{1}{|\mathbf{r}_{ij} - \mathbf{R}_S|}\,\mathrm{erfc}(\alpha|\mathbf{r}_{ij} - \mathbf{R}_S|)$$
$$+ \frac{2\pi}{\Omega}\sum_{\mathbf{k}\neq 0}\frac{1}{k^2}\,e^{-k^2/(4\alpha^2)}\sum_{i\neq j} e^{i\mathbf{k}\cdot\mathbf{r}_{ij}}$$
$$- \frac{1}{2}N^2\frac{\pi}{\Omega\alpha^2} - N\frac{\alpha}{\sqrt{\pi}} + \frac{1}{2}N\sum_{\mathbf{R}_S\neq 0}\frac{1}{|\mathbf{R}_S|}\,\mathrm{erfc}(\alpha|\mathbf{R}_S|)$$

# FeO, part I

# Cohesive energy

$$E_{coh} = E_{atom}[\mathrm{TM}] + E_{atom}[\mathrm{O}] - \frac{1}{\mathcal{N}_{\mathrm{TMO}}} E_{supercell}[\mathrm{TMO}]$$

## Simulation parameters

- simulation cell size: 8 FeO (176 electrons)
- further corrections towards infinite system (will discuss later)
- Ne-core pseudopotentials for Fe and Mn, He-core for O (Dirac-Fock, Troullier-Martins)

$\det[\psi_i^{HF}(j)]$

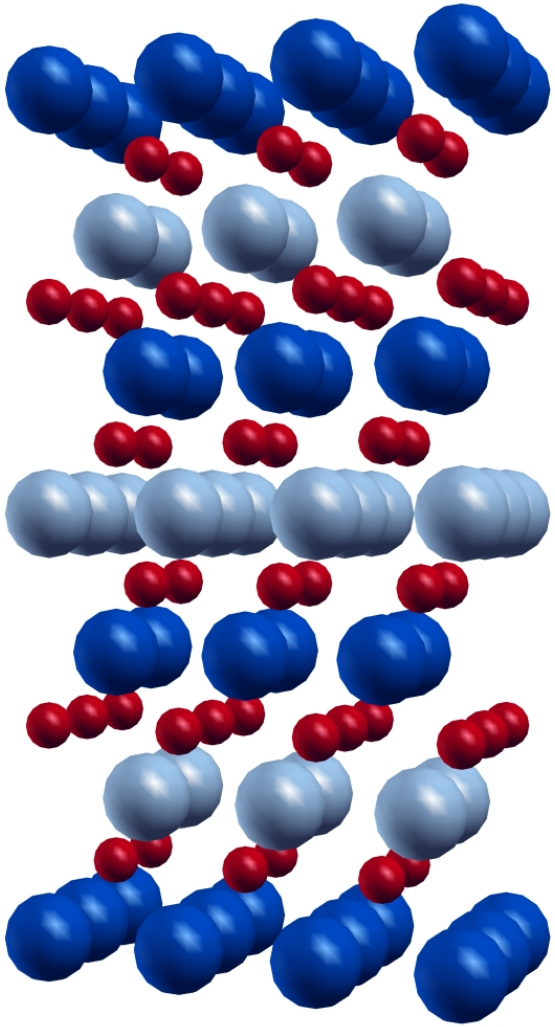
$\det[\psi_i^{PBE0_{20}}(j)]$

| | LDA | HF | B3LYP | DMC[HF] | DMC[PBE0$_{20}$] | exp. |
|---|---|---|---|---|---|---|
| FeO | 11.68 | 5.69 | 7.95 | 9.23(6) | **9.47(4)** | **9.7** |
| MnO | 10.57 | 5.44 | 7.71 | | **9.26(4)** | **9.5** |

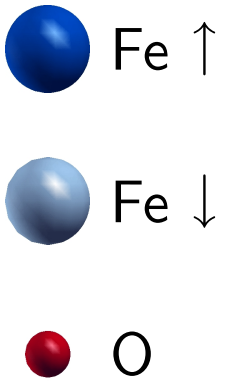
* all calculations at experimental lattice constant

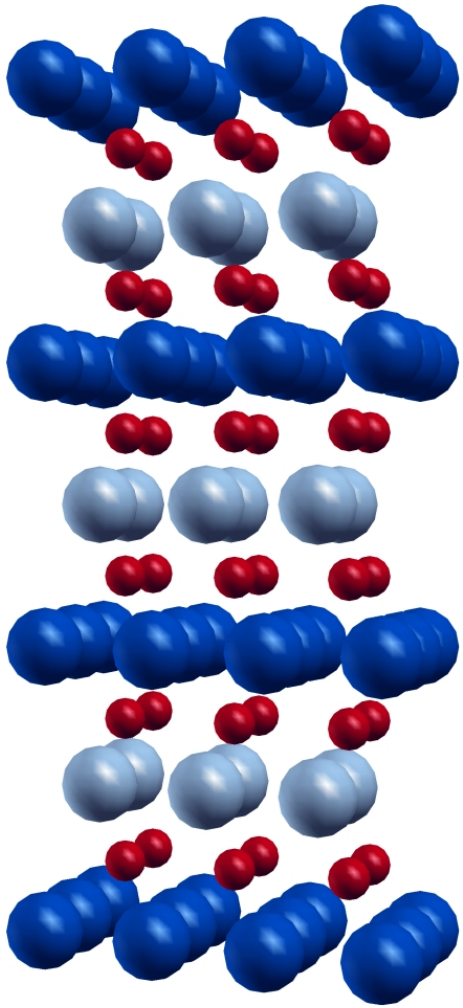
| | | |
|---|---|---|
| FeO total energy (hartree) | −139.6105(8) | **−139.6210(5)** |

# Competing crystal structures in FeO



B1 (NaCl) AFM-II

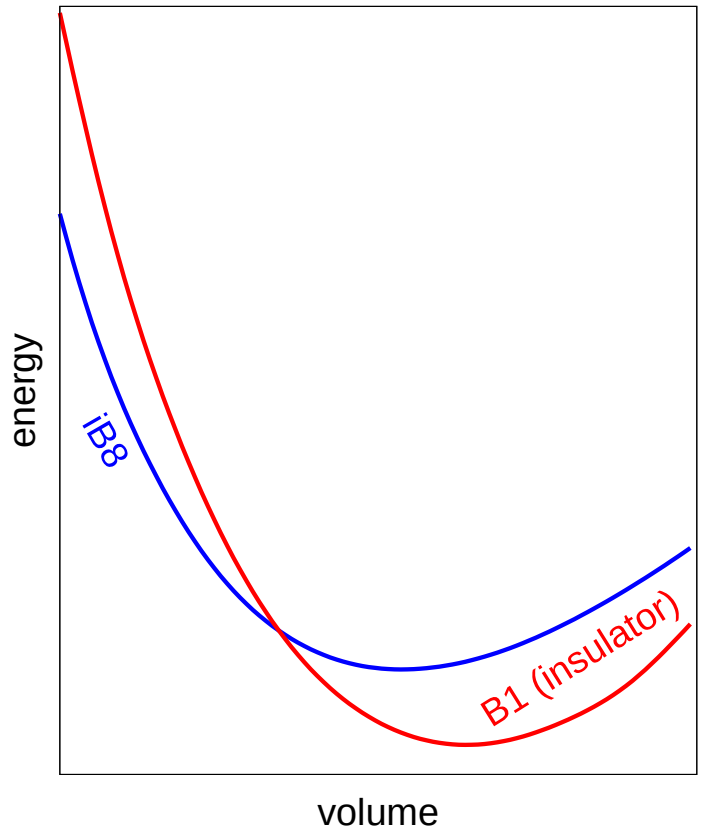


iB8 (NiAs) AFM

# Equation of state: Experimental estimates

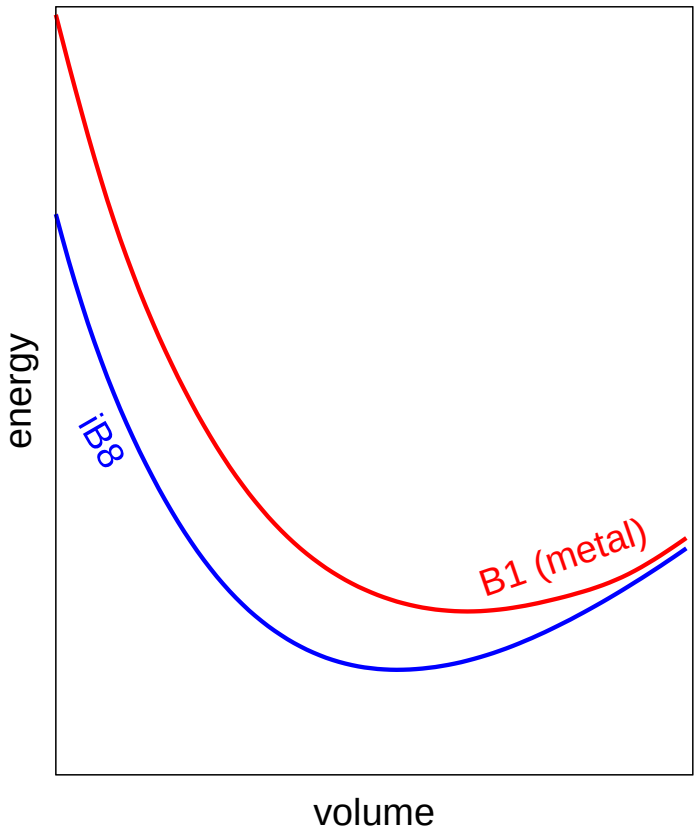
Experiments are not particularly conclusive so far.




