A Stochastic Approach for Thermal DFT

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Putting the Theory Back in Density Functional Theory 2016

Outline

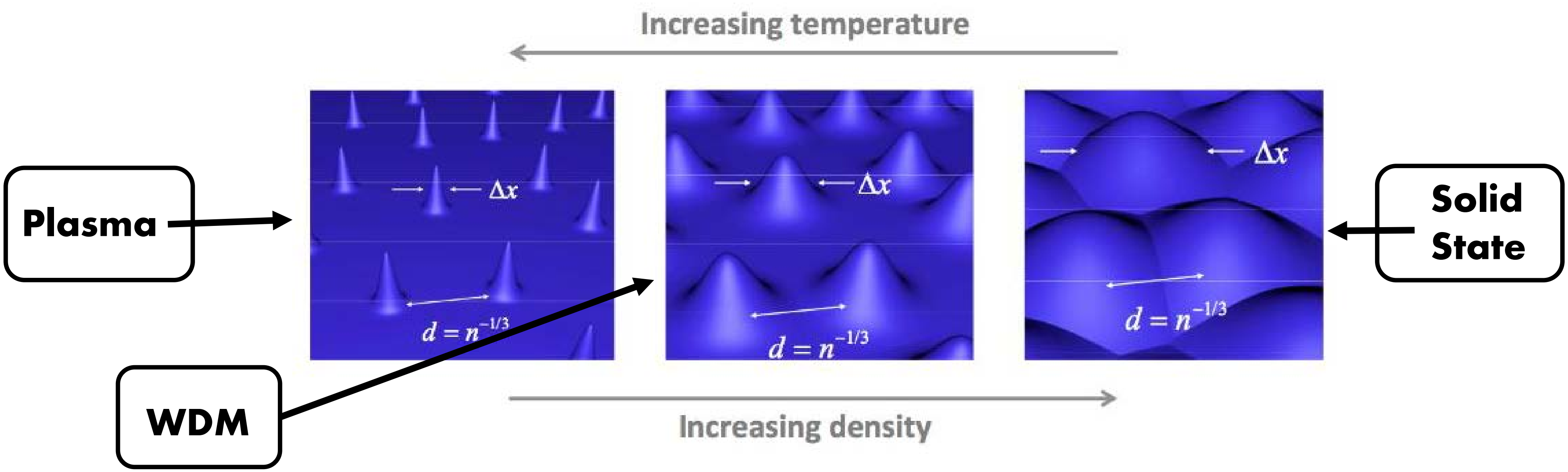
1. **Introduction**

- **Warm Dense Matter (WDM) regime**
- **Thermal Density Functional Theory (TDFT),**

2. **Stochastic TDFT: Theory and computational advantage**

3. **Preliminary results**

Introduction- WDM Regime



$$\tau \sim 10^3 - 10^5 K$$

$$Density = \ n \sim 1 \ \frac{gr}{cm^3}$$

Figure is taken from: http://www.lanl.gov/projects/dense-plasma-theory/background/warm-dense-matter.php (Los Alamos National Labs website)

Introduction - TDFT

$\boldsymbol{\tau = 0}$

Hohenberg & Kohn

$$\hat{H} = \hat{T} + \hat{U}_{ee} + \hat{V}$$
$$\Downarrow$$
$$E[n(\boldsymbol{r})] = \underbrace{T[n(\boldsymbol{r})] + U_{ee}[n(\boldsymbol{r})]}_{F_{HK}[n(\boldsymbol{r})]} + \int v(\boldsymbol{r})n(\boldsymbol{r})$$

$\boldsymbol{\tau > 0}$

Mermin

$$\hat{\Omega} = \hat{H} - \tau\hat{S} - \mu\hat{N}$$
$$\Downarrow$$
$$\Omega^{\tau}_{v-\mu}[n(\boldsymbol{r})] = \underbrace{T[n(\boldsymbol{r})] + U_{ee}[n(\boldsymbol{r})] - \tau S[n(r)]}_{F_M[n(\boldsymbol{r})]} + \int (v(\boldsymbol{r}) - \mu)n(\boldsymbol{r})$$

$$v(\boldsymbol{r}) \leftrightarrow n(\boldsymbol{r})$$

$$\min_{n(\boldsymbol{r})} \Omega^{\tau}_{v-\mu} \rightarrow Free\ Energy$$

N. David Mermin, Phys. Rev. **137**, A1441 – Published 1 March 1965

Introduction- Thermal Kohn-Sham DFT

$$F_M[n(r)] = (T_s[\boldsymbol{n}(\boldsymbol{r})] - \tau \boldsymbol{S}_s[\boldsymbol{n}(\boldsymbol{r})] + \boldsymbol{E}_H[\boldsymbol{n}(\boldsymbol{r})]) + F_{XC}[n(\boldsymbol{r})]$$

$$\boldsymbol{F}_{XC}[\boldsymbol{n}(\boldsymbol{r})] = (\boldsymbol{T}[\boldsymbol{n}] - \boldsymbol{T}_s[\boldsymbol{n}]) - \boldsymbol{\tau}(\boldsymbol{S}[\boldsymbol{n}] - \boldsymbol{S}_s[\boldsymbol{n}]) + (\boldsymbol{V}_{ee}[\boldsymbol{n}] - \boldsymbol{E}_H[\boldsymbol{n}])$$

$$T_s[n(r)] = \sum_i f_i \int \phi_i^*(\boldsymbol{r}) \left(-\frac{1}{2}\nabla^2\right) \phi_i(\boldsymbol{r})$$

$$E_H[n(r)] = \frac{1}{2} \iint \frac{n(r)n(r')}{|r - r'|} d^3r\, d^3r'$$

$$S_s[n(r)] = -k_B \cdot tr\left\{f_{FD}(\hat{h}) \cdot \ln f_{FD}(\hat{h}) + \left(1 - f_{FD}(\hat{h})\right) \ln\left(1 - f_{FD}(\hat{h})\right)\right\}$$
$$= -k_B \sum_i f_i \cdot \ln f_i + (1 - f_i) \cdot \ln(1 - f_i)$$

