

Diffusion Monte Carlo simulations of crystalline FeO under pressure

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FeO

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

quantum Monte Carlo

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

The method

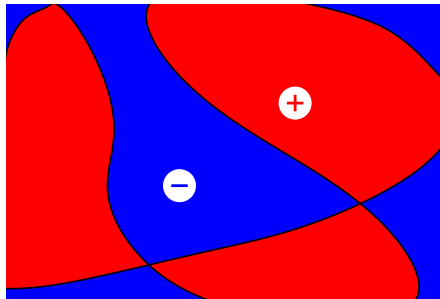
Diffusion quantum Monte Carlo (DMC)

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

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

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

- fermionic Ψ changes sign (antisymmetry w.r.t. particle exchanges) \rightarrow **fixed-node approximation**



$$\begin{aligned} \text{sign } \Psi(1, \dots, N) \\ = \text{sign } \Psi_T(1, \dots, N) \end{aligned}$$

DMC and DFT

diffusive projection

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

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

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

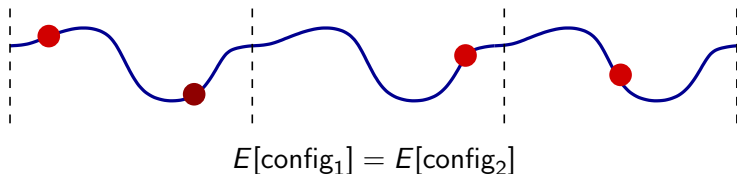
Slater determinant of 1-body orbitals Jastrow many-body correlation factor

- 1-body orbitals = variational “parameters”
 - Hartree-Fock approximation
 - PBE0_x — PBE-GGA mixed with x % of exact exchange
- Jastrow factor

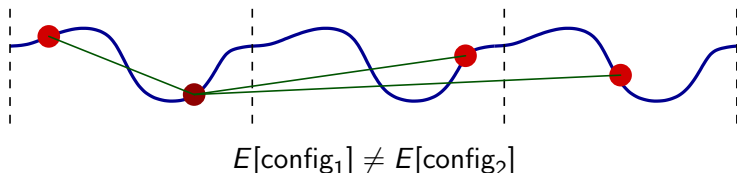
$$J(1, \dots, N) = \sum_i f_e(\mathbf{r}_i) + \sum_{ij} f_{ee}(\mathbf{r}_i - \mathbf{r}_j) + \sum_{i,\alpha} f_{el}(\mathbf{r}_i - \mathbf{R}_\alpha)$$

Reduction to the primitive cell?

non-interacting particles in a periodic potential



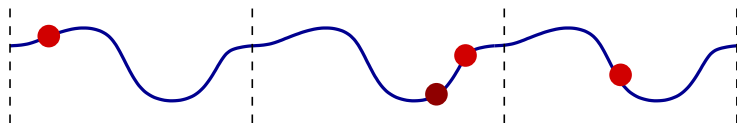
interacting particles in a periodic potential



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

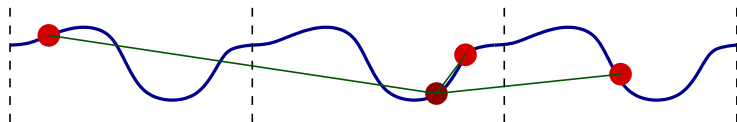
Reduction to the primitive cell?

non-interacting particles in a periodic potential



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

interacting particles in a periodic potential



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

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

Periodic Coulomb interaction

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

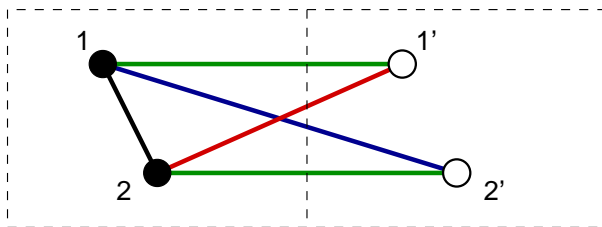
$$v_{ee}(\mathbf{r}) = \sum_{\mathbf{R}_S} \frac{1}{|\mathbf{r} - \mathbf{R}_S|} \simeq \frac{4\pi}{\Omega} \sum_{\mathbf{k} \neq 0} \frac{1}{k^2} e^{i\mathbf{k} \cdot \mathbf{r}}$$