- **shock-wave compression**
  - **$P_c \sim 70$ GPa**
    *[Jeanloz&Ahrens (1980)]*
- **static compression**
  - **900 K: $P_c \sim 74$ GPa**
  - **600 K: $P_c \sim 90$ GPa**
    *[Fei&Mao (1994)]*
  - **300 K: $P_c > 220$ GPa**

  ? large barrier & slow kinetic ?
  *[Yagi,Suzuki,&Akimoto (1985)]*
  *[Mao,Shu,Fei,Hu&Hemley (1996)]*

# Equation of state: Failure of LDA/GGA




- **iB8 stable at all pressures**

  *[Mazin,Fei,Downs&Cohen (1998)]*

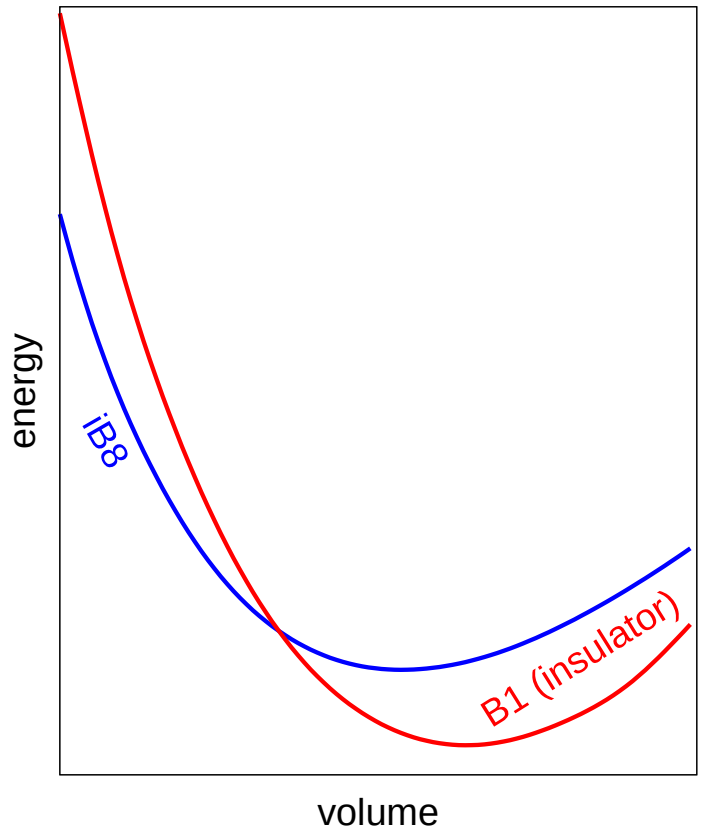
  *[Fang,Terakura,Sawada,Miyazaki &Solovyev (1998)]*

- **B1 has no gap (metal)**

# Equation of state: "Correlated" band theories

Inclusion of **Coulomb U stabilizes B1 phase**.

*[Fang, Terakura, Sawada, Miyazaki&Solovyev (1998)]*



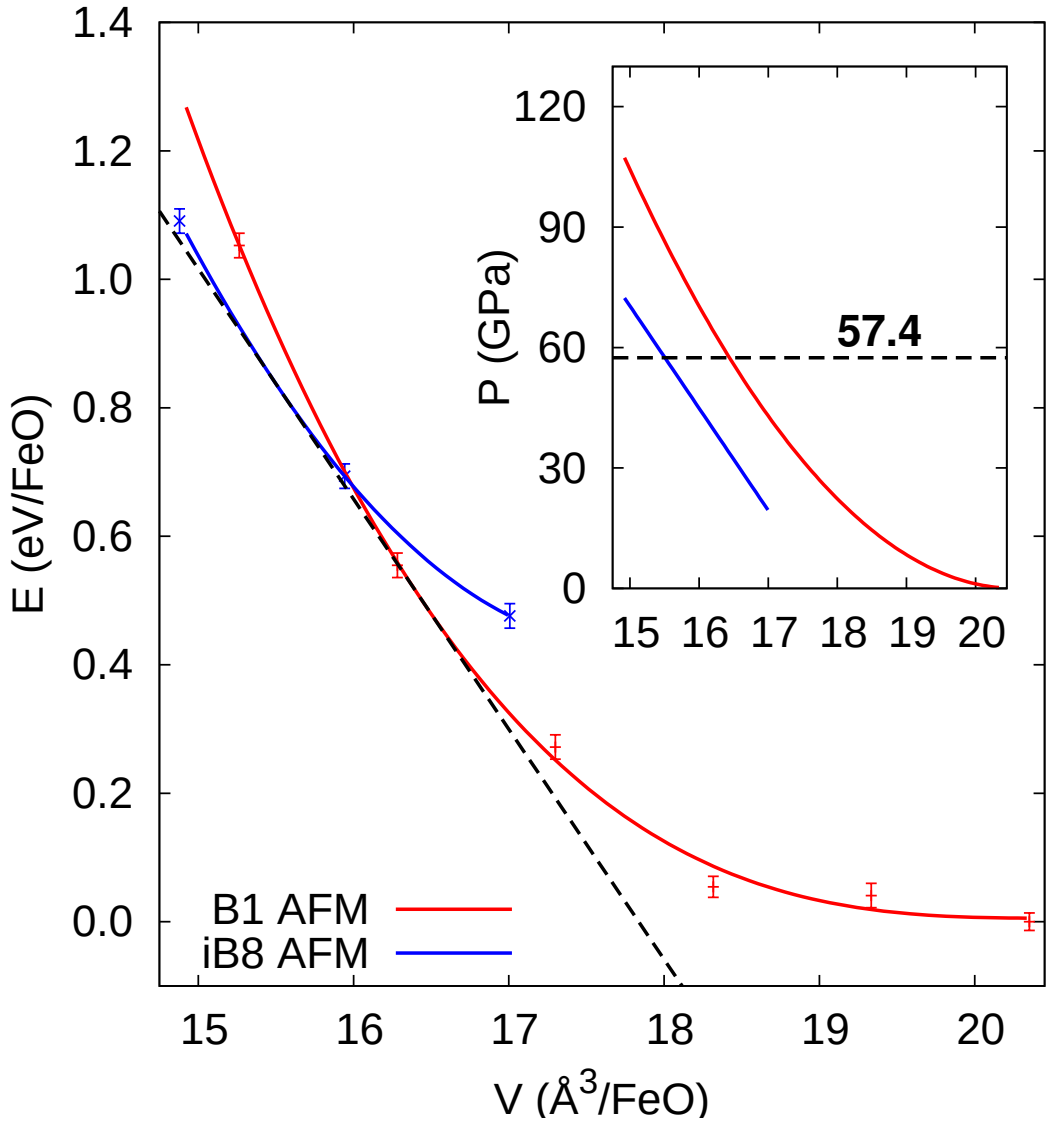

FeO

| *method* | $P_c$ (GPa) |
|---|---|
| $PBE0_{10}$ | 7 |
| $PBE0_{20}$ | 43 |
| **exp.** | $\gtrsim$ **70** |

MnO

| *method* | $P_c$ (GPa) |
|---|---|
| $PBE0_{10}$ | 117 |
| **exp.** | $\sim$ **100** |

# Equation of state: DMC[PBE0$_{20}$]




| *method* | $P_c$ (GPa) |
|---|---|
| PBE-GGA | — |
| PBE0$_{10}$ | 7 |
| PBE0$_{20}$ | 43 |
| **DMC** | **57 ± 5*** |
| **exp.** | **$\gtrsim$ 70** |