Thermal Kohn-Sham DFT Scaling

$$\{\phi(\boldsymbol{r})\}$$

$$\boldsymbol{f_i = \left(1 + e^{\beta(\epsilon_i - \mu)}\right)^{-1}}$$

$$n(r) = \sum_i f_i |\phi_i(\boldsymbol{r})|^2$$

$$\left[-\frac{1}{2}\nabla^2 + v_s(r)\right]\phi_i(\boldsymbol{r}) = \epsilon_i \phi_i(\boldsymbol{r})$$

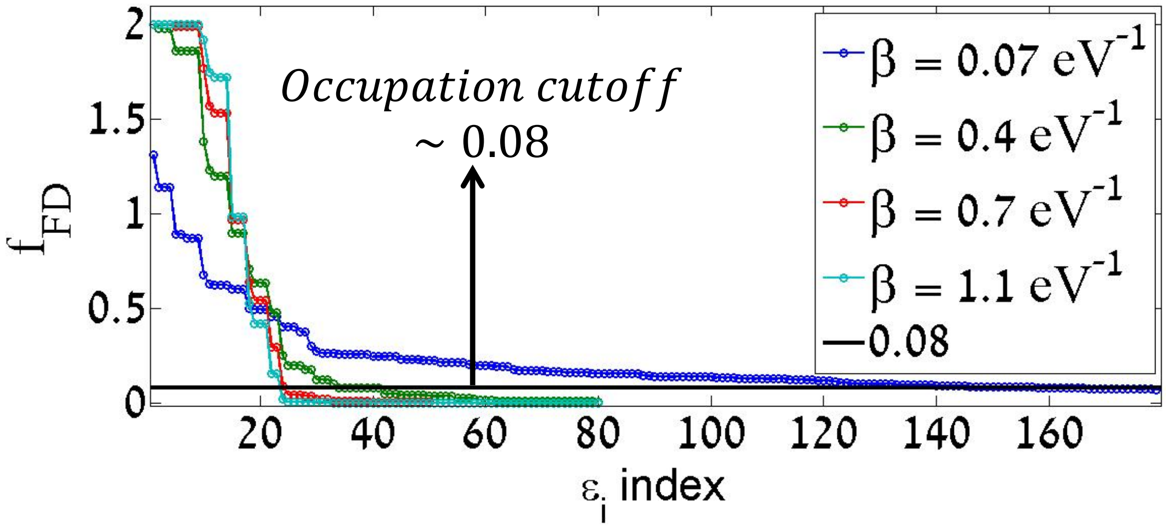
$$v_s(\boldsymbol{r}) = v_H[n](\boldsymbol{r}) + v_{XC}[n](\boldsymbol{r}) + v(\boldsymbol{r})$$

$$\langle \phi_i | \hat{h} | \phi_j \rangle$$

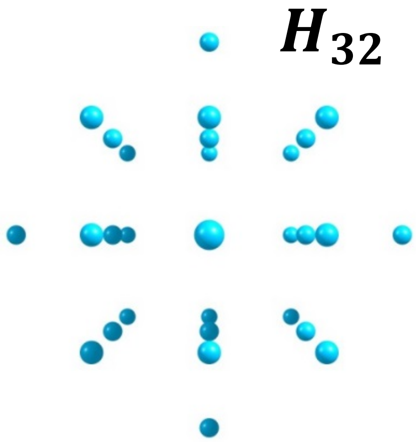
$$\propto N_g \log N_g \cdot N_{occ}^2$$

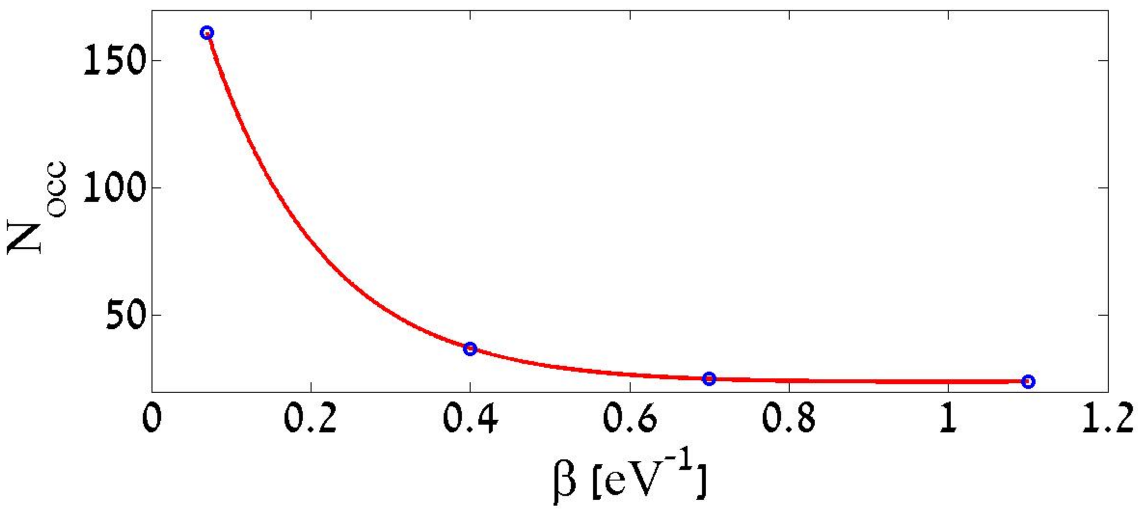
$$Diagonalization \;\; \propto N_{occ}^3$$

Thermal Kohn-Sham dDFT
Occupied States



$$f_i = \left(1 + e^{\beta(\epsilon_i - \mu)}\right)^{-1}$$





Kohn-Sham Orbital-Free DFT

$$Scaling \propto System\ Size$$

Orbital-Free DFT:

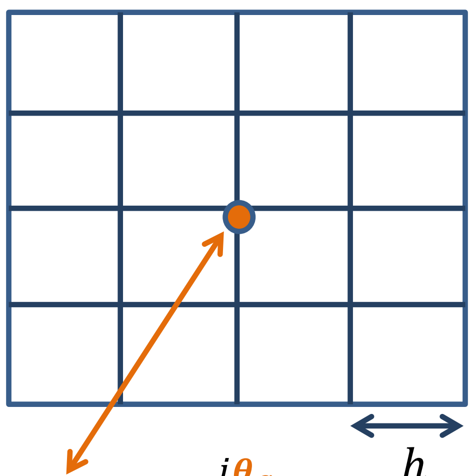
Corrections to Thomas-Fermi for kinetic energy

Stochastic DFT:

$$\hat{h} \rightarrow \{\phi_i\} \rightarrow n(\boldsymbol{r})$$

R. Baer, D. Neuhauser, E. Rabani "Self-averaging stochastic Kohn-Sham density functional theory", Phys. Rev. Lett. 111, 106402 (2013)

Stochastic representation of the unit operator



$$\chi(r_g) = \frac{e^{i\theta_g}}{\sqrt{h^3}}$$

Random val. $[0,2\pi]$

$$|\chi_m\rangle = \sum_i \alpha_i^m |\psi_i\rangle$$

$$\alpha_i^m = \langle\psi_i|\chi_m\rangle = \sum_g h^3 \psi^*(r_g)\left(\frac{e^{i\theta_g}}{\sqrt{h^3}}\right)$$

$$\langle\alpha_i^m \alpha_j^m\rangle = \sum_{g,g'} h^3 \psi_i^*(r_g)\psi_j(r_{g'})\underbrace{\left\langle e^{i\left(\theta_g^m - \theta_{g'}^m\right)}\right\rangle}_{\delta_{g,g'}}$$

$$= \sum_g h^3 \psi_i^*(r_g)\psi_j(r_g) = \delta_{i,j}$$

$$\langle|\chi\rangle\langle\chi|\rangle = \frac{1}{M}\sum_m^{M\to\infty} |\chi_m\rangle\langle\chi_m| = \sum_{i,j}\langle\alpha_i^*\alpha_j\rangle|\psi_j\rangle\langle\psi_i| = \sum_i |\psi_i\rangle\langle\psi_i| = \hat{I}$$

Stochastic TDFT- Trace

$$tr\{\hat{A}\} = tr\{\langle|\chi\rangle\langle\chi|\rangle\hat{A}\} =$$

$$\frac{1}{M}\sum_{m}\sum_{i}\langle\psi_i|\chi_m\rangle\langle\chi_m|A|\psi_i\rangle =$$

$$\frac{1}{M}\sum_{m}\sum_{i}\langle\chi_m|A|\psi_i\rangle\langle\psi_i|\chi_m\rangle =$$

$$\frac{1}{M}\sum_{m}\langle\chi_m|A|\chi_m\rangle = \langle\langle\chi|A|\chi\rangle\rangle$$

M. F. Hutchinson, Comm. Stat., Simul. and Comp., 19, 433 (1990)

Stochastic TDFT- Trace

$$\hat{A} \rightarrow f_{FD}(\hat{h})\hat{n}(\boldsymbol{r})$$

$$n(\boldsymbol{r}) = tr\{f_{FD}(\hat{h})\hat{n}(\boldsymbol{r})\} = \langle\langle\chi|f_{FD}(\hat{h})\hat{n}(\boldsymbol{r})|\chi\rangle\rangle$$

$$|\zeta\rangle = \sqrt{f_{FD}(\hat{h})}|\chi\rangle$$

$$\Downarrow$$

$$\langle\langle\zeta|\hat{n}(\boldsymbol{r})|\zeta\rangle\rangle = n(\boldsymbol{r})$$

Stochastic TDFT- SCF

$$|\zeta_m\rangle = \sqrt{f_{FD}(\hat{h})}|\chi_m\rangle$$

Expansion using Chebyshev

Rescaling $\mathrm{h}, \beta, \mu \rightarrow [-1,1]$

$\boldsymbol{\kappa} \propto \boldsymbol{\beta \Delta E}$ *

$$\sqrt{f_{FD}(\hat{h}_s)} = \sum_{n=0}^{\kappa} \alpha(\mu_s, \beta_s) T_n(\hat{h}_s)$$

$$\langle\zeta|n(\boldsymbol{r})|\zeta\rangle = n_m(\boldsymbol{r})$$

✕ $\boldsymbol{M}$

$$n(\boldsymbol{r}) = \frac{1}{M}\sum_{m}^{M} n_m(\boldsymbol{r})$$

* R. Baer and M. Head-Gordon,"Electronic structure of large systems: coping with small gaps using the energy renormalization group method", J. Chem. Phys. 109, 10159 (1998).

Stochastic TDFT-SCF

$$E + -\tau S + -\mu N$$

$$\Omega_{\mathrm{new}} - \Omega_{old} \leq tolerance\,?$$

no

yes

$$|\zeta_m\rangle = \sqrt{f_{FD}(\hat{h})}|\chi_m\rangle$$

Done!