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

$$\begin{aligned} \sum_{\mathbf{k} \neq 0} \frac{1}{k^2} e^{i\mathbf{k} \cdot \mathbf{r}} &= \sum_{\mathbf{k} \neq 0} \frac{1}{k^2} e^{-k^2/(4\alpha^2)} e^{i\mathbf{k} \cdot \mathbf{r}} - \lim_{\mathbf{k} \rightarrow 0} \frac{1}{k^2} \left(1 - e^{-k^2/(4\alpha^2)}\right) \\ &\quad + \sum_{\mathbf{k}} \frac{1}{k^2} \left(1 - e^{-k^2/(4\alpha^2)}\right) e^{i\mathbf{k} \cdot \mathbf{r}} \\ &= \sum_{\mathbf{k} \neq 0} \frac{1}{k^2} e^{-k^2/(4\alpha^2)} e^{i\mathbf{k} \cdot \mathbf{r}} - \frac{1}{4\alpha^2} \\ &\quad + \frac{\Omega}{4\pi} \sum_{\mathbf{R}_S} \frac{1}{|\mathbf{r} - \mathbf{R}_S|} \operatorname{erfc}(\alpha|\mathbf{r} - \mathbf{R}_S|) \end{aligned}$$

Total interaction energy (Ewald)

Total e-e interaction energy per simulation cell.



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

Total interaction energy (Ewald), cont.

The same formula once more in B&W.

$$\begin{aligned}
 V_{ee} &= \underbrace{\frac{1}{2} \sum_{i \neq j} v_{ee}(\mathbf{r}_{ij})}_{\text{interaction of } i \text{ with } j \text{ and with images of } j} + \underbrace{\frac{1}{2} \sum_i \lim_{r_{ii} \rightarrow 0} \left[v_{ee}(\mathbf{r}_{ii}) - \frac{1}{r_{ii}} \right]}_{\text{interaction of } i \text{ with its periodic images}} \\
 &= \frac{1}{2} \sum_{i \neq j} \sum_{\mathbf{R}_S} \frac{1}{|\mathbf{r}_{ij} - \mathbf{R}_S|} \operatorname{erfc}(\alpha |\mathbf{r}_{ij} - \mathbf{R}_S|) \\
 &\quad + \frac{2\pi}{\Omega} \sum_{\mathbf{k} \neq 0} \frac{1}{k^2} e^{-k^2/(4\alpha^2)} \sum_{i \neq j} e^{i\mathbf{k} \cdot \mathbf{r}_{ij}} \\
 &\quad - \frac{1}{2} N^2 \frac{\pi}{\Omega \alpha^2} - N \frac{\alpha}{\sqrt{\pi}} + \frac{1}{2} N \sum_{\mathbf{R}_S \neq 0} \frac{1}{|\mathbf{R}_S|} \operatorname{erfc}(\alpha |\mathbf{R}_S|)
 \end{aligned}$$

FeO, part I

Cohesive energy

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

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)

	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)**

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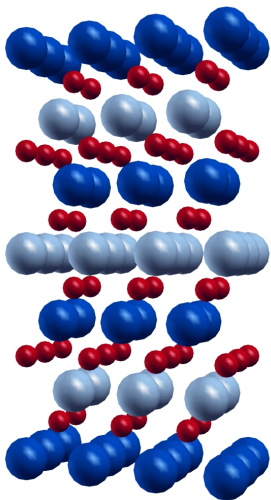
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FeO total energy (hartree)

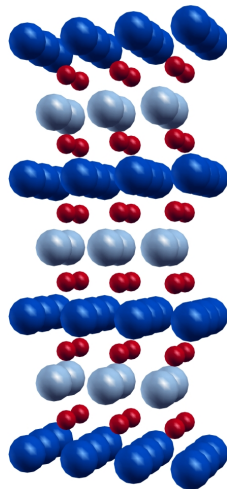
-139.6105(8)

-139.6210(5)