* pure Ewald formula

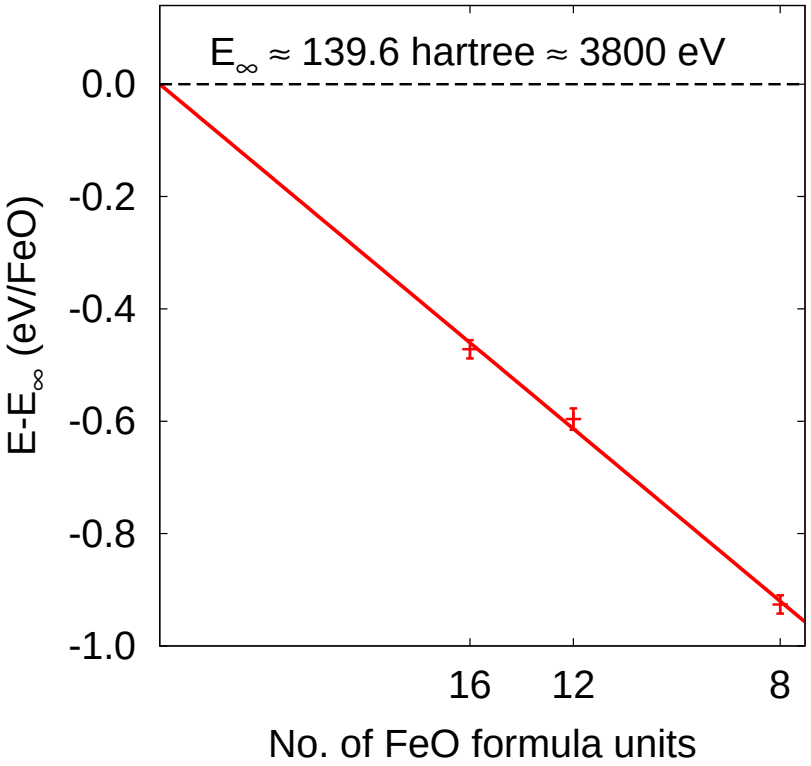
*geometry optimization:*

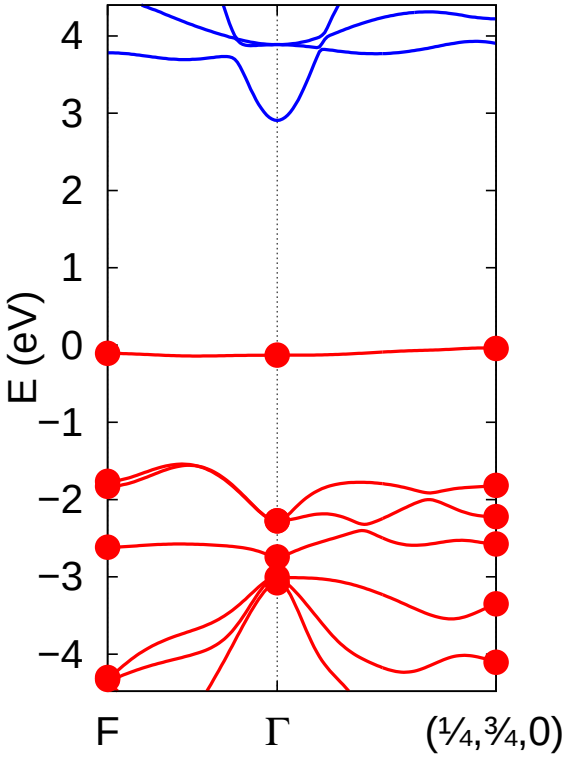
| | |
|---|---|
| iB8 | $c/a$ (PBE0$_{20}$) |
| B1 | none |

# Finite size errors

# Only 8 FeO in the simulation cell: Finite-size errors

- **kinetic energy FSE**
  average over 8 $k$-points (a.k.a. twists of boundary conditions) $\longrightarrow$ only $\sim$ **0.01 eV/FeO** away from converged Brillouin zone integral
- **potential energy FSE (beyond Ewald)**

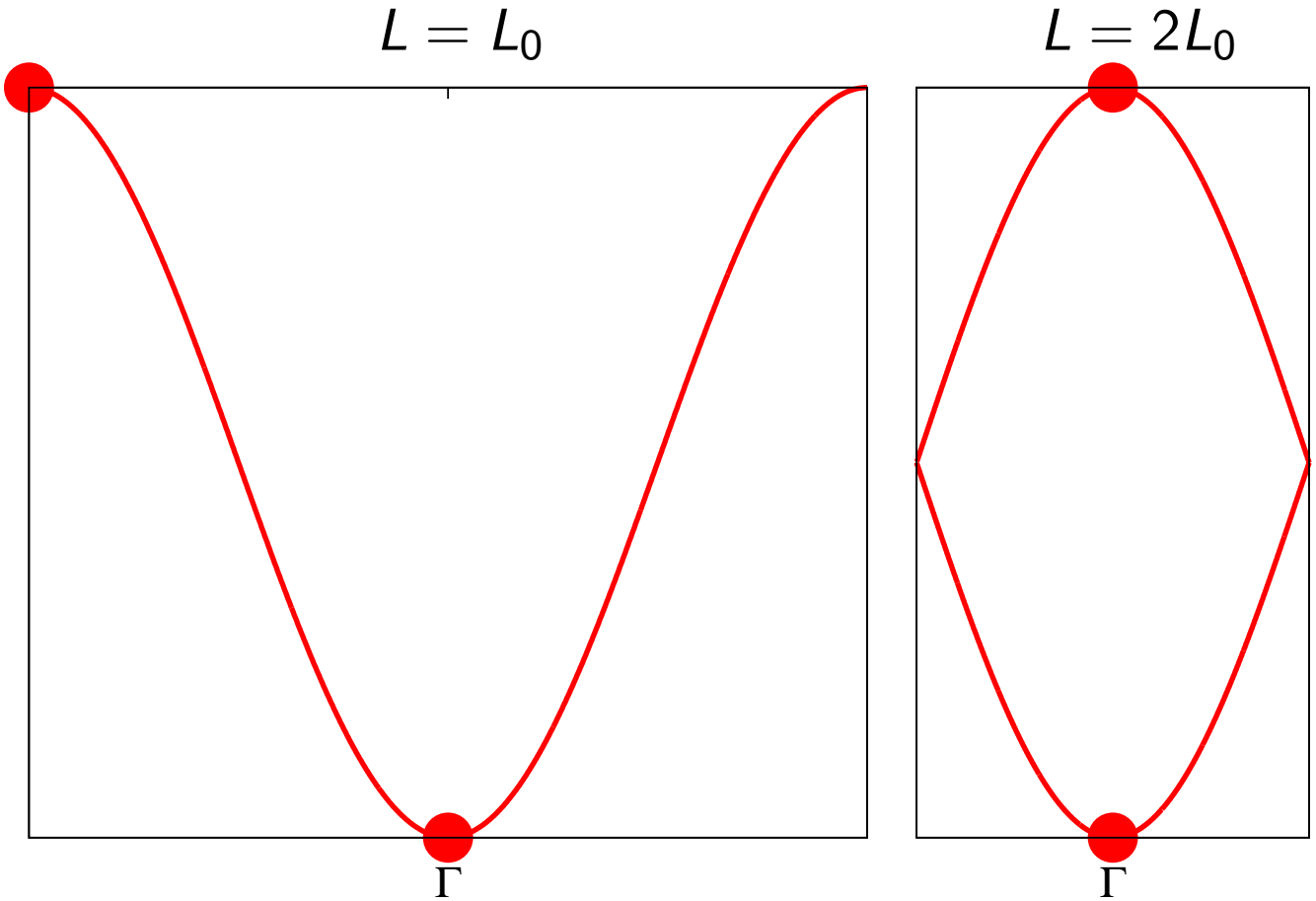



- $E - E_\infty$ comparable to the scale of our physics ($\sim$ **1 eV/FeO**)
- finite-size scaling at every volume too expensive

# Improving kinetic energy — $k$-point average

Adding $k$-points effectively increases simulation cell size...




...but not quite when interactions are in the game.