Stochastic TDFT-
Free Energy Calculation

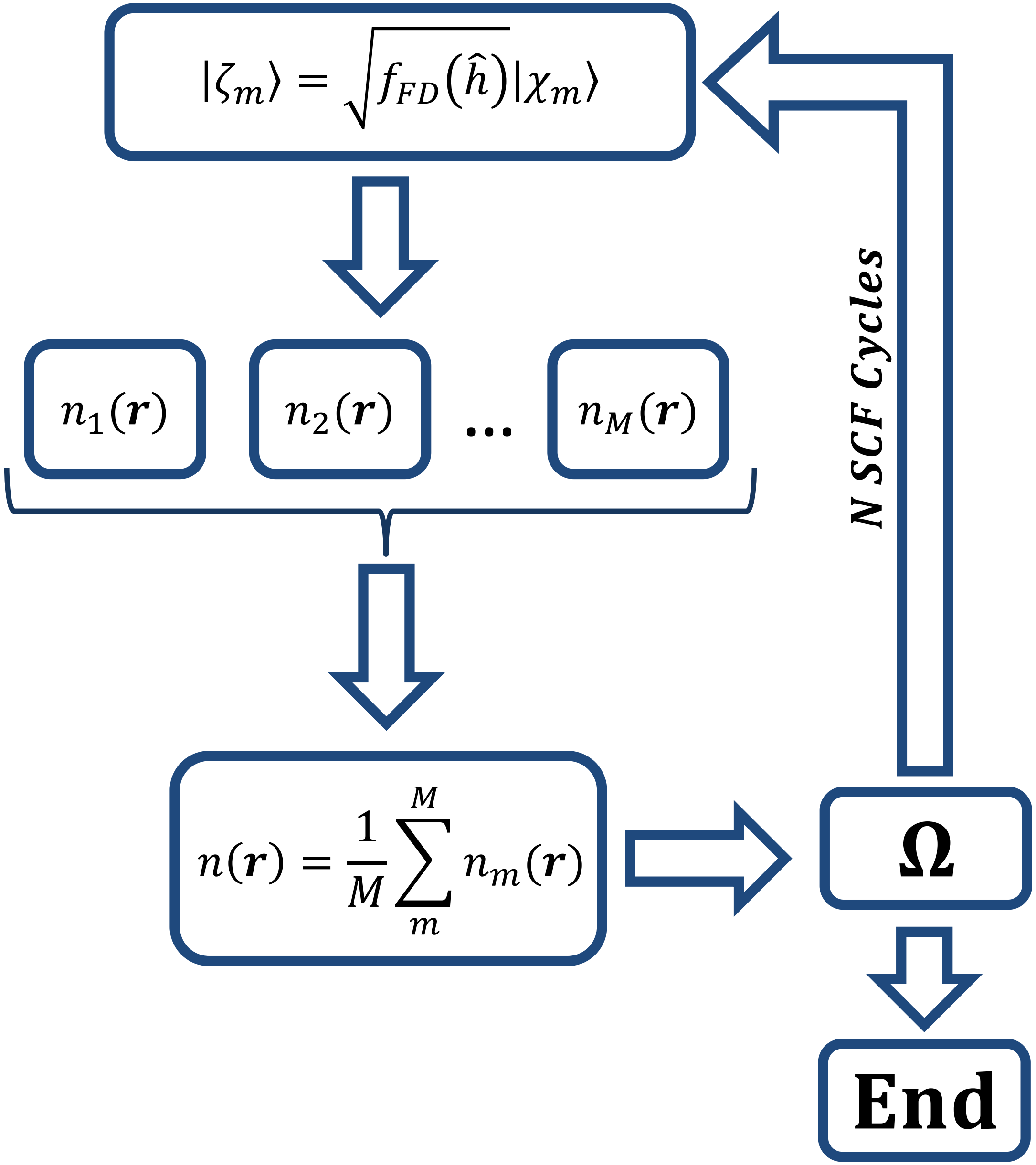
$$\Omega = \boldsymbol{T_s} - \tau S_s + \int n(r)(v(r) - \mu) d^3 r + E_H[n] + E_{XC}[n]$$

$$\boldsymbol{n(r) = \langle \langle \zeta | \delta(r - \hat{r}) | \zeta \rangle \rangle = \langle \zeta(r)^2 \rangle}$$

$$\boldsymbol{T_s = \left\langle \langle \zeta | \hat{T} | \zeta \rangle \right\rangle = -\frac{1}{2m} \left\langle \langle \zeta | \nabla^2 \zeta \rangle \right\rangle}$$

$$\boldsymbol{S_s = \langle \langle \chi | f \ln f + (1 - f) \ln (1 - f) | \chi \rangle \rangle}$$

