Towards efficient excited state calculations at high temperatures with mixed deterministic-stochastic hybrid exchange

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Center for Nonlinear Studies Postdoctoral Fellow
T-1 / CNLS
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Los Alamos
NATIONAL LABORATORY

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Acknowledgments

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Center for Nonlinear Studies

U.S. DEPARTMENT OF ENERGY

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My Background

Postdoc 2 – LANL
T1/CNLS
2023-Present

Los Alamos
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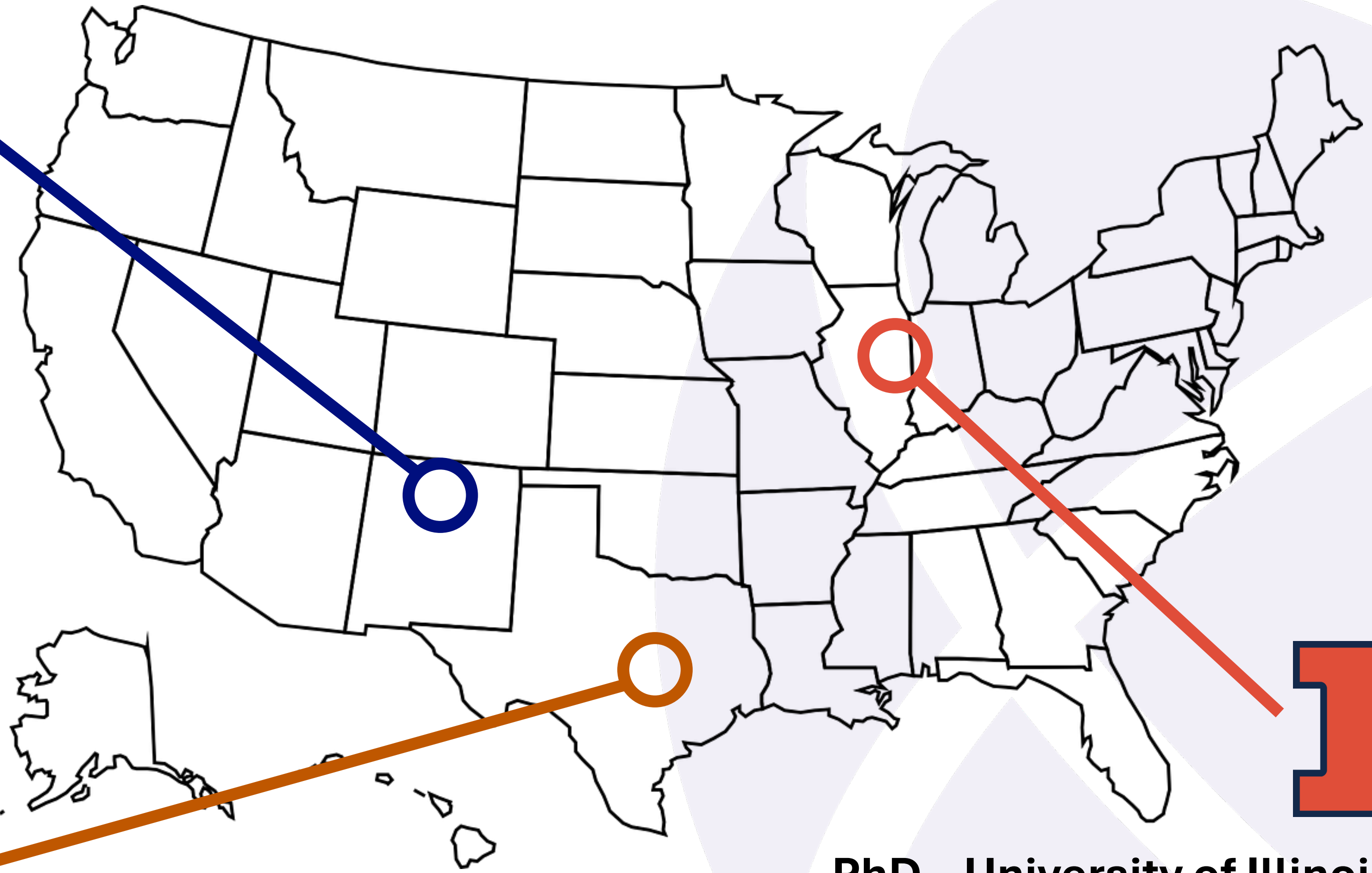
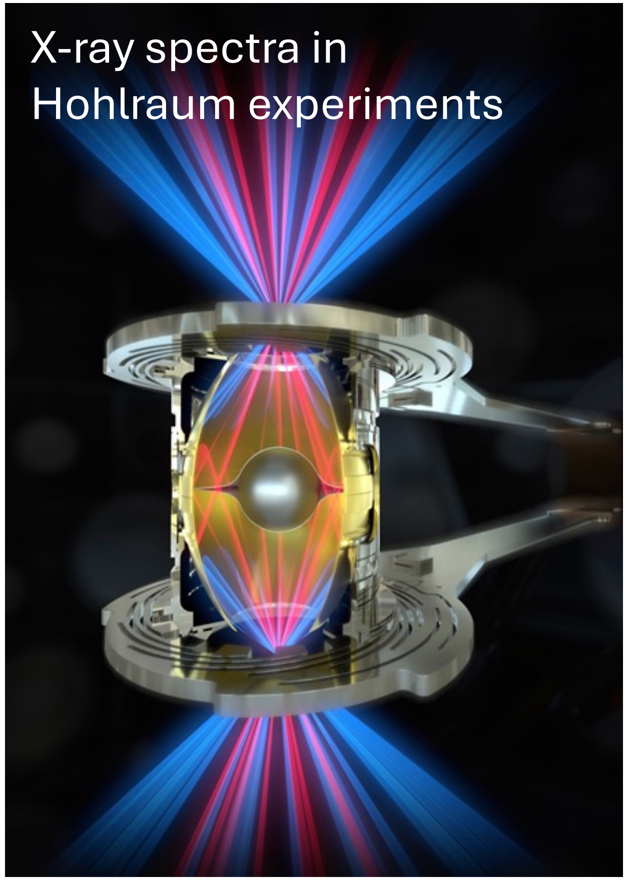


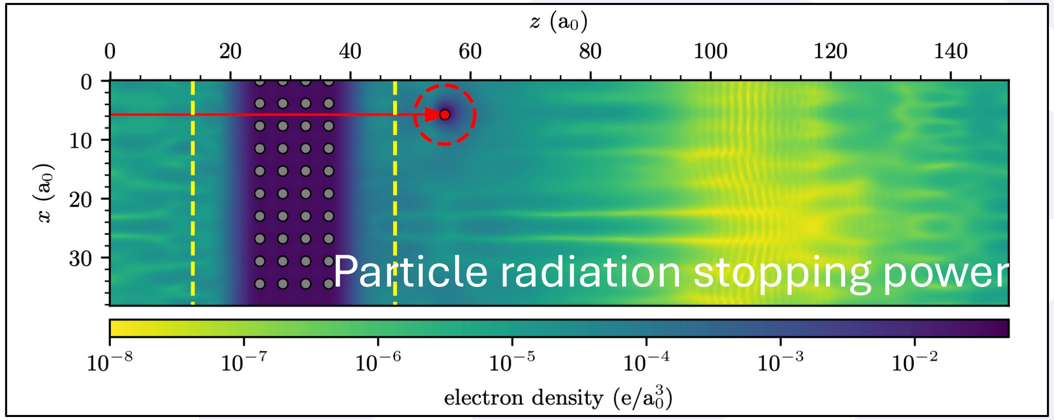
TEXAS
The University of Texas at Austin

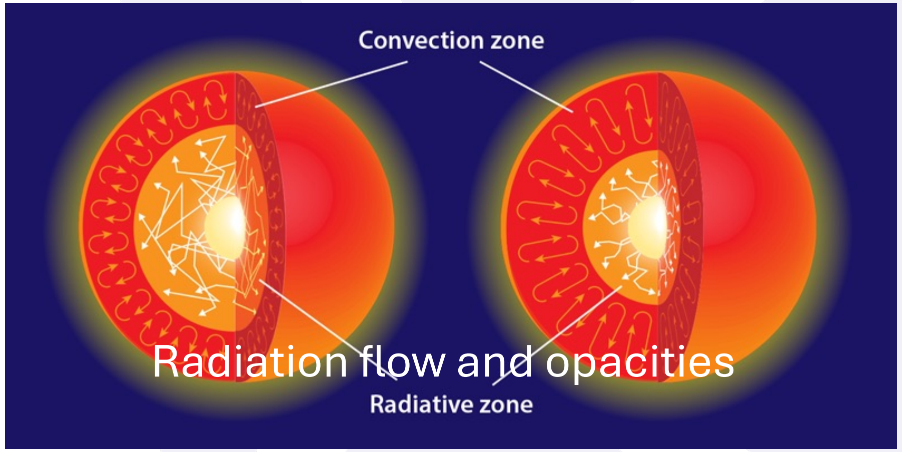
Postdoc 1 – University of Texas, Austin
Physics + The Oden Institute
2020-2023