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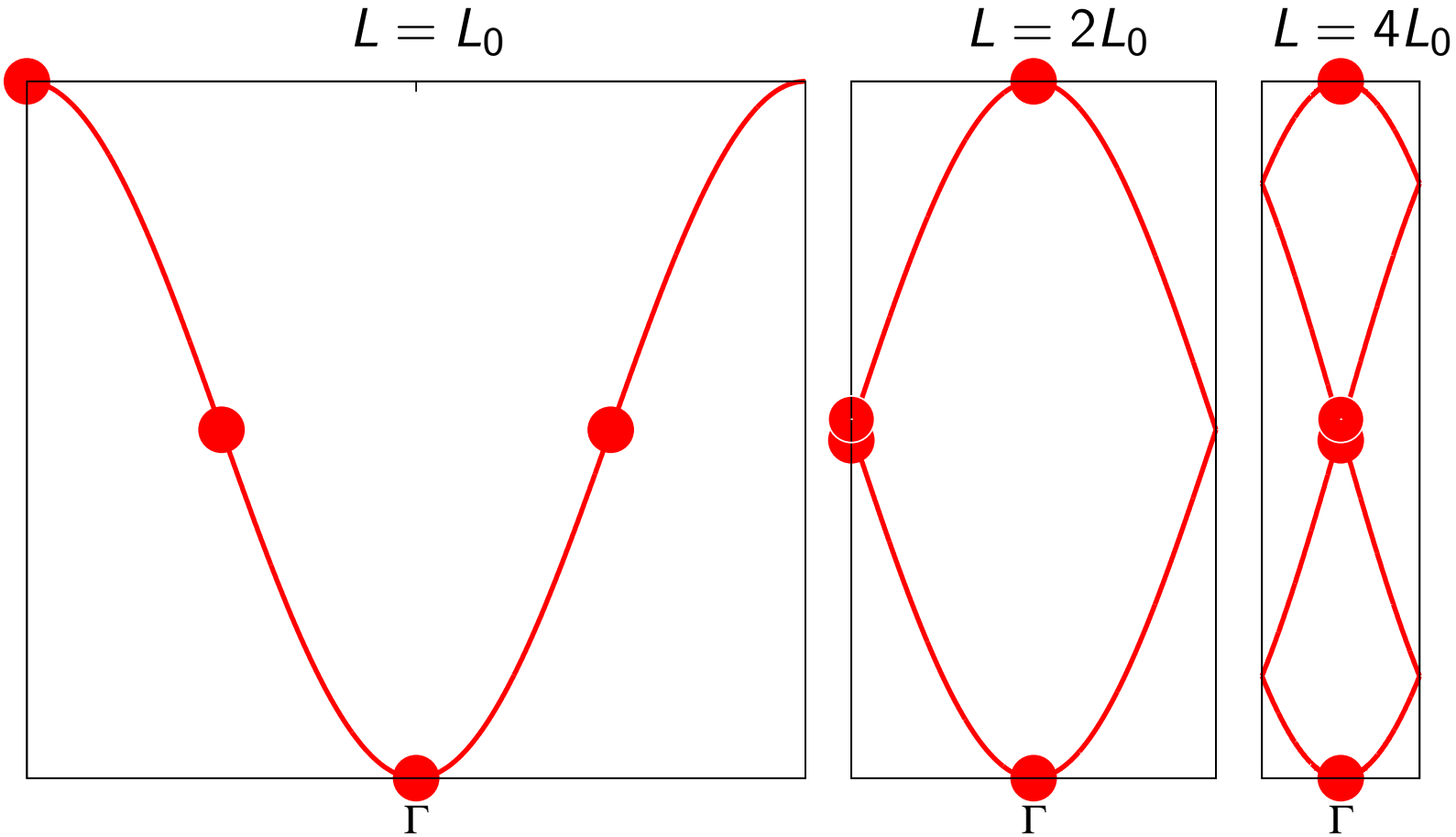


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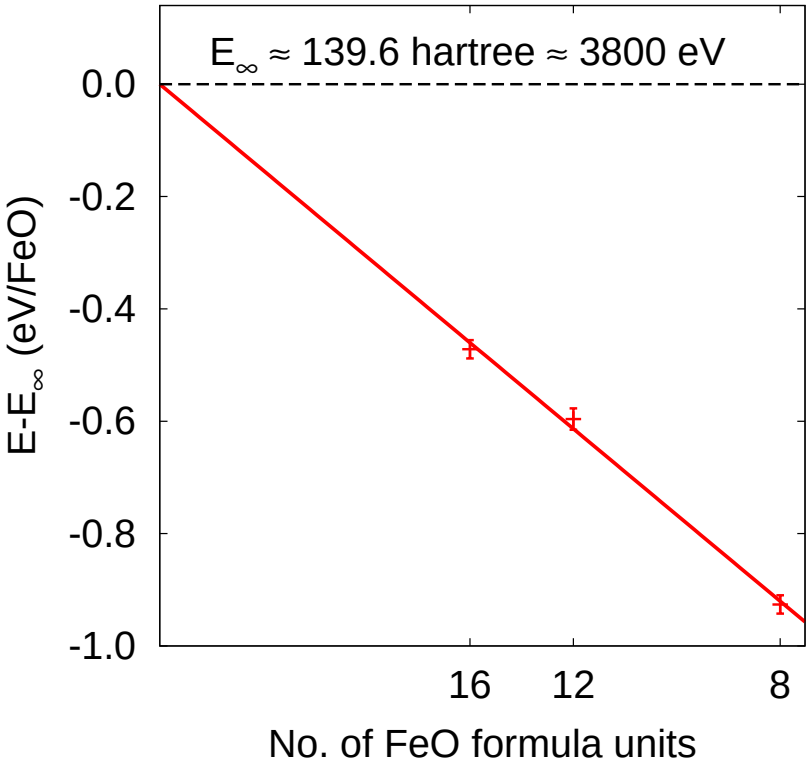


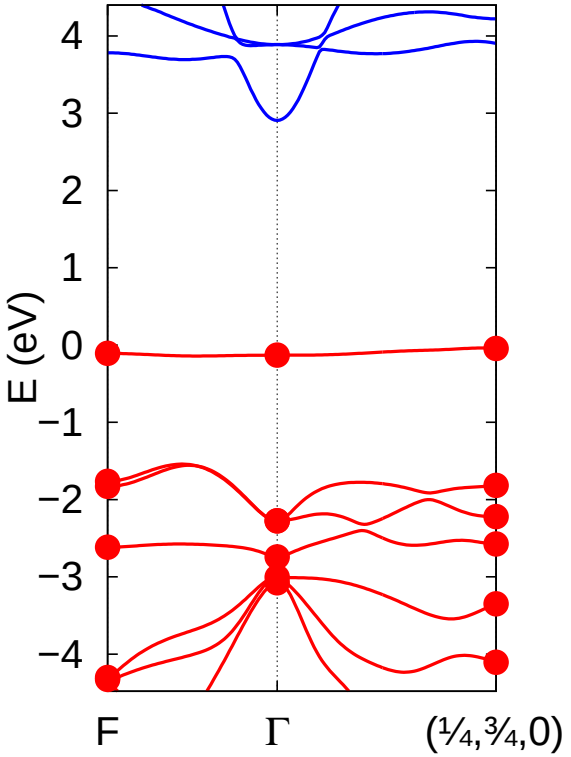


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# Potential energy & static structure factor

*[after Chiesa,Ceperley,Martin&Holzmann (2006)]*

$$V_{ee} = \frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}} = \frac{2\pi N}{\Omega}\sum_{\mathbf{k}}\left(\frac{\rho_{\mathbf{k}}\rho_{-\mathbf{k}}}{N} - 1\right) = \frac{2\pi N}{\Omega}\sum_{\mathbf{k}}\Big(S_N(\mathbf{k}) - 1\Big)$$

Correction $\Delta_{FS} = \left(\lim_{\Omega\to\infty} V_{ee} - V_{ee}\right)/N$ has two parts

- $\Delta_{FS}^{(1)} = \dfrac{2\pi}{\Omega}\sum_{\mathbf{k}\neq 0}\dfrac{1}{k^2} - \dfrac{1}{4\pi^2}\int d^3k\,\dfrac{1}{k^2} = \lim_{\mathbf{r}_{ii}\to 0}\left[v_{ee}(\mathbf{r}_{ii}) - \dfrac{1}{r_{ii}}\right]$

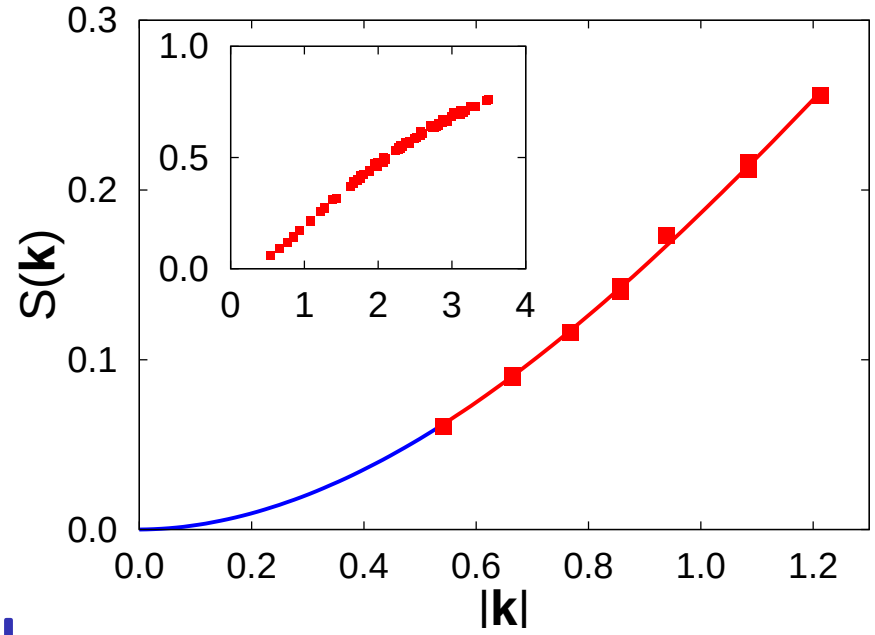
  ... this one we already know (and have in Ewald formula)