Expected Scaling



Scaling

Applying Chebyshev $\propto \boldsymbol{\kappa}$

⨯

Applying Hamiltonian $\propto N_g \log N_g$

⨯

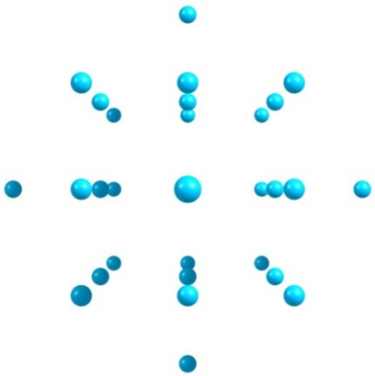
Stochastic Orbitals M

⨯

SCF Cycles N

Linear Scaling

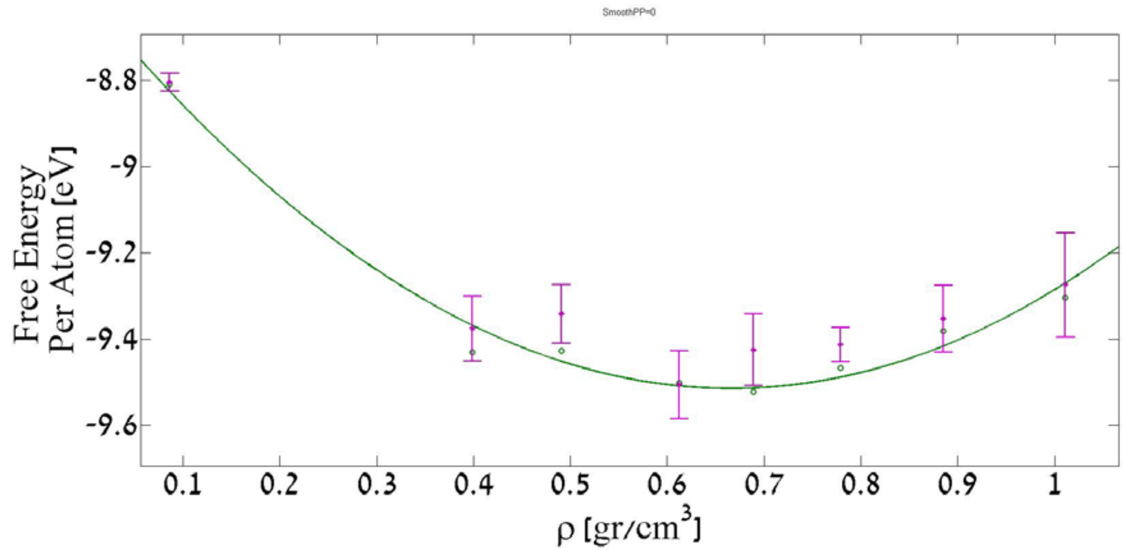
sDFT vs. dDFT for H_{32} Cluster

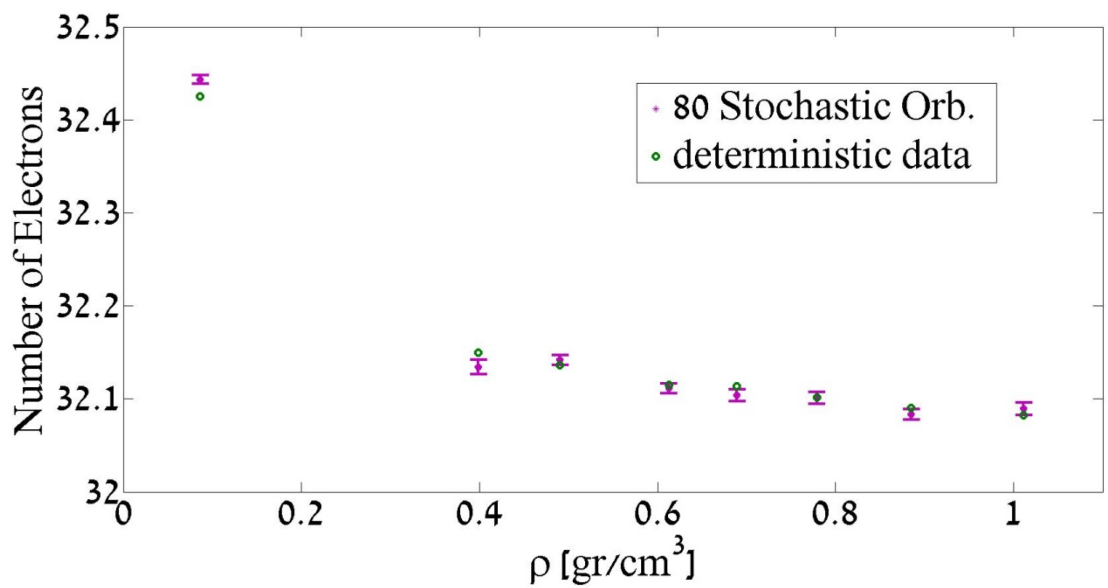


$\beta = 20 E_h^{-1}$

$\tau = 1.6 \cdot 10^4 K$

$\mu = -0.2\ E_h$





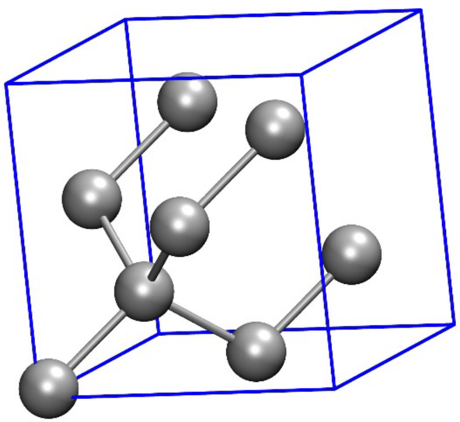