PhD – University of Illinois, Urbana-Champaign
Materials Science and Engineering
2014-2019

Excited state physics in hot materials/matter





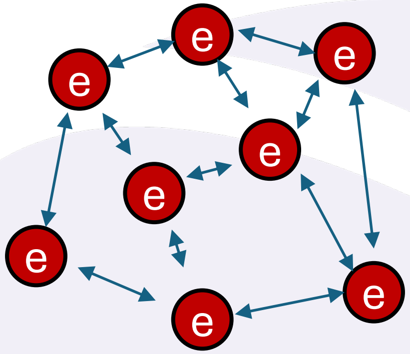


Kononov and Schleife, *Phys. Rev. B.*, 102, 165401 (2020)

https://physics.aps.org/articles/v12/65
https://lasers.llnl.gov/news/rugby-hohlraum-kicks-up-nif-energy-efficiency

Foundation for this work – density functional theory (DFT)

Schrödinger Equation
Linear PDE describing many-electron state, fully interacting



$$\hat{H}\Psi_n(\mathbf{r}_1, ..., \mathbf{r}_{N_e}) =$$

$$\left[-\frac{1}{2}\sum_{i=1}^{N_e}\nabla^2 + \sum_{i}^{N_e}\sum_{I}^{N_N}\frac{Ze}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i}^{N_e}\sum_{j\neq i}^{N_e}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}\right]\Psi_n(\mathbf{r}_1, ..., \mathbf{r}_{N_e}) = E_n\Psi_n(\mathbf{r}_1, ..., \mathbf{r}_{N_e})$$

Kohn and Sham, *Phys. Rev.,* 140, A1133 (1965)

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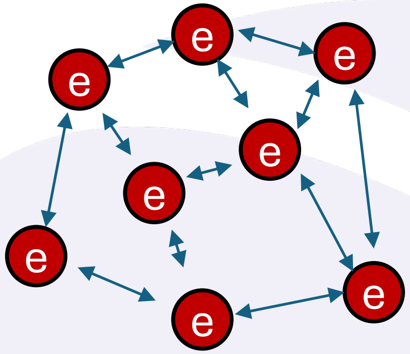

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Density Functional Theory (DFT) – Define an auxiliary system that shares the same ground state energy and density

Kohn and Sham, *Phys. Rev.,* 140, A1133 (1965)

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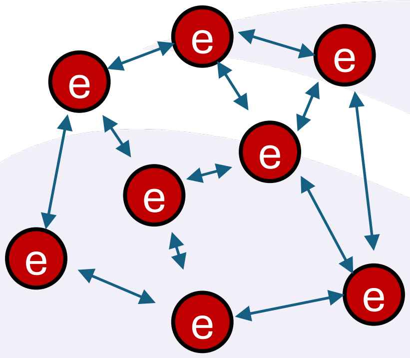

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Kohn-Sham Equation
Nonlinear set of equations to solve for single particle states in ***mean field***

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}[\rho(\mathbf{r})] + e^2\int d\mathbf{r}'\frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[\rho(\mathbf{r})]\right)\phi_n(\mathbf{r}) = \epsilon_n\phi_n(\mathbf{r})$$

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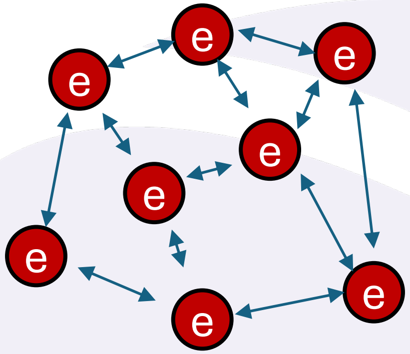

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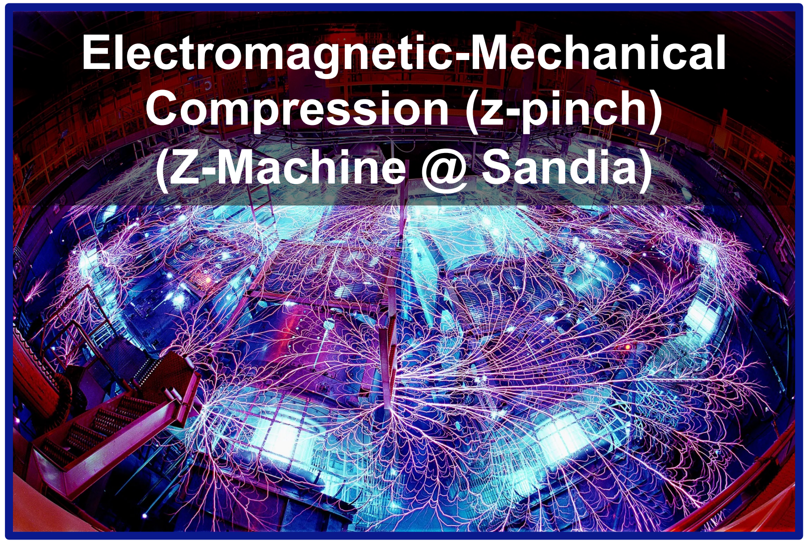
$$\hat{H}_{\text{KS}}\phi_n(\mathbf{r}) = \epsilon_n\phi_n(\mathbf{r})$$

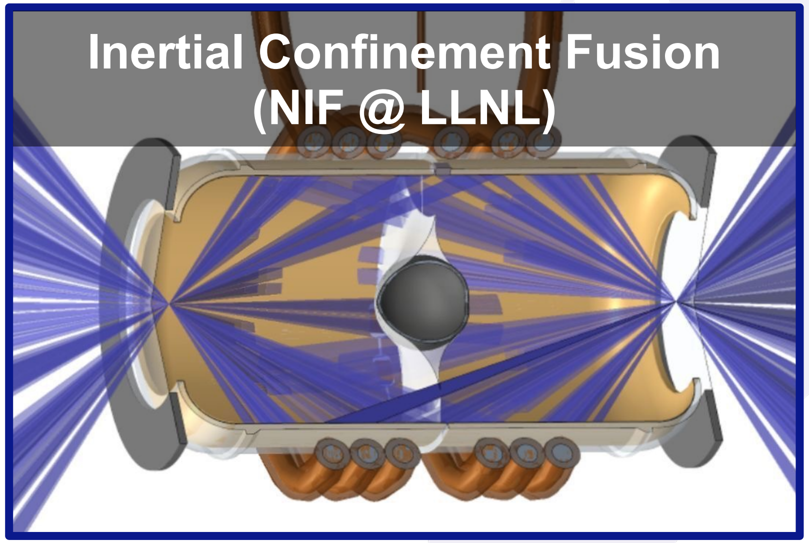
Eigenvalue Equation
Deterministic DFT (dDFT)

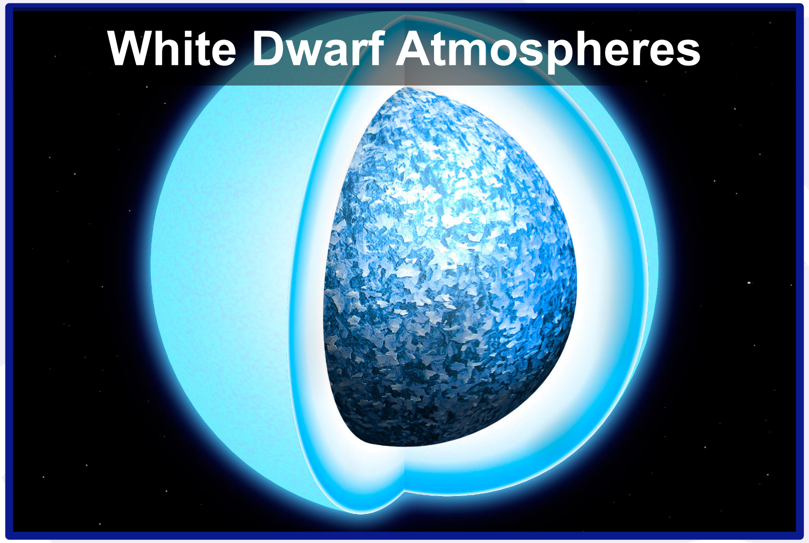
Kohn and Sham, *Phys. Rev.,* 140, A1133 (1965)

Finite temperature DFT

Can we utilize DFT to study states of matter at extreme temperatures and densities?