- $\Delta_{FS}^{(2)} = \dfrac{1}{4\pi^2}\int d^3k\,\dfrac{S_\infty(\mathbf{k})}{k^2} - \dfrac{2\pi}{\Omega}\sum_{\mathbf{k}\neq 0}\dfrac{S_N(\mathbf{k})}{k^2} \simeq \dfrac{1}{4\pi^2}\int_0^{(2\pi/L)^3} d^3k\,\dfrac{S_\infty(\mathbf{k})}{k^2}$

  ... this contribution is new

# Potential energy & static structure factor, cont.

$$\Delta_{FS}^{(2)} = \frac{1}{4\pi^2} \int_0^{(2\pi/L)^3} d^3k \, \frac{S_\infty(\mathbf{k})}{k^2}$$




## We need $S_\infty(\mathbf{k})$ at $k \leq 2\pi/L$

- $S_N(\mathbf{k})$ does not depend much on $N \longrightarrow S_\infty(\mathbf{k}) \simeq S_N(\mathbf{k})$
- $k \leq 2\pi/L$ correspond to wavelengths longer than the size of our simulation cell, i.e., no direct access to $S_N(\mathbf{k})$ there $\longrightarrow$ extrapolation needed
- fortunately, exact identity fixes $S_N(\mathbf{0}) = 0$, so that the extrapolation is under control

# Extrapolated estimate for $S(\mathbf{k})$

- **mixed estimate**
  DMC with guiding wave function samples the mixed distribution $f(\mathbf{R}) = \Psi_0(\mathbf{R})\Psi_T(\mathbf{R})$

$$\langle\Psi_0|\hat{S}|\Psi_T\rangle = \int d^{3N}R \underbrace{\Psi_0(\mathbf{R})\Psi_T(\mathbf{R})}_{f(\mathbf{R})} \underbrace{\frac{\hat{S}(\mathbf{R})\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}}_{S_L(\mathbf{R})} = \frac{1}{N_w}\sum_w S_L(\mathbf{R}_w)$$

  $\Psi_T(\mathbf{R})$ known in explicit form $\longrightarrow$ derivatives in $\hat{S}(\mathbf{R})$ would be no problem in evaluation of $S_L(\mathbf{R})$

- **extrapolated estimate**
  approximate expression for the desired matrix element

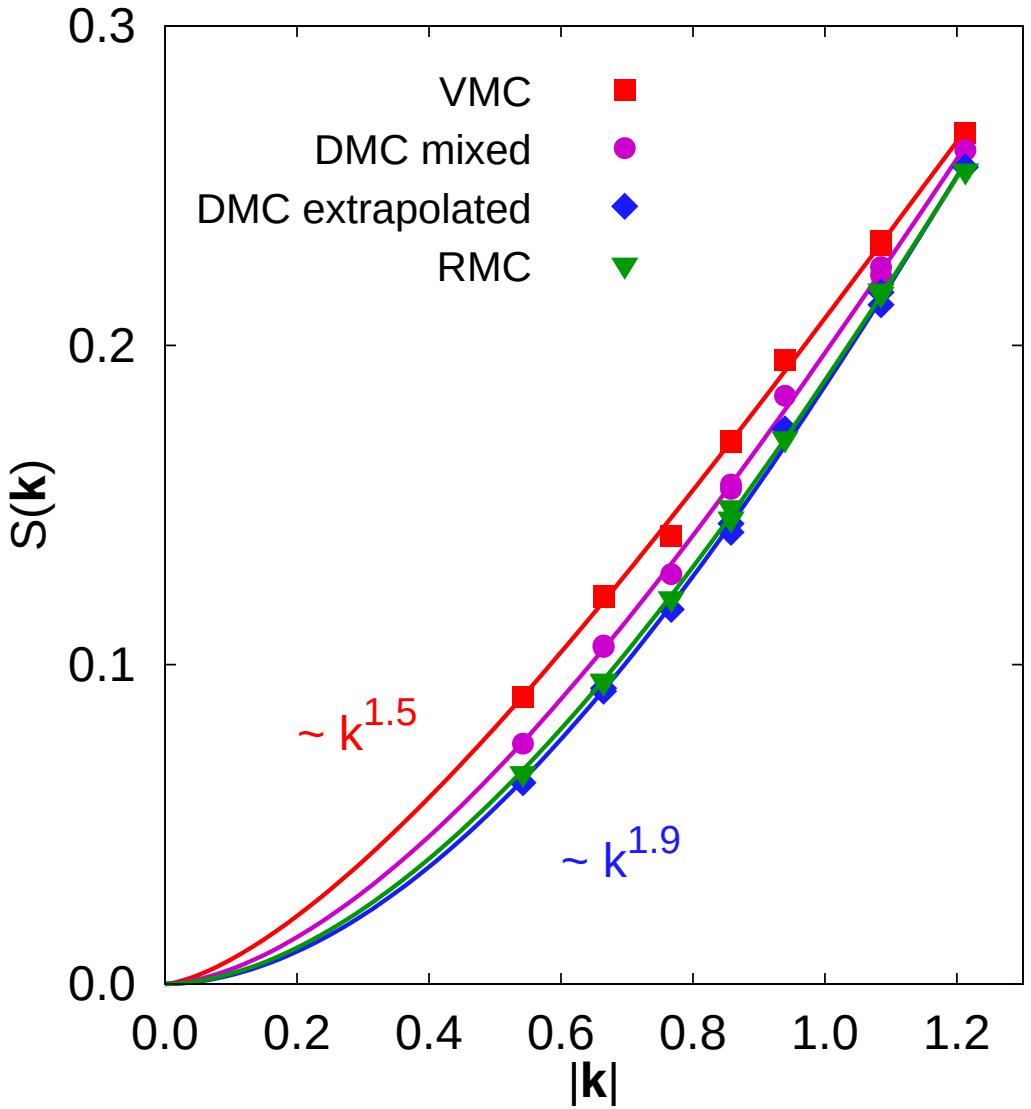
$$\langle\Psi_0|\hat{S}|\Psi_0\rangle = 2\langle\Psi_0|\hat{S}|\Psi_T\rangle - \langle\Psi_T|\hat{S}|\Psi_T\rangle + \mathcal{O}\big((\Psi_0 - \Psi_T)^2\big)$$

---

$$|\Psi_0\rangle = |\Psi_T + \Delta\rangle : \quad \langle\Psi_T + \Delta|\hat{S}|\Psi_T + \Delta\rangle = \langle\Psi_T|\hat{S}|\Psi_T\rangle + 2\langle\Delta|\hat{S}|\Psi_T\rangle + \langle\Delta|\hat{S}|\Delta\rangle$$

$$\langle\Psi_T + \Delta|\hat{S}|\Psi_T\rangle = \langle\Psi_T|\hat{S}|\Psi_T\rangle + \langle\Delta|\hat{S}|\Psi_T\rangle$$

# Comparison of various estimates for $S(\mathbf{k})$




Reptation Monte Carlo (RMC)

- provides pure estimates for local ("density-type") quantities
- quickly loses efficiency with increasing system size

# Expectation values in DMC and DFT

## DMC

- expectation values calculated using explicitly correlated many-body wave function
- in general, only mixed estimators $\langle \Psi_0 | \hat{A} | \Psi_T \rangle$ available; these depend on quality of $|\Psi_T\rangle$
- for the total energy and all $\left[\hat{B}, \hat{H}\right] = 0$ we have $\langle \Psi_0 | \hat{B} | \Psi_T \rangle = \langle \Psi_0 | \hat{B} | \Psi_0 \rangle$