Competing crystal structures in FeO



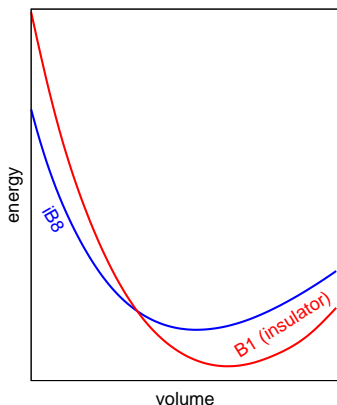
B1 (NaCl) AFM-II



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)]

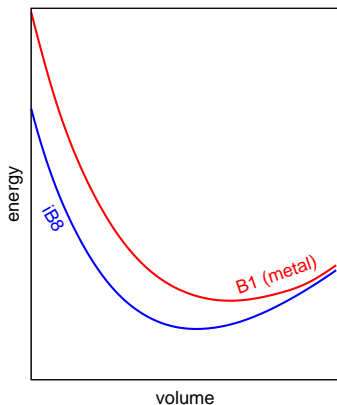
- 300 K: $P_c > 220$ GPa

? 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)]

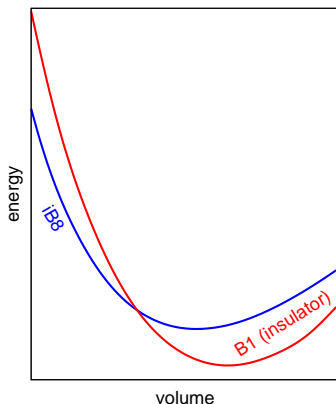
*[Fang, Terakura, Sawada, Miyazaki
& Solovyev (1998)]*

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

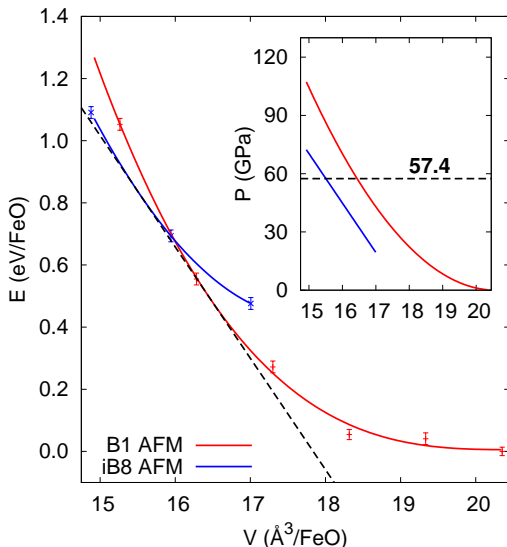
Equation of state: “Correlated” band theories

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

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



	<i>method</i>	P_c (GPa)
FeO	PBE0 ₁₀	7
	PBE0 ₂₀	43
	exp.	≥ 70
	<i>method</i>	P_c (GPa)
MnO	PBE0 ₁₀	117
	exp.	~ 100

Equation of state: DMC[PBE0₂₀]

<i>method</i>	P_c (GPa)
PBE-GGA	—
PBE0 ₁₀	7
PBE0 ₂₀	43
DMC	$57 \pm 5^*$
exp.	$\gtrsim 70$

* pure Ewald formula

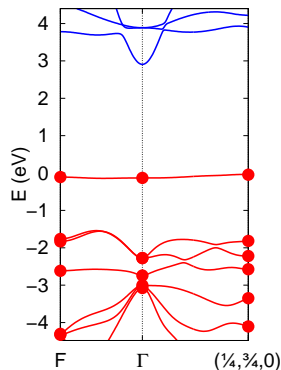
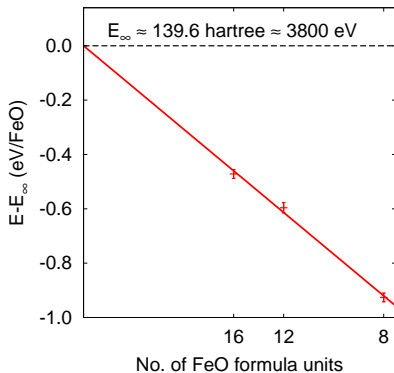
geometry optimization:

iB8	c/a (PBE0 ₂₀)
B1	none

Finite size errors

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

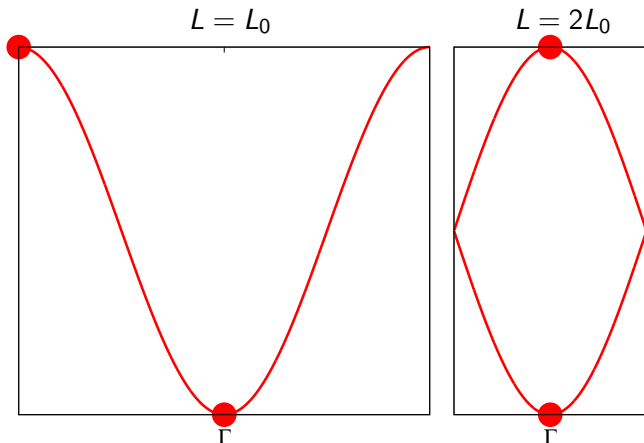
- **kinetic energy FSE**
average over 8 k -points (a.k.a. twists of boundary conditions) \rightarrow only ~ 0.01 eV/FeO away from converged Brillouin zone integral
- **potential energy FSE (beyond Ewald)**



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

Improving kinetic energy — k -point average

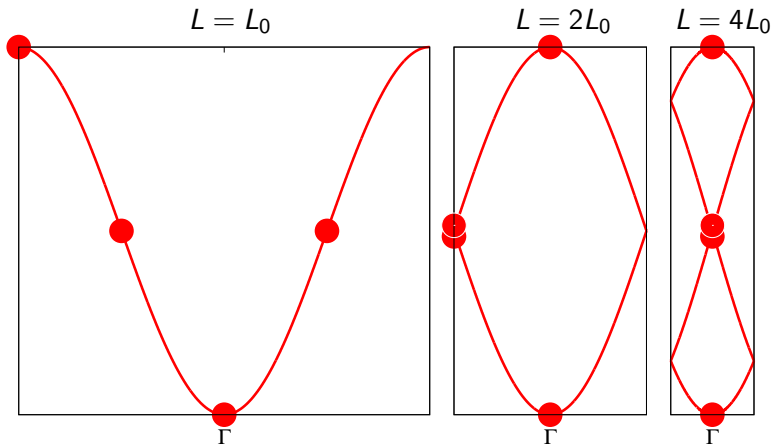
Adding k -points effectively increases simulation cell size...



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

Improving kinetic energy — k -point average

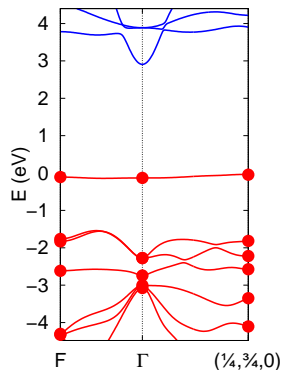
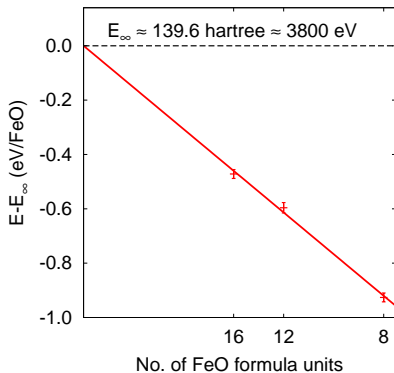
Adding k -points effectively increases simulation cell size. . .



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

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) \rightarrow 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

Potential energy & static structure factor

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

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

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

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

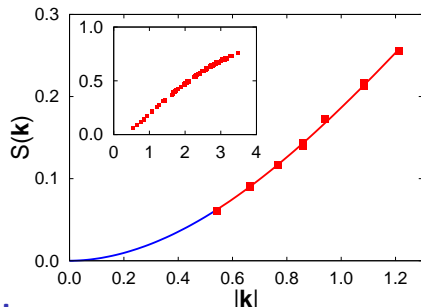
... this one we already know (and have in Ewald formula)

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

... 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 \rightarrow derivatives in $\hat{S}(\mathbf{R})$ would be no problem in evaluation of $S_L(\mathbf{R})$