Convergence with M: Si at Γ point

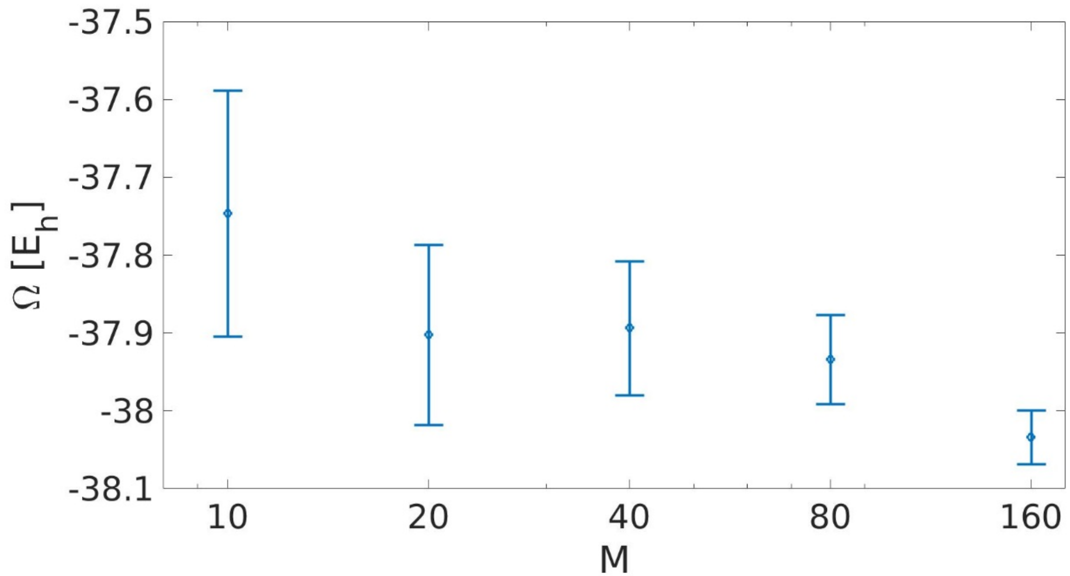
$$\beta = 40\ E_h^{-1}$$

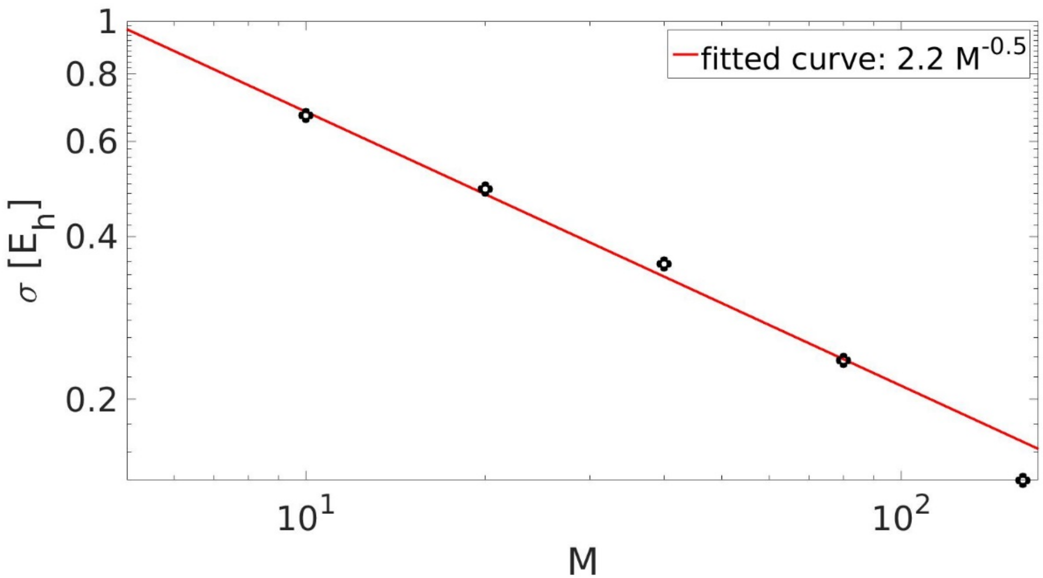
$$\tau = 7.9 \cdot 10^3\ K$$

$$\mu = 0.2 E_h$$

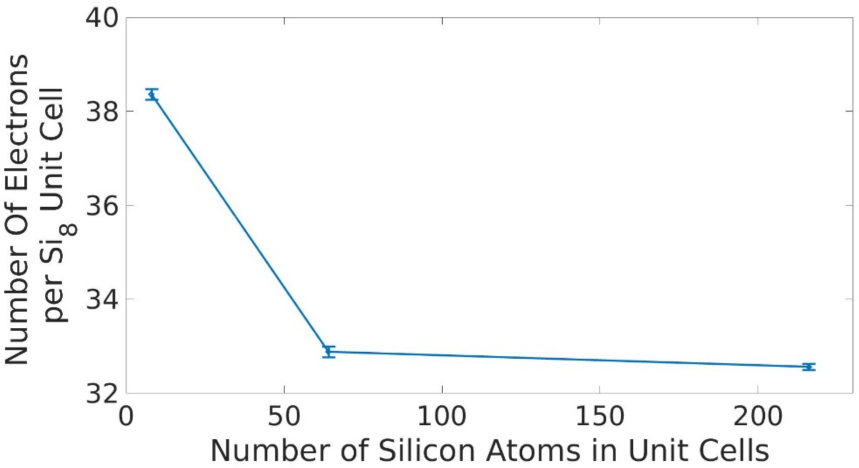
$$lattice\ constant = 10.6\ a_0$$

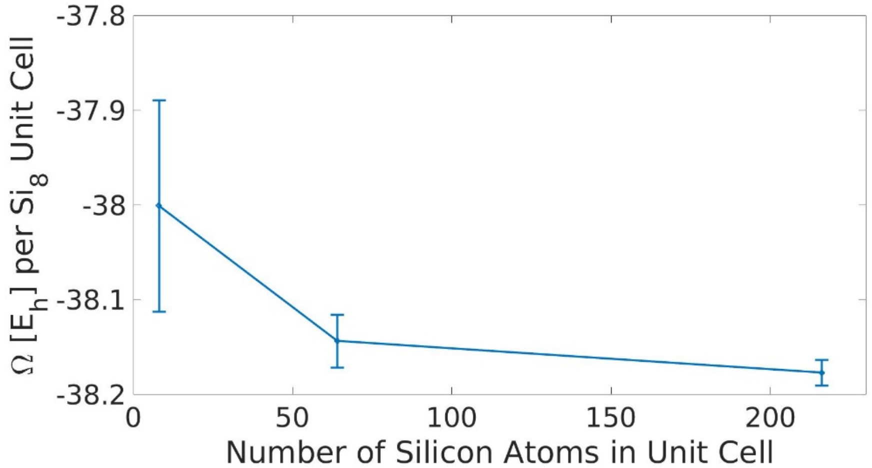


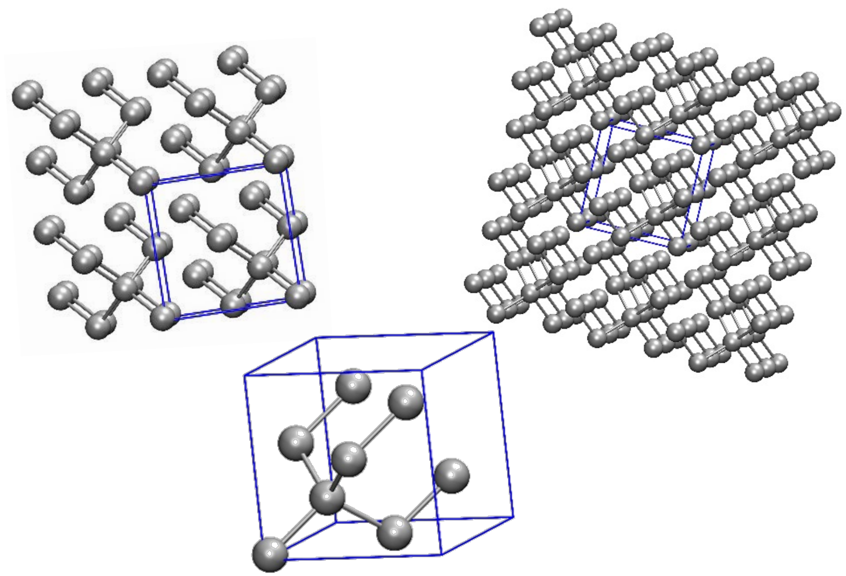


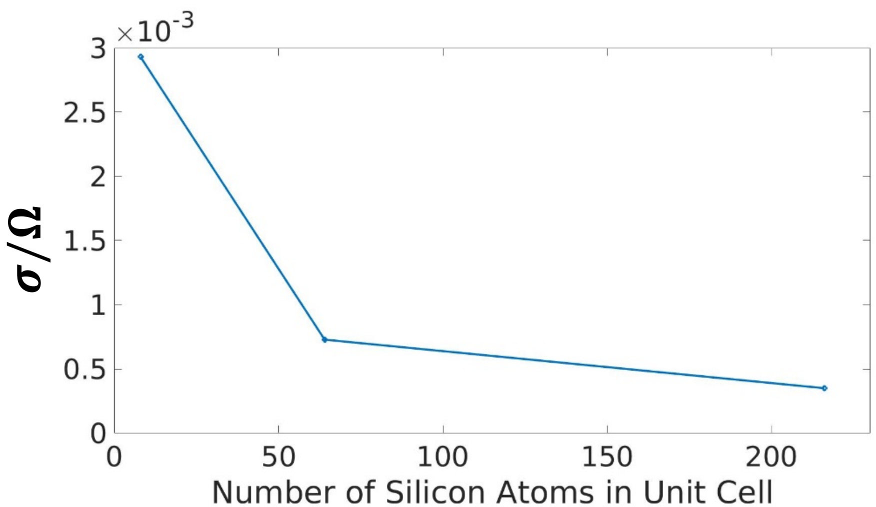


Convergence of Γ point calculation as function of system size