## DFT

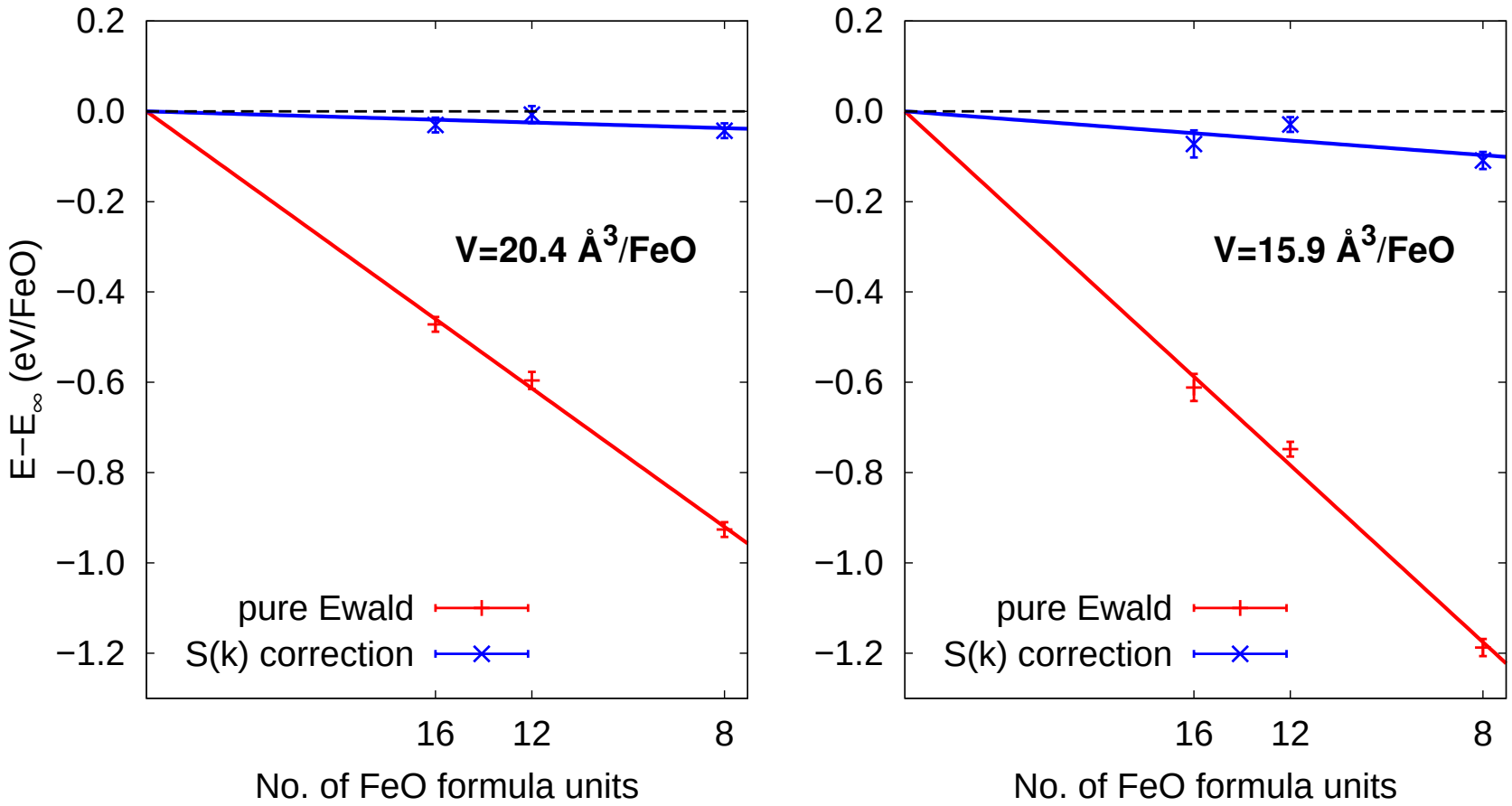
- quantities calculated from eigenfunctions of artificial non-interacting Kohn-Sham system
- these eigenfunctions (and eigenvalues) not guaranteed to have direct physical content (but often seem to be close)
- total energy prominent — K-S system constructed to have the same total energy as the original interacting system

# Back to FeO

# "$S(\mathbf{k})$ correction" does a good job

Finite size errors at different levels of compression

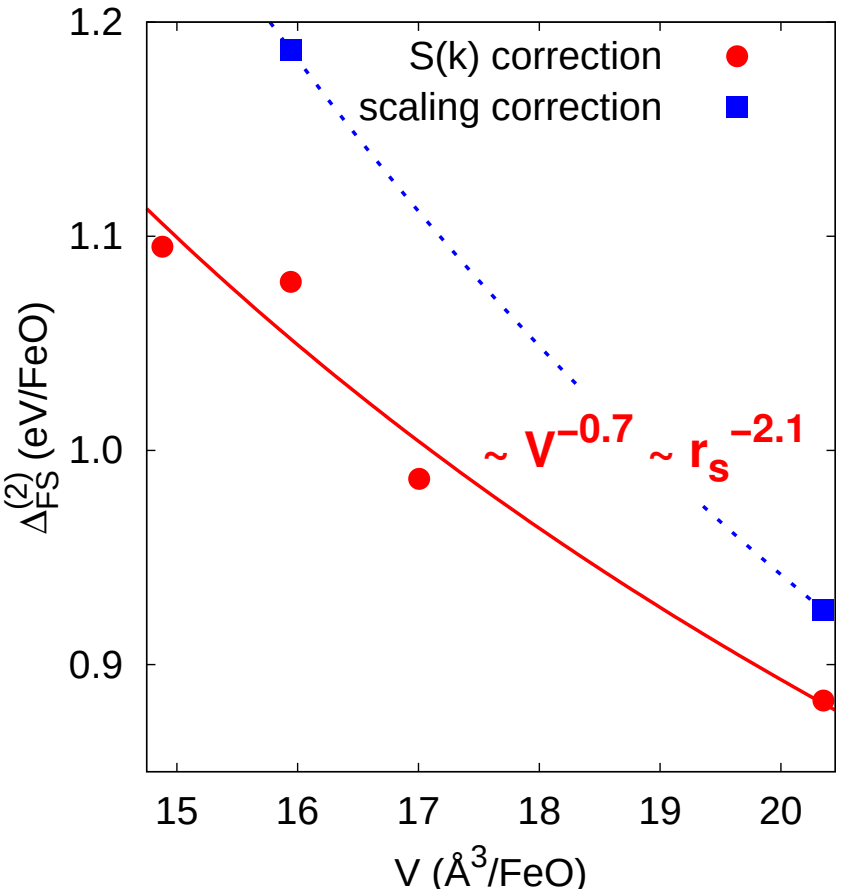
$\longrightarrow$ errors grow as electron density increases

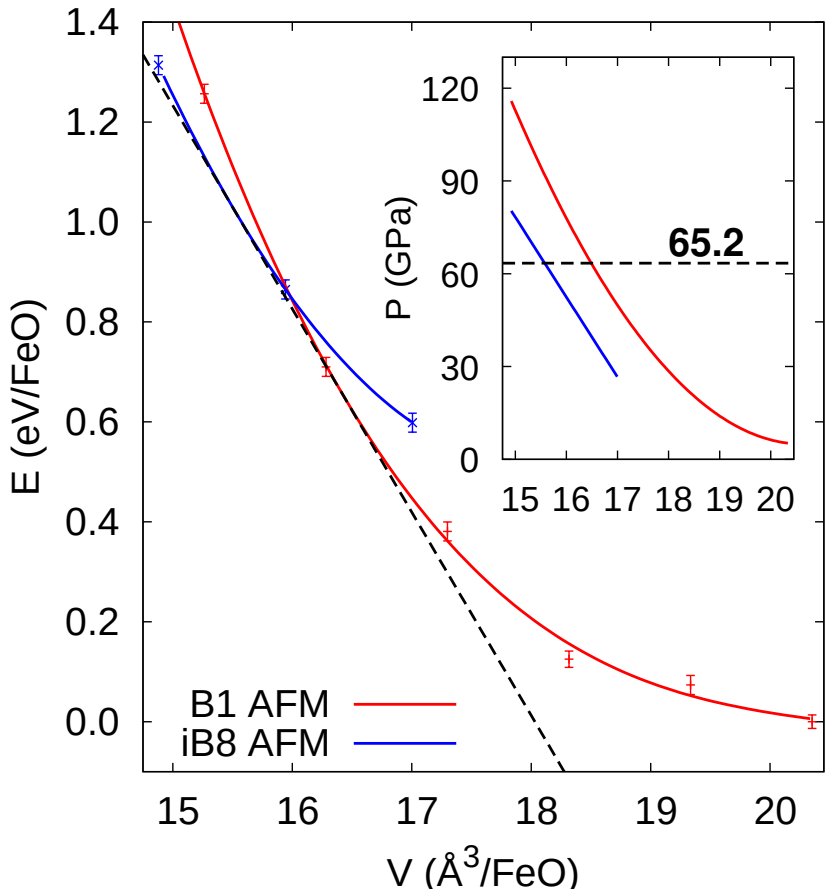


# Transition pressure $P_c$ revisited

Finite-size corrections (slightly) increase $P_c$ .