- **extrapolated estimate**

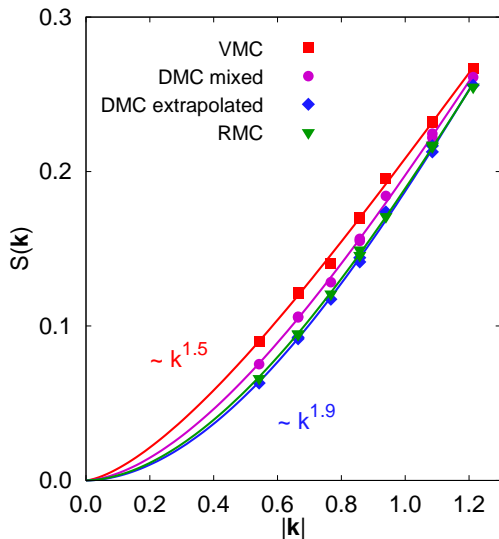
approximate expression for the desired matrix element

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

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

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

Comparison of various estimates for $S(k)$



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 $[\hat{B}, \hat{H}] = 0$ we have $\langle \Psi_0 | \hat{B} | \Psi_T \rangle = \langle \Psi_0 | \hat{B} | \Psi_0 \rangle$

DFT

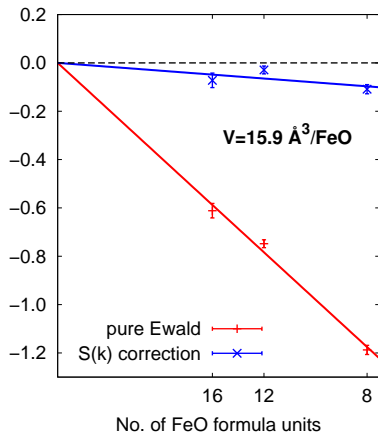
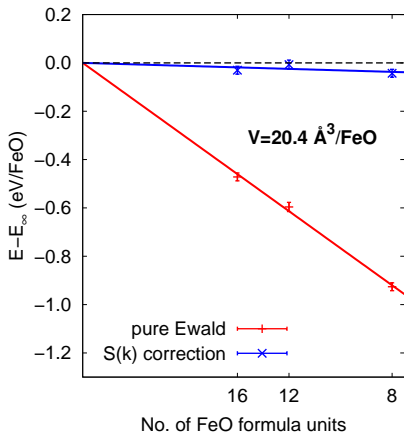
- quantities calculated from eigenfunctions of artificial non-interacting Kohn-Sham system
- these eigenfunctions (and eigenvalues) not guaranteed to have direct physical content (but often seem to be close)
- total energy prominent — K-S system constructed to have the same total energy as the original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

Back to FeO

“S(k) correction” does a good job

Finite size errors at different levels of compression

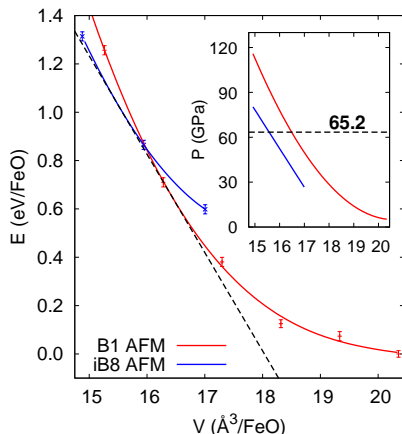
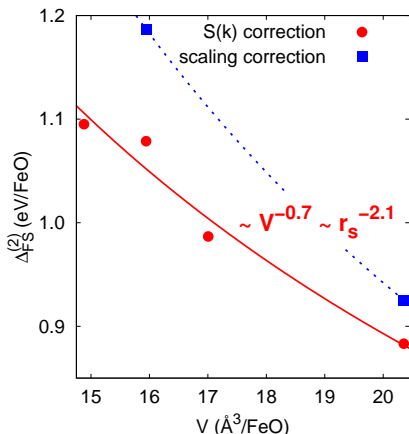
→ errors grow as electron density increases



Transition pressure P_c revisited

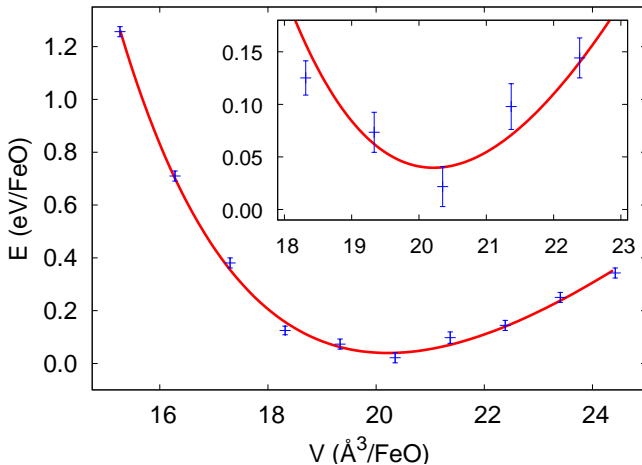
Finite-size corrections (slightly) increase P_c .