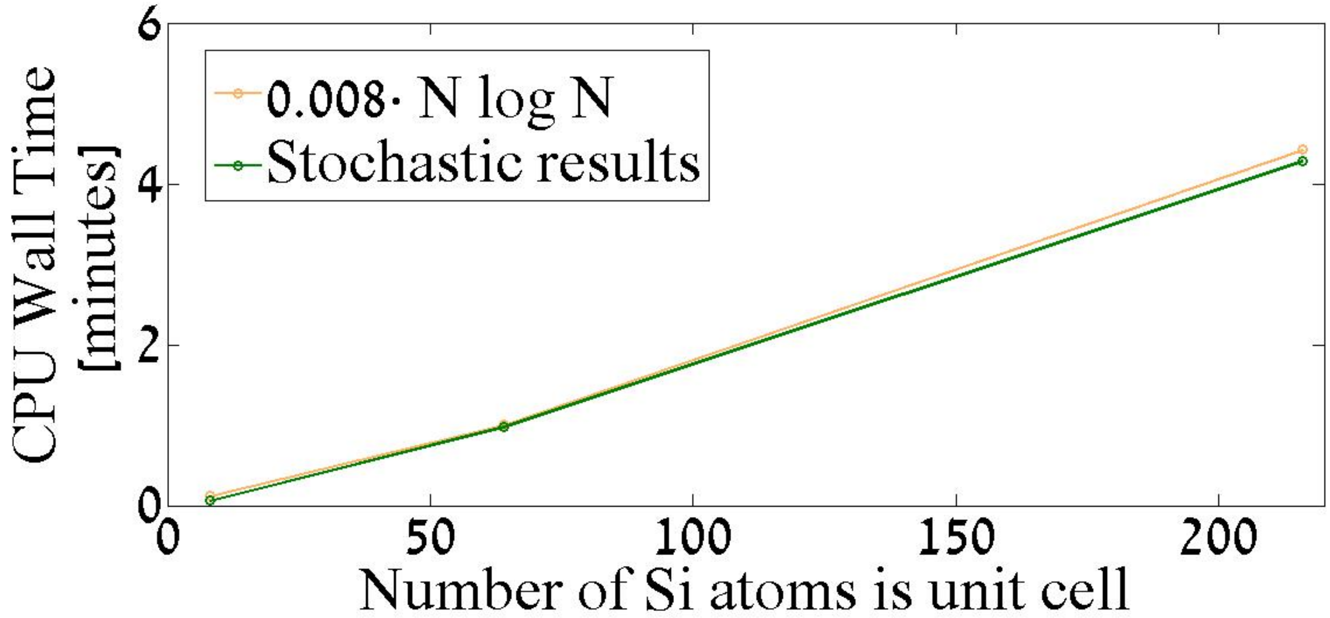




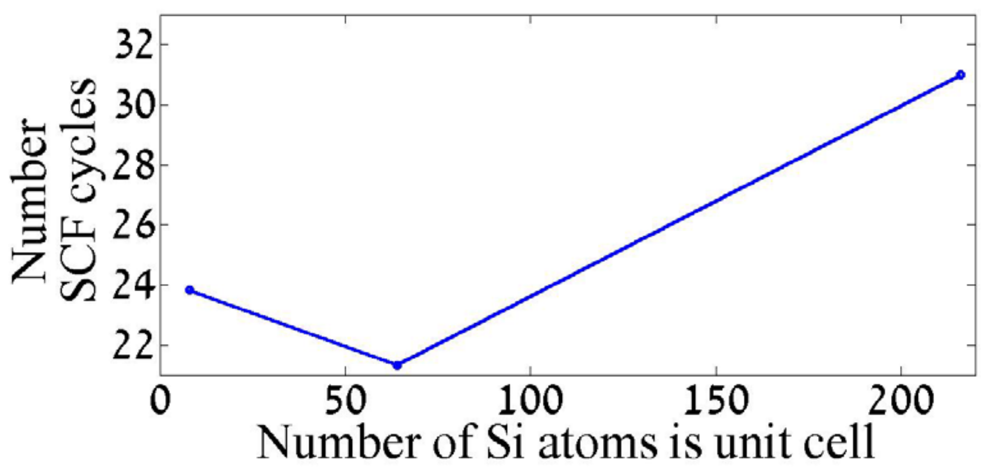




Scaling as a function of System size



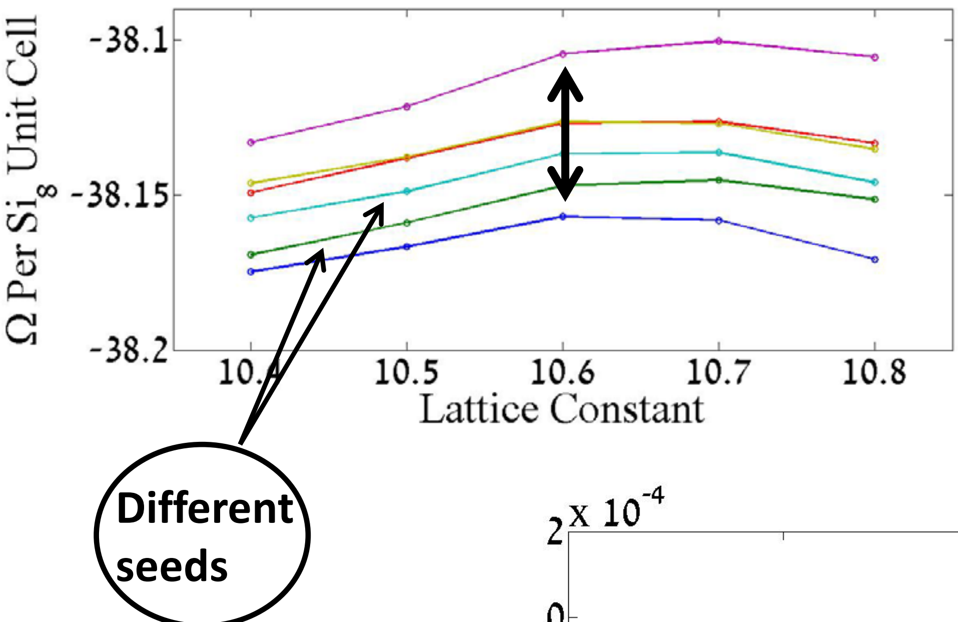
80 Stochastic Orbitals

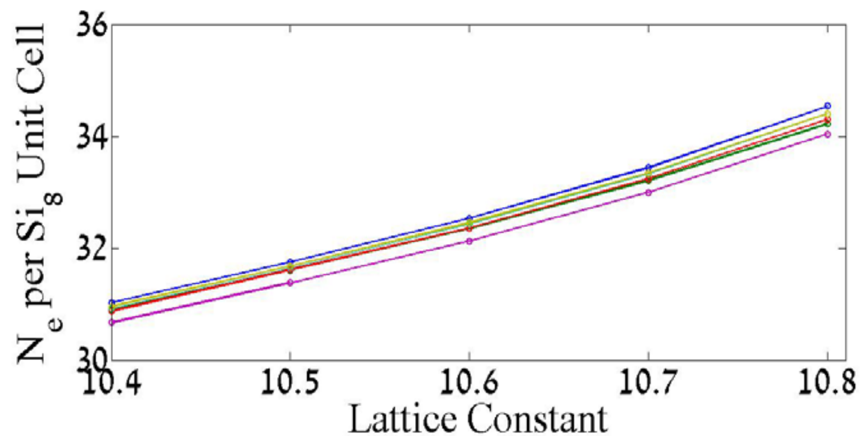


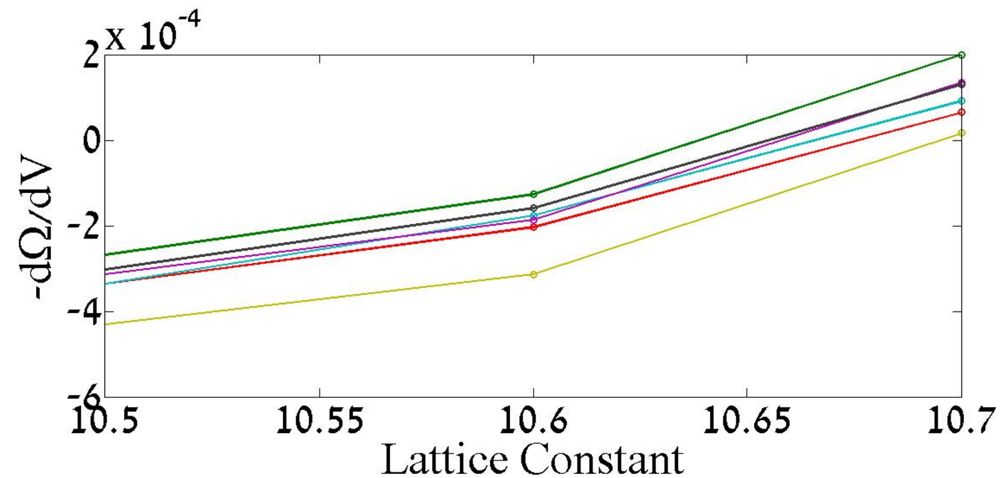
✓ **Linear Scaling**

Preliminary results: $\Omega(V), \Omega'(V)$

$$M = 80$$
$$\beta = 40\ E_h^{-1}, \mu = 0.2\ E_h$$







Conclusions & Future Plans

- **Linear-scaling calculation (or better) of free-energy using sDFT**
- **More efficient the higher the temperature**
- **Error controlled by number of stochastic orbitals**
- **Enable calculation of equation of state** $p(\beta, \mu)$

Future Plans:

- **Mean force calculations for nuclear dynamics**
- **Calculations of impurities (perhaps using the fragment method)**
- **Implement a "more suitable" XC functional for finite temperature**
- **Suggestions are welcome!**