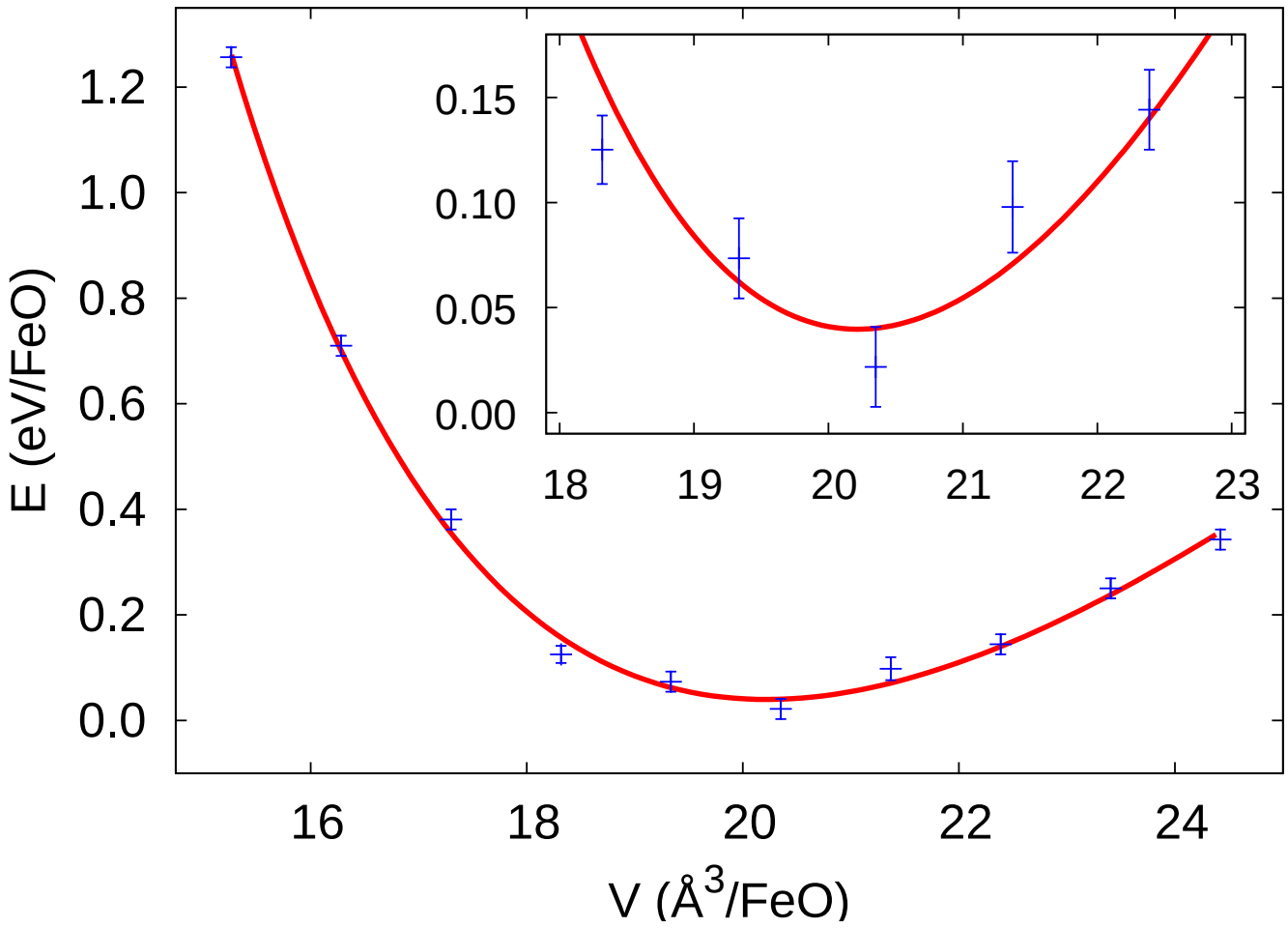
- pure Ewald formula $\longrightarrow$ $P_c = \mathbf{57} \pm \mathbf{5}$ GPa
- $S(\mathbf{k})$ correction $\longrightarrow$ $P_c = \mathbf{65} \pm \mathbf{5}$ GPa



# Equilibrium volume and related properties

Murnaghan equation of state fits the B1 AFM-II data nicely.



# Equilibrium volume and related properties, cont.

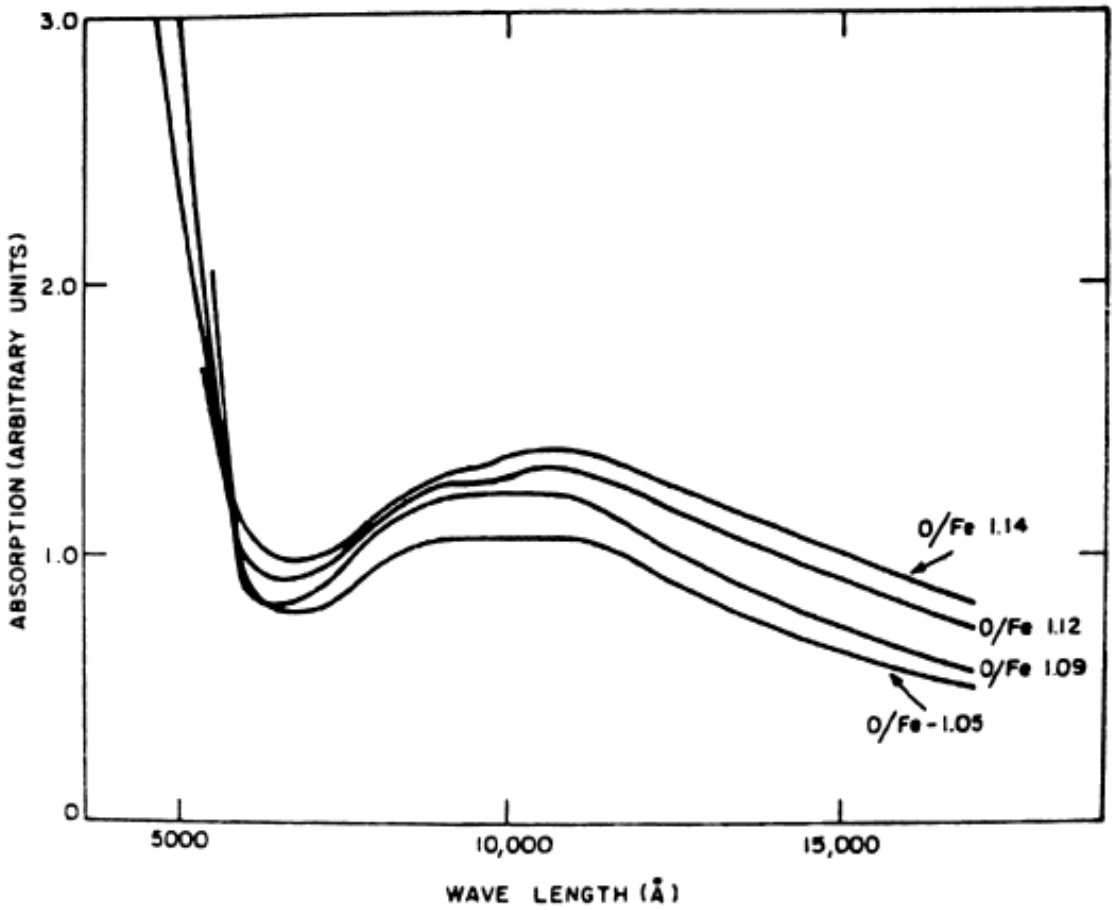
$$E(V) = E_0 + \frac{K_0 V}{K_0'}\left(\frac{(V_0/V)^{K_0'}}{K_0' - 1} + 1\right) - \frac{K_0 V_0}{K_0' - 1}$$

$$K_0 = -V\left(\partial P/\partial V\right)_T \qquad K_0' = \left(\partial K_0/\partial P\right)_T$$

| | $a_0$ (Å) | $K_0$ (GPa) | $K_0'$ |
|---|---|---|---|
| DMC, pure Ewald | 4.283(7) | 189(8) | 5.5(7) |
| **DMC + $S(\mathbf{k})$ correction** | **4.324(6)** | **170(10)** | **5.3(7)** |
| $PBE0_{20}$ | 4.328 | 182 | 3.7 |
| $PBE0_{10}$ | 4.327 | 177 | 3.7 |
| PBE | 4.300 | 191 | 3.5 |
| LDA | 4.185 | 224 | 4.0 |
| **experiment** | **4.307–4.334** | **140–180** | **2.1–5.6** |