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



Equilibrium volume and related properties

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



Equilibrium volume and related properties, cont.

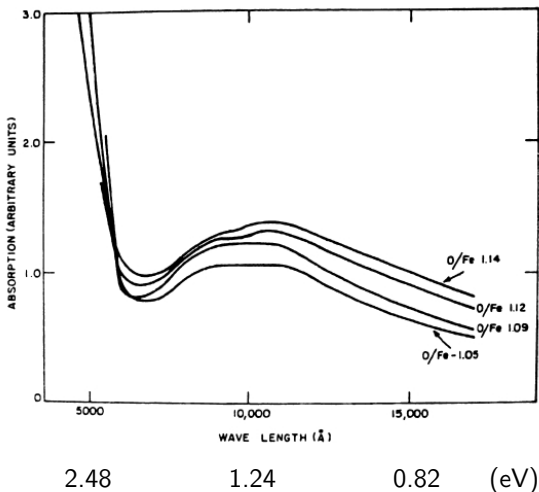
$$E(V) = E_0 + \frac{K_0 V}{K'_0} \left(\frac{(V_0/V)^{K'_0}}{K'_0 - 1} + 1 \right) - \frac{K_0 V_0}{K'_0 - 1}$$

$$K_0 = -V(\partial P/\partial V)_T \quad K'_0 = (\partial K_0/\partial P)_T$$

	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

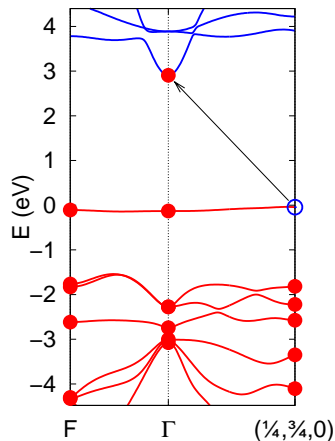
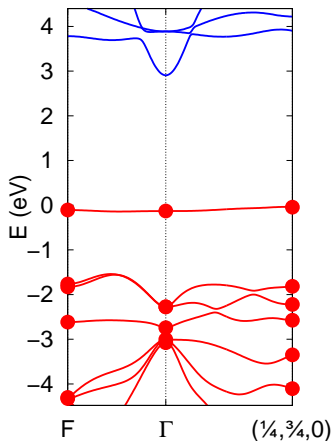
Can we access also spectral information?

[Bowen, Adler & Auker (1975)]



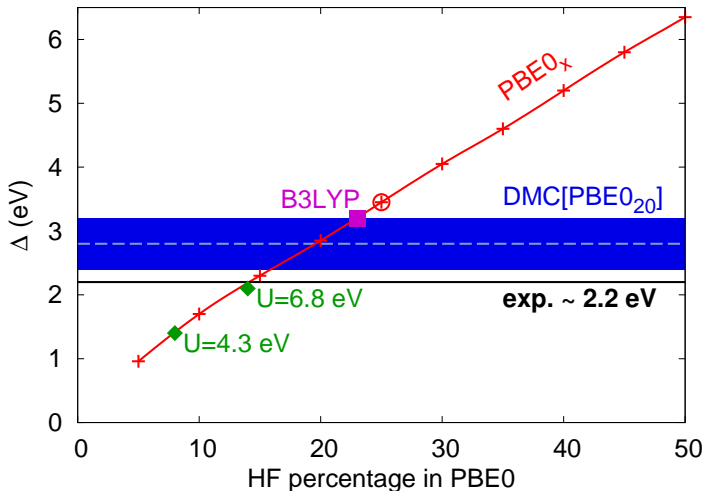
Band gap estimate in B1 at ambient pressure

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



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 Δ is calculated from extensive energies
→ 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
→ 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)
→ 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

-
- *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)