Mermin, *Phys. Rev.*, 137, 5A (1965)

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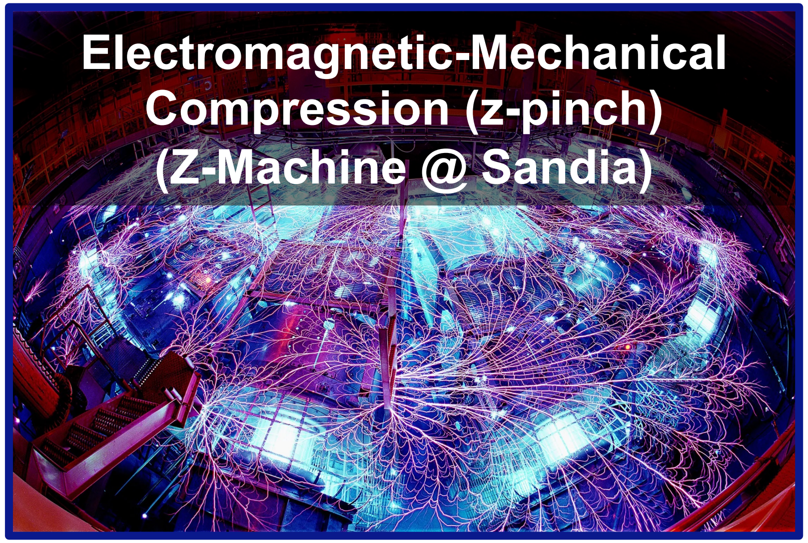
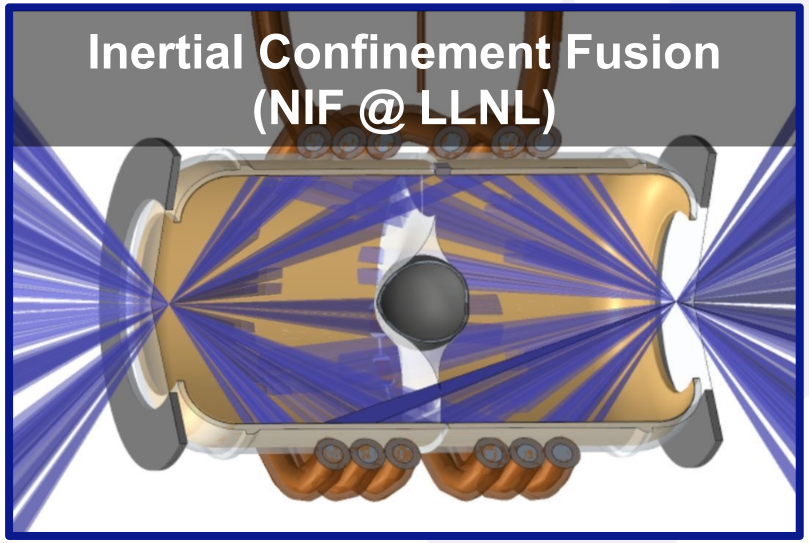
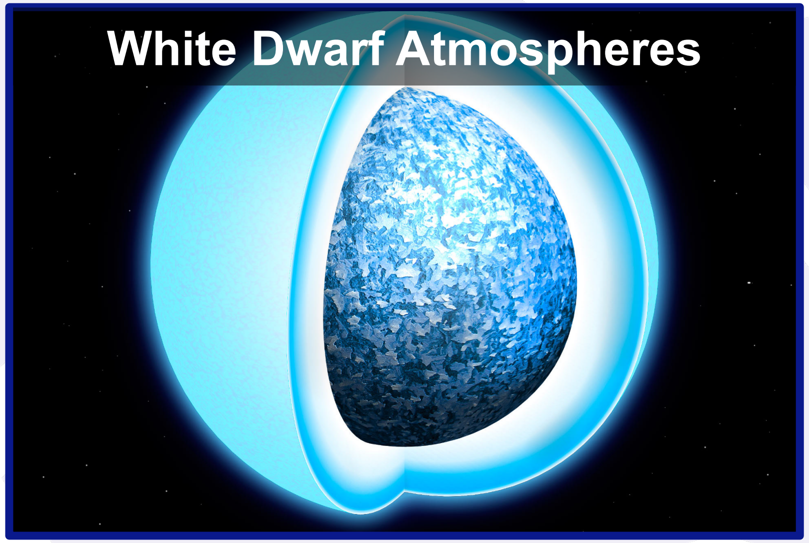




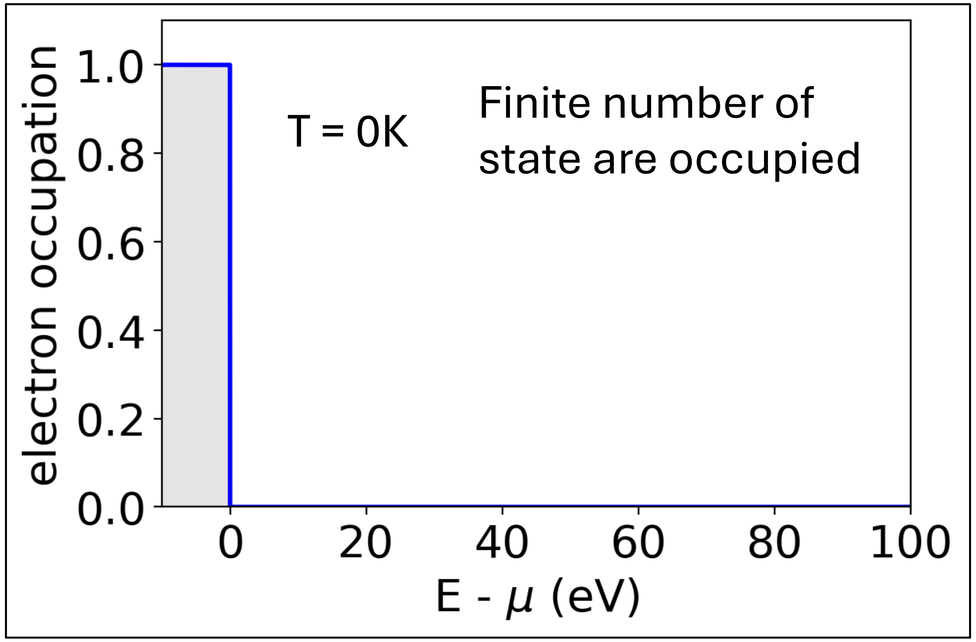


Yes! We can use the Mermin extension of DFT

Mermin, *Phys. Rev.*, 137, 5A (1965)

Temperature scaling of deterministic DFT

$$\hat{H}_{\mathrm{KS}}\phi_n(\mathbf{r}) = \epsilon_n\phi_n(\mathbf{r})$$



$$\rho(\mathbf{r}) = \sum_{n}^{N_{occ}} \phi_n^*(\mathbf{r})\phi_n(\mathbf{r})$$

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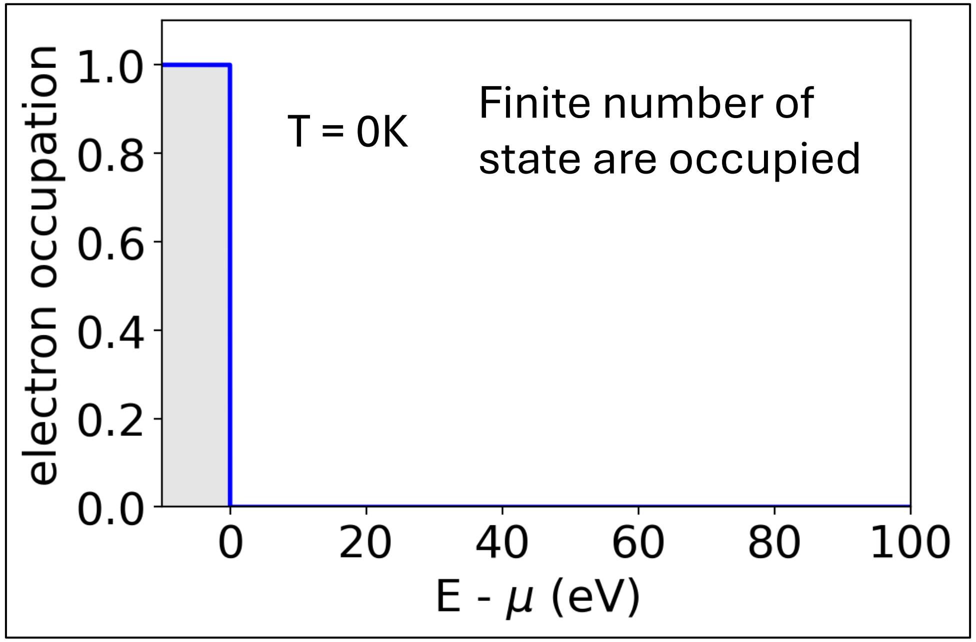

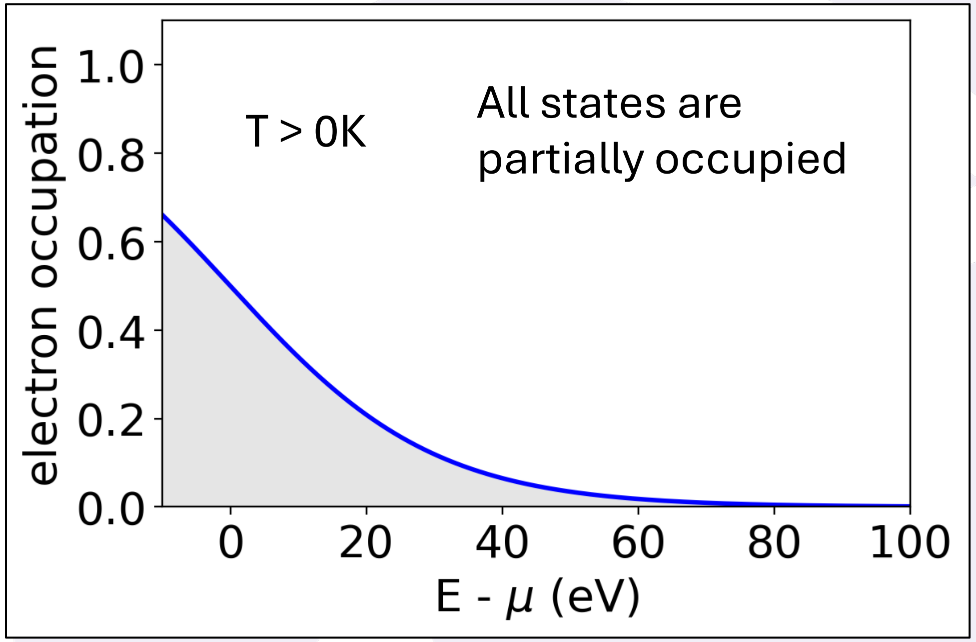

$$\rho(\mathbf{r}) = \sum_n^{N_{occ}} \phi_n^*(\mathbf{r})\phi_n(\mathbf{r}) \qquad \rho(\mathbf{r},T) = \sum_n^{\infty} f_n(T,\mu)\phi_n^*(\mathbf{r})\phi_n(\mathbf{r}) \approx \sum_n^{N_{\rm conv.}} f_n(T,\mu)\phi_n^*(\mathbf{r})\phi_n(\mathbf{r})$$

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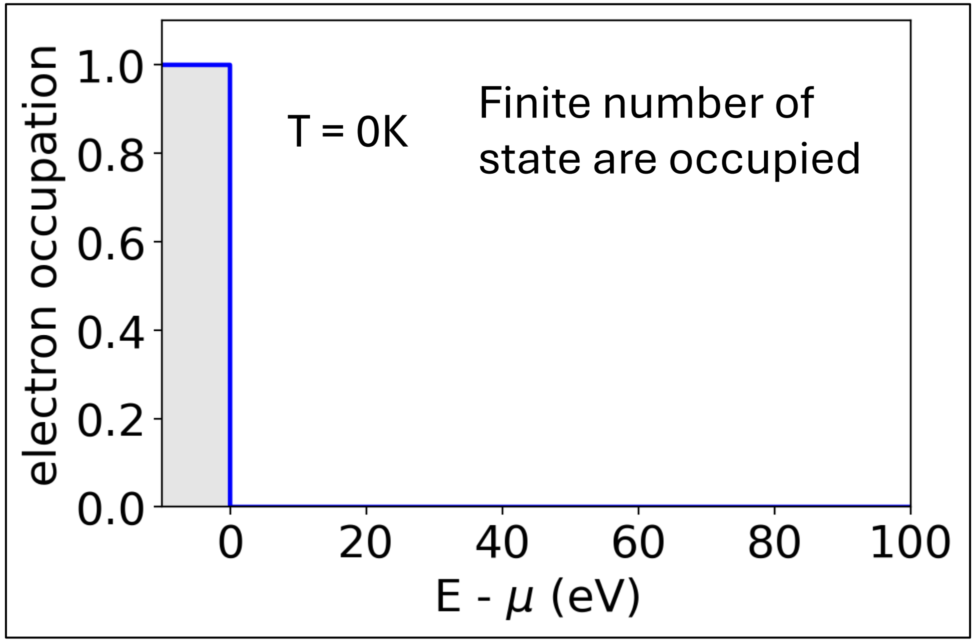

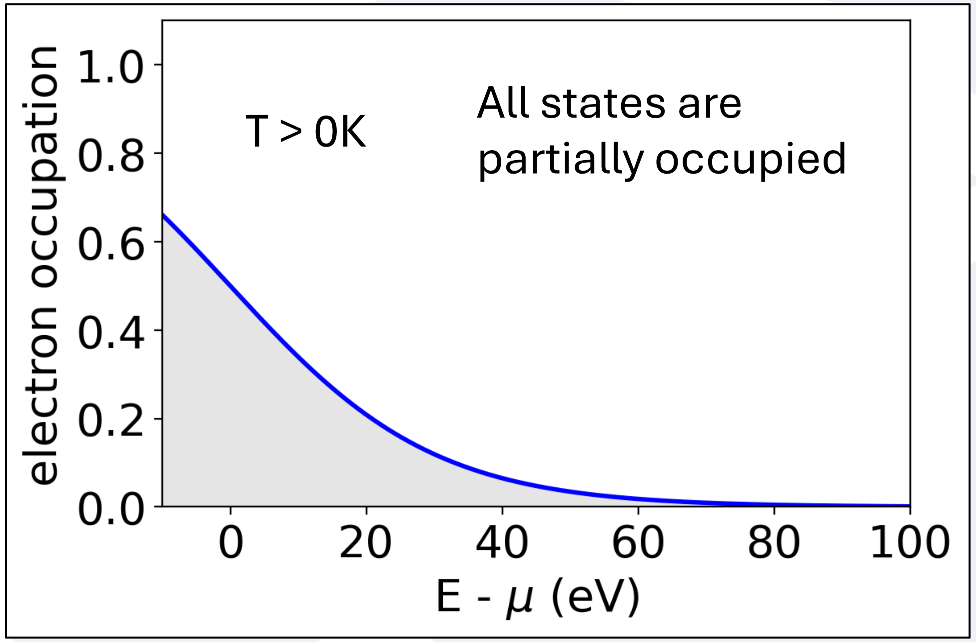

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Need to compute and orthogonalize many more eigenvalue/vectors of KS Hamiltonian

dDFT scales ~O(T^3)

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How can we overcome cubic temperature scaling in dDFT?

If we want to compute an observable associated with an operator in the single-particle DFT formalism, we can use either the ***KS Wavefunctions*** ***or*** the ***Density Matrix***.

$$\langle \hat{O} \rangle = \sum_n^{\infty} f_n(T,\mu) \langle \phi_n | \hat{O} | \phi_n \rangle = \mathrm{Tr}[\hat{\rho}(\hat{H},T,\mu)\hat{O}]$$

Fabien *at al.*, *WIREs Comp. Mol. Sci.* (2019)

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If we are okay with predicting the observables to within some finite degree of accuracy, we can approximate the trace – **Stochastic Resolution of a Matrix Trace**

$$\mathrm{Tr}[\mathbf{M}] \approx \frac{1}{N_\alpha} \sum_{\alpha=1}^{N_\alpha} \vec{\chi}_\alpha^T \mathbf{M} \vec{\chi}_\alpha$$

Fabien ***at al.***, *WIREs Comp. Mol. Sci.* (2019)

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Finally, we can recast the trace over a density matrix times an observable by:

$$\mathrm{Tr}[\hat{\rho}\hat{O}] \approx \frac{1}{N_\alpha} \sum_{\alpha=1}^{N_\alpha} (\hat{\rho}\vec{\chi}_\alpha)^T \hat{O} \vec{\chi}_\alpha$$

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We need to compute a matrix vector multiplication without computing the actual matrix

$$\hat{\rho}(\hat{H}, T, \mu) = (e^{\beta(\hat{H}-\mu)} + 1)^{-1}$$

Fabien ***at al.***, *WIREs Comp. Mol. Sci.* (2019)

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We need to compute a matrix vector multiplication without computing the actual matrix

$$\hat{\rho}(\hat{H},T,\mu) = (e^{\beta(\hat{H}-\mu)}+1)^{-1}$$

This can be approximate through a Chebyshev expansion with cost ~O(T^{-1})

$$\hat{\rho}\vec{\chi} = \sum_{l=0}^{N_c} a_l(T)\chi^l$$

$$\chi^0 = \vec{\chi} \rightarrow \chi^1 = \hat{H}\chi^0 \rightarrow \chi^{l+1} = 2\hat{H}\chi^l - \chi^{l-1}$$

Fabien **at al.**, *WIREs Comp. Mol. Sci.* (2019)

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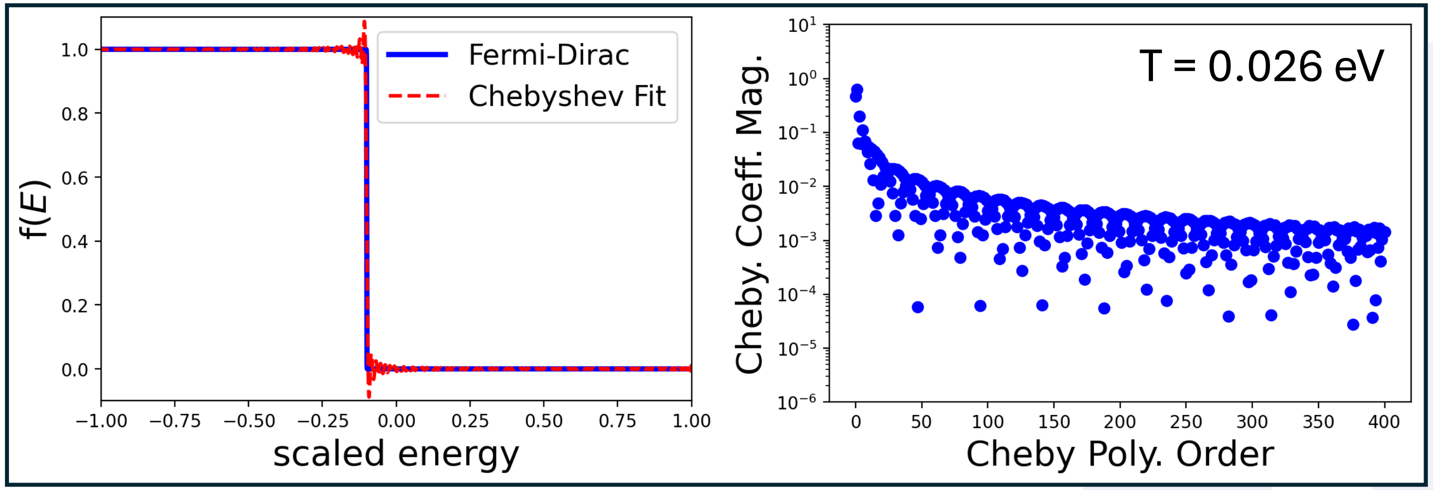
Inverse temperature scaling for Chebyshev expansion



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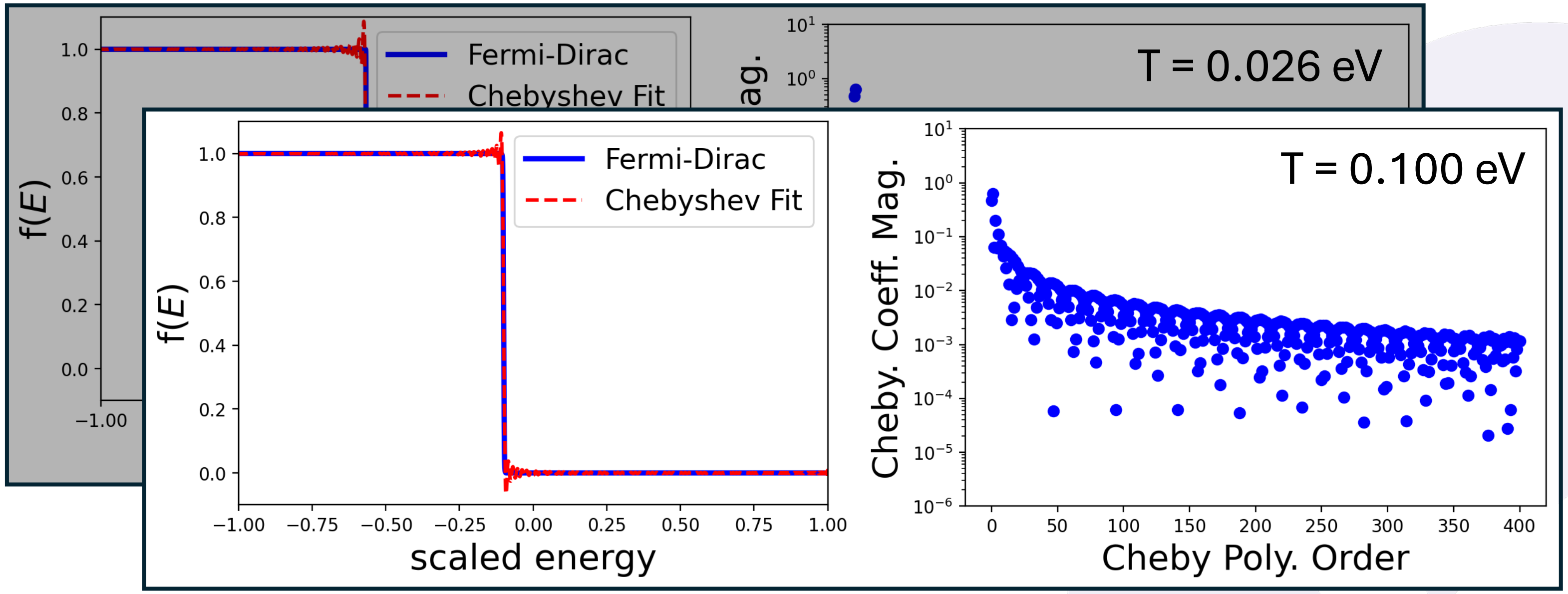

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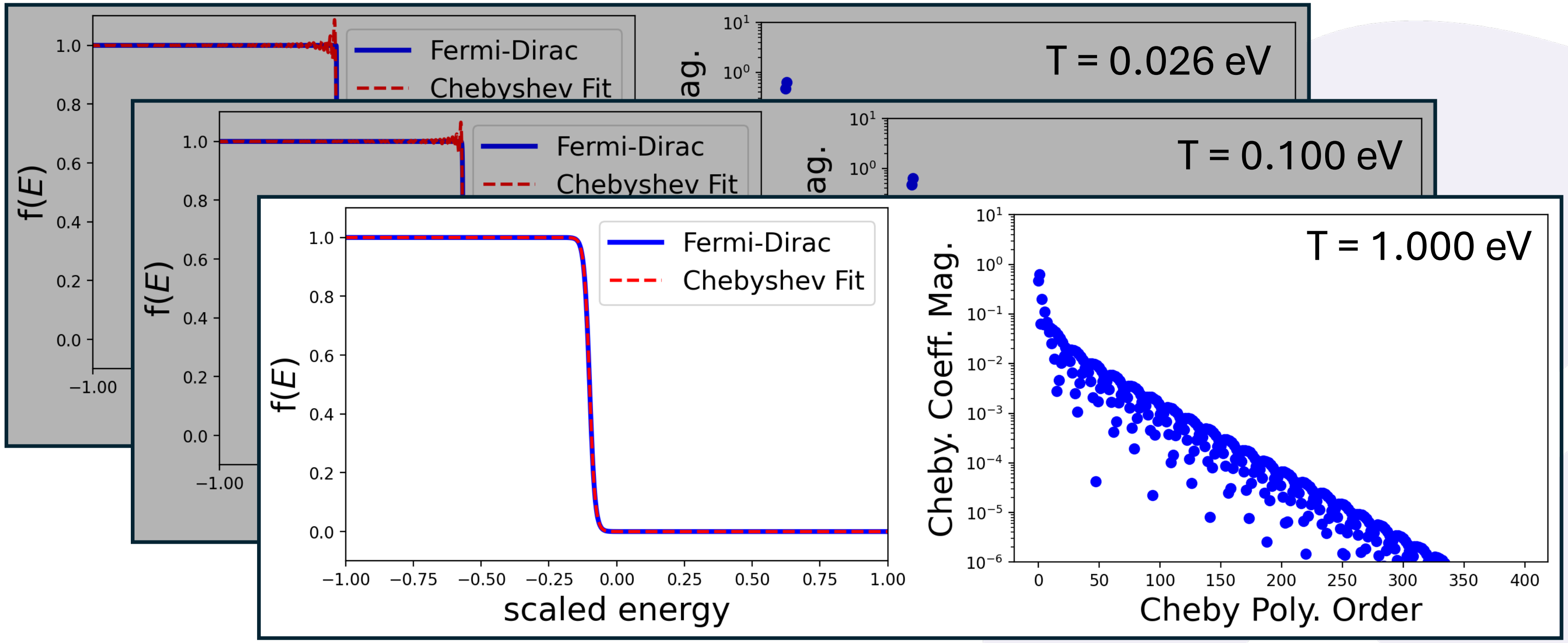

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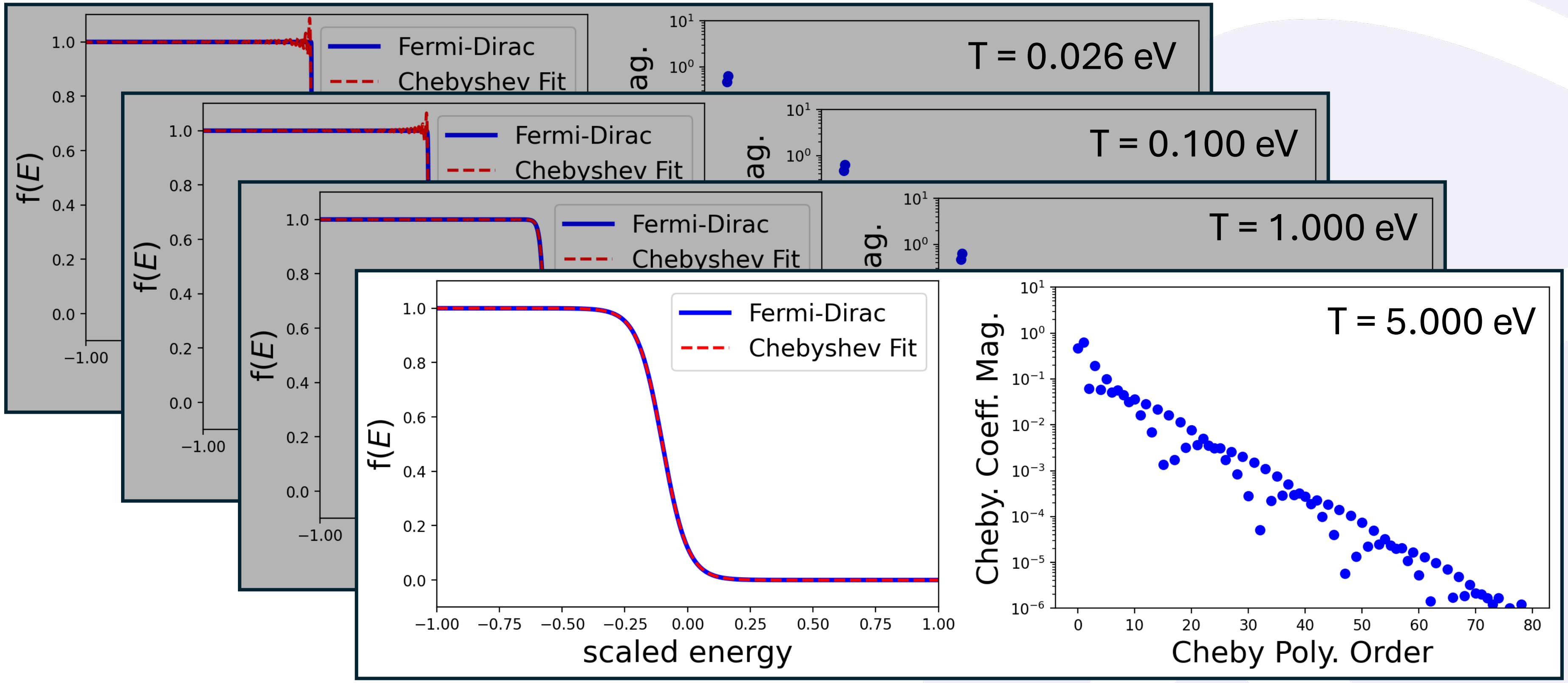

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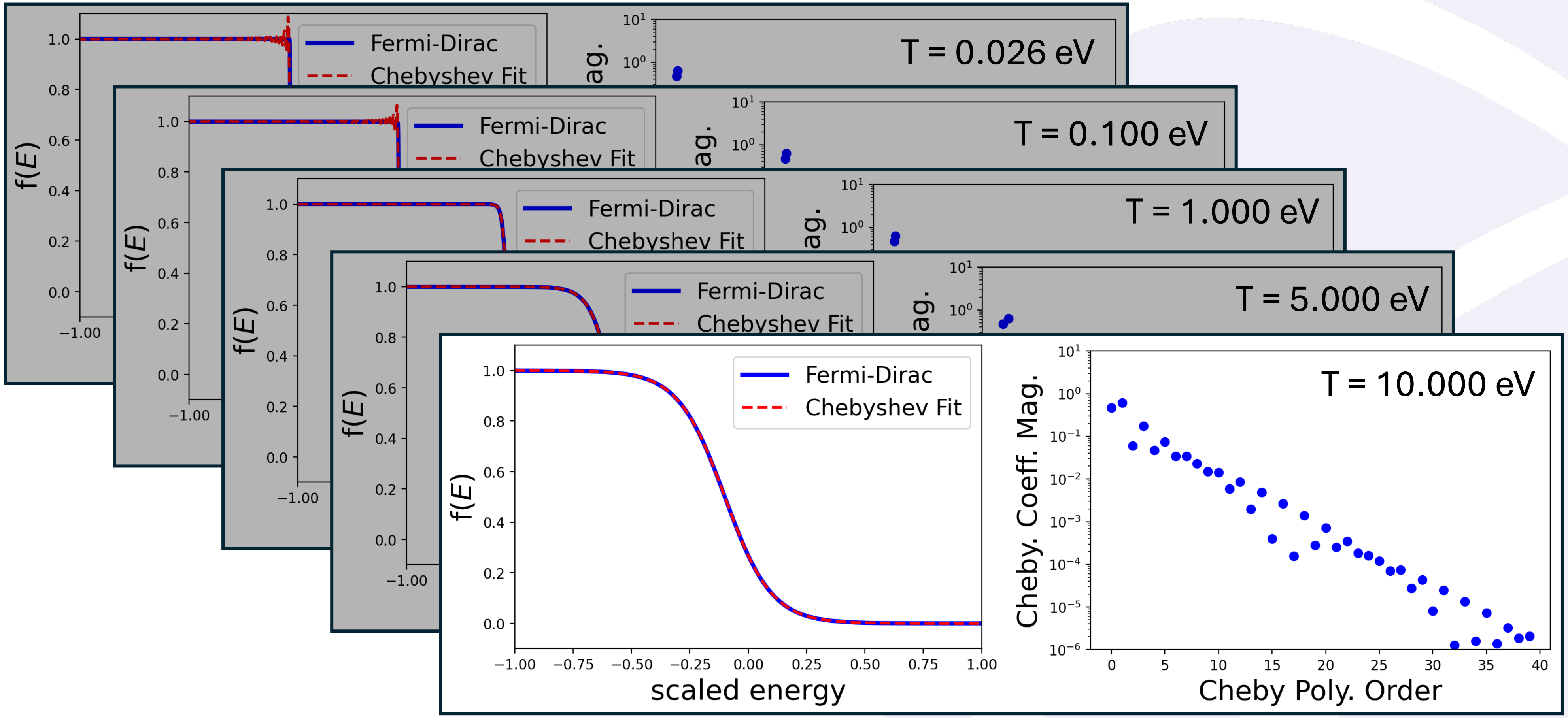

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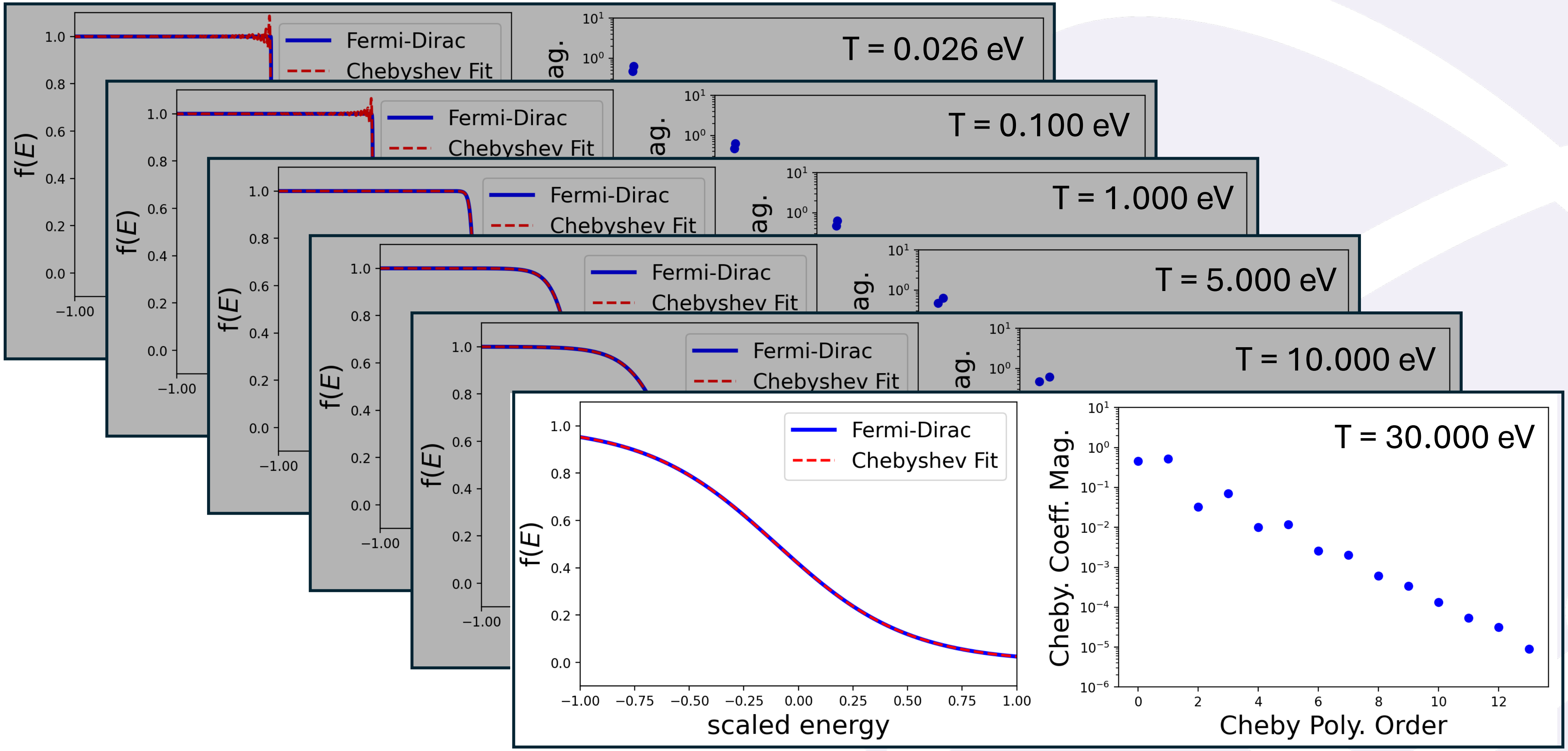

SCF Scheme

1. Guess Density $\rho(\mathbf{r})$

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2. Compute Hamiltonian

$$\hat{H} = \left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}[\rho(\mathbf{r})] + e^2 \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[\rho(\mathbf{r})] \right)$$

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3. Deterministic calculation of electron density – scales as ~O(n³) ~ T³

Eigenvalue Solve

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}[\rho(\mathbf{r})] + e^2 \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{\text{xc}}[\rho(\mathbf{r})] \right) \longrightarrow (\phi_n(\mathbf{r}), \epsilon_n) \longrightarrow \rho(\mathbf{r}) = \sum_n f_n(T)\phi_n^*(\mathbf{r})\phi_n(\mathbf{r})$$

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4. Compute the energy as a functional of the density

$$E_0[\rho(\mathbf{r})] = \hat{T}[\phi(r)] + \int d\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) + \frac{e^2}{2}\int d\mathbf{r} \int \mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|r-r'|} + E_{\text{xc}}[\rho(\mathbf{r})]$$

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SCF Cycle

3. Deterministic calculation of electron density – scales as ~O(n^3) ~ T^3

Eigenvalue Solve

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}[\rho(\mathbf{r})] + e^2 \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{\text{xc}}[\rho(\mathbf{r})] \right) \longrightarrow (\phi_n(\mathbf{r}), \epsilon_n) \longrightarrow \rho(\mathbf{r}) = \sum_n f_n(T)\phi_n^*(\mathbf{r})\phi_n(\mathbf{r})$$

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5. Is the energy converged to a minimum?

- If yes, **STOP…You're Done!**
- If no, feed density back into Hamiltonian, repeat

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SCF Scheme

1. Guess Density $\rho(\mathbf{r})$

2. Compute Hamiltonian

$$\hat{H} = \left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}[\rho(\mathbf{r})] + e^2 \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{\text{xc}}[\rho(\mathbf{r})] \right)$$

SCF Cycle

3. Stochastic calculation of electron density – scales as ~O(N_c) and ~T^{-1}

$$\hat{\rho}_0(T)\vec{\chi} = \sum_{l=0}^{N_C} a_l(T)\chi^l \qquad \chi^0 = \vec{\chi} \rightarrow \chi^1 = \hat{H}\chi^0 \rightarrow \chi^{l+1} = 2\hat{H}\chi^l - \chi^{l-1}$$

$$\rho(\mathbf{r}) \approx \sum_{\alpha=1}^{N_\alpha} (\hat{\rho}_0\vec{\chi}_{\alpha,\mathbf{r}})^T \vec{\chi}_{\alpha,\mathbf{r}'}\delta^3(\mathbf{r}-\mathbf{r}')$$

4. Compute the energy as a functional of the density

$$E_0[\rho(\mathbf{r})] = \hat{T}[\vec{\chi}(\mathbf{r})] + \int d\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) + \frac{e^2}{2}\int d\mathbf{r} \int \mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\text{xc}}[\rho(\mathbf{r})]$$

5. Is the energy converged to a minimum?

- If yes, **STOP…You're Done!**
- If no, feed density back into Hamiltonian, repeat

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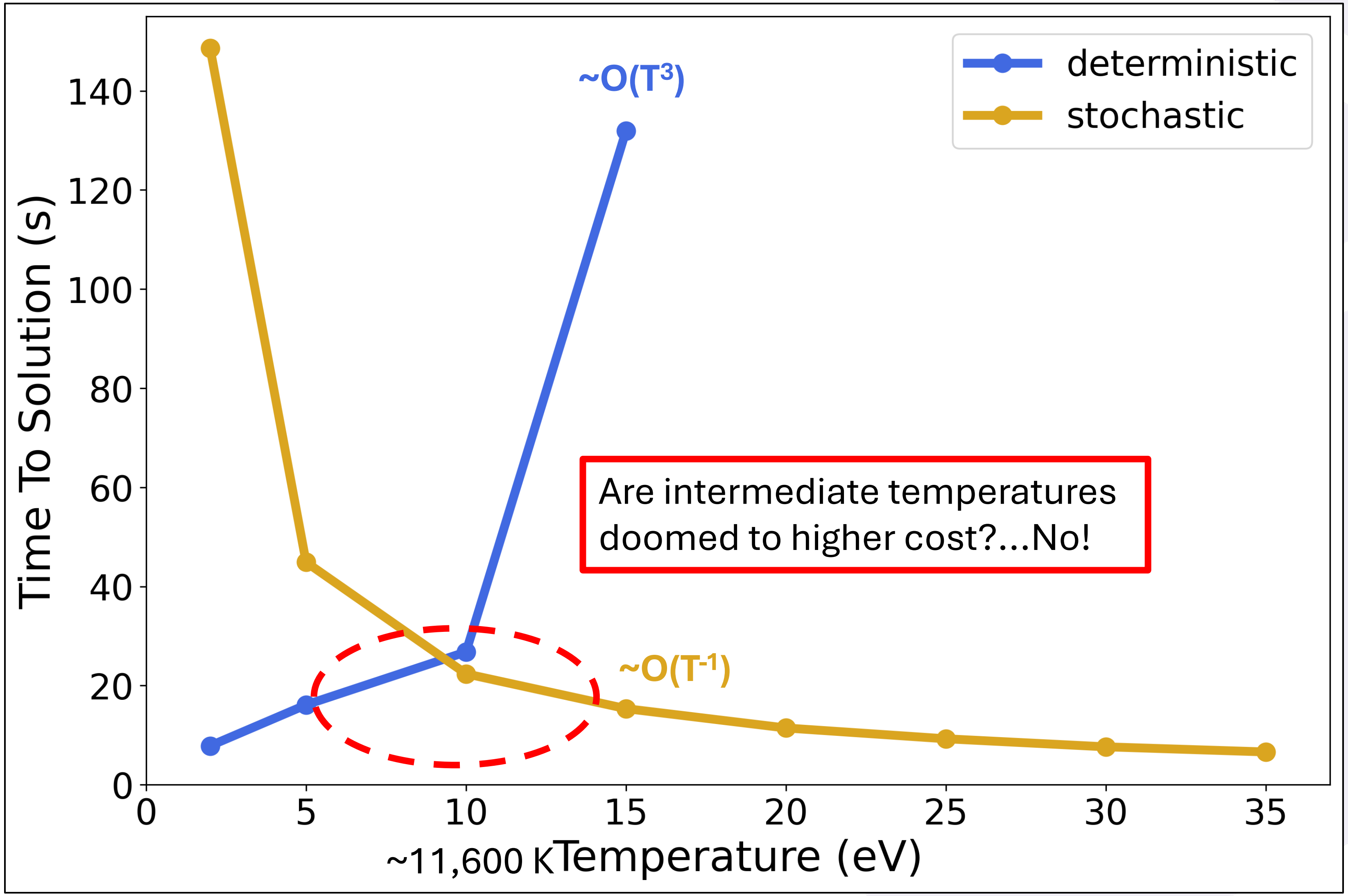
Efficiency of sDFT with temperature



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Can we mix dDFT with sDFT? Yes, and we get mixed DFT (mDFT)

$$\psi \subset \{\phi, \tilde{X}\}$$

Partially occupied deterministic

Thermally filtered stochastic

White and Collins *Phys. Rev. Lett.*, 125, 055002 (2020)

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Project random vectors out of deterministic subspace

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$$\tilde{\chi}_b = \chi_b - \sum_{n}^{N_\phi} c_{ab}\phi_a$$

Thermally filter by applying square root of density matrix to unfiltered out-projected random vectors (Chebyshev expansion)

$$\tilde{X}_b = \sqrt{\hat{\rho}(\hat{H}, T, \mu)}\tilde{\chi}_b$$

White and Collins *Phys. Rev. Lett.*, 125, 055002 (2020)

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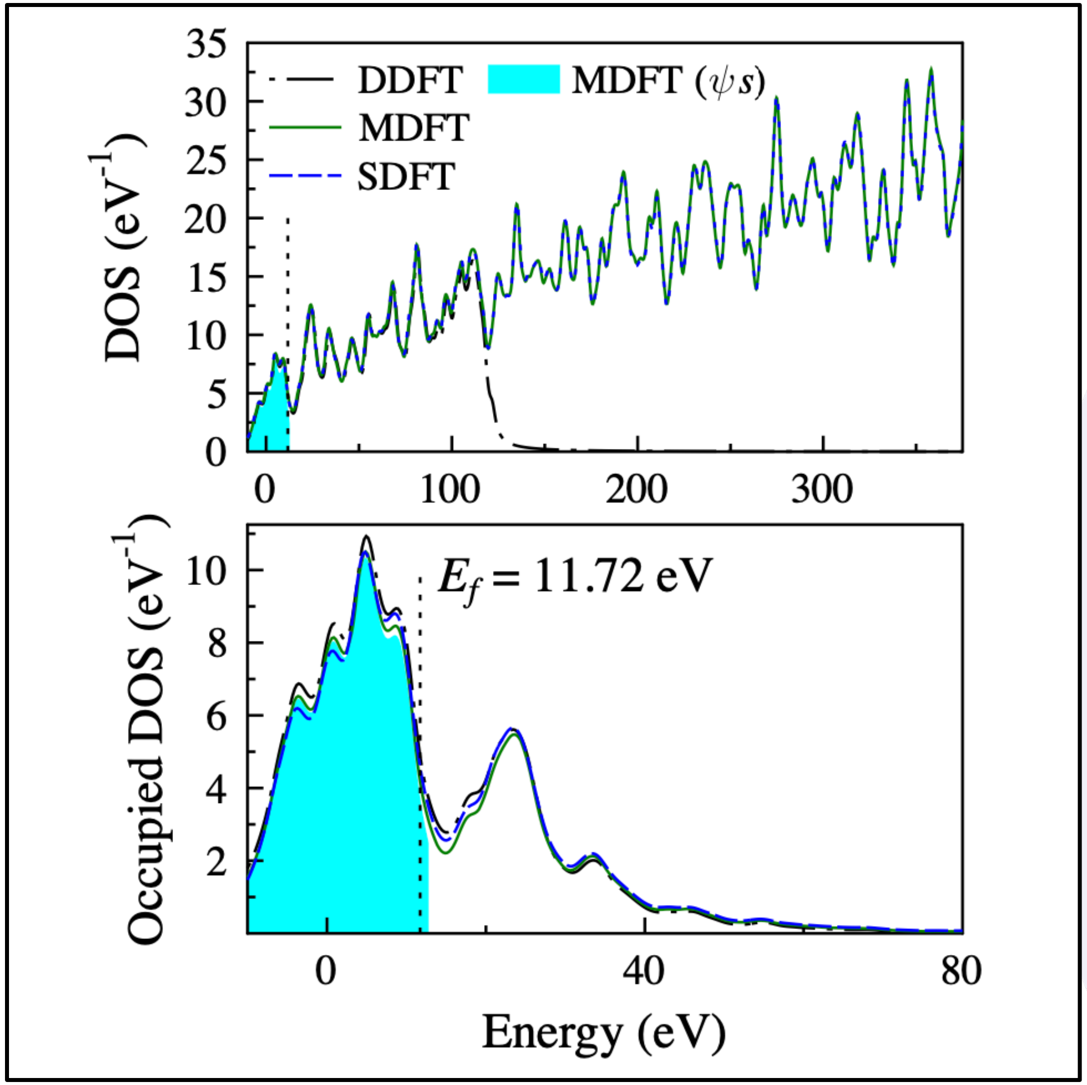