# Can we access also spectral information?

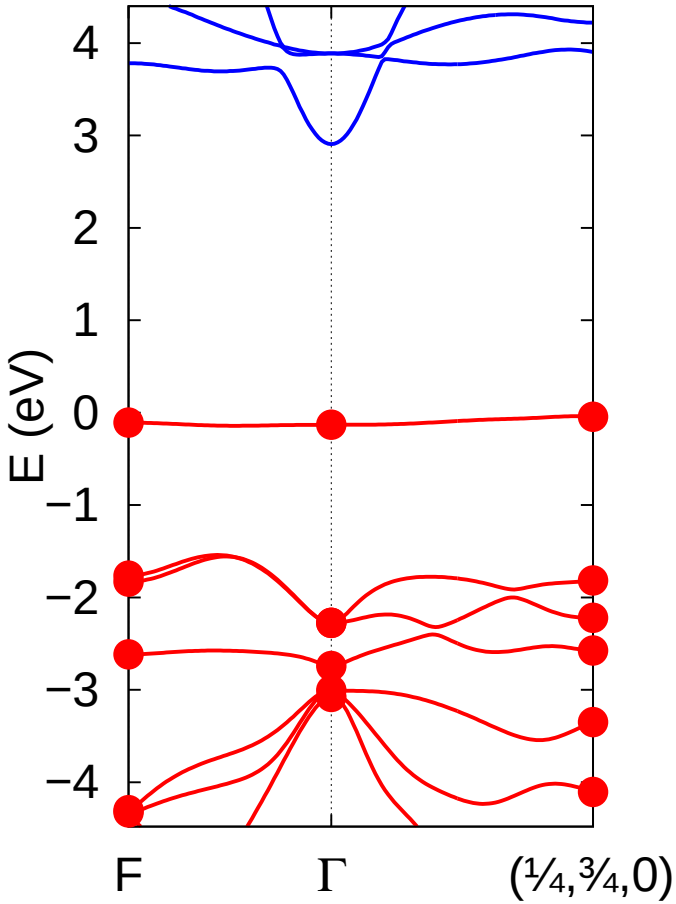
*[Bowen,Adler&Auker (1975)]*

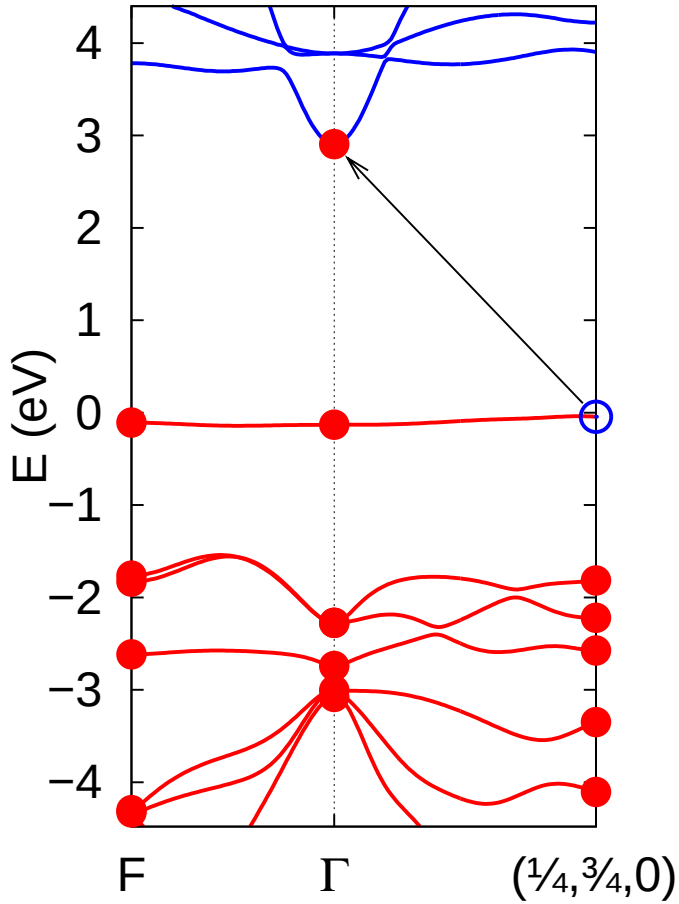



2.48 1.24 0.82 (eV)

# Band gap estimate in B1 at ambient pressure

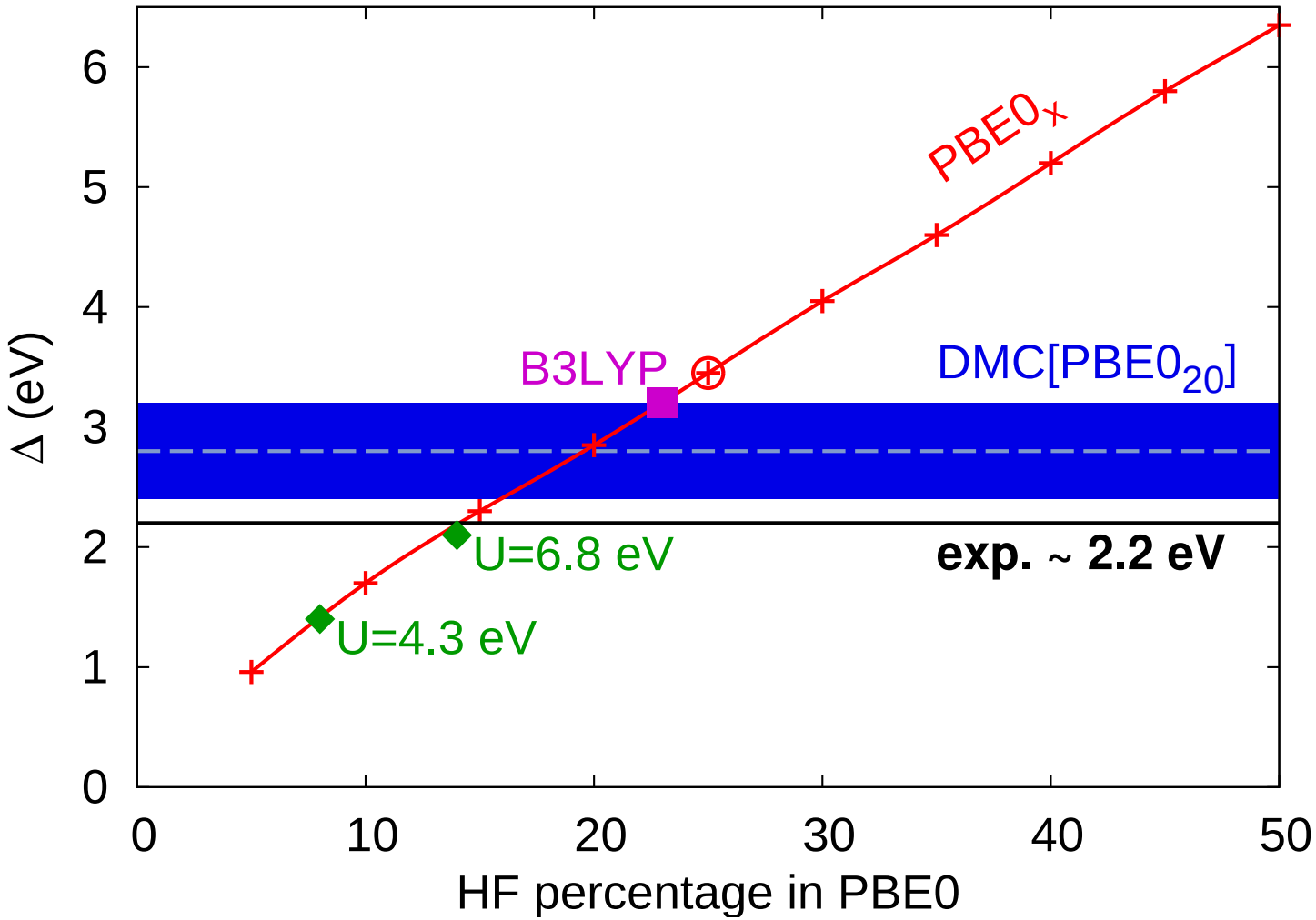
$$\Delta = E^{s.cell}_{solid}[e.s.] - E^{s.cell}_{solid}[g.s.] = \mathbf{2.8 \pm 0.4\ eV}$$



# Band gap estimate in B1 at ambient pressure, cont.

DMC, hybrid-functional DFT and LDA+U compared.



# Notes on band gaps in DMC

- in $\Delta = E[e.s.] - E[g.s.]$, the intensive quantity $\Delta$ is calculated from extensive energies
  $\longrightarrow$ unfavorable for errorbars
- single $k$-point quantities; although large cancellation of kinetic energy finite-size errors is likely ($E[e.s.]$ and $E[g.s.]$ are at the same $k$-point), safe elimination of these is through a large simulation cell
  $\longrightarrow$ unfavorable for errorbars
- (the lowest) excited state must have a different symmetry than the ground state (exc. state is then a groundstate within that symmetry)
  $\longrightarrow$ might not be the case in large supercell with small number of symmetry operations
- other methods for extracting excited-state information from DMC available, but considerably more costly

# Final words

- quantum Monte Carlo is ready to be applied to solids with correlated $d$ electrons
- FeO case study is very encouraging
  - good agreement with experimental data at both ambient conditions and elevated pressure
  - consistently accurate for various quantities (cohesion, $P_c(\text{B1} \rightarrow \text{iB8})$, equilibrium lattice constant, bulk modulus, ...)
- computer time provided by INCITE ORNL and NCSA

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- *more good news*: you can try it at home

  **www.qwalk.org**

  (Lucas Wagner, Michal Bajdich and Lubos Mitas)

  *the bad news*: you need some 100,000+ CPU hours (for EoS)

# DMC projection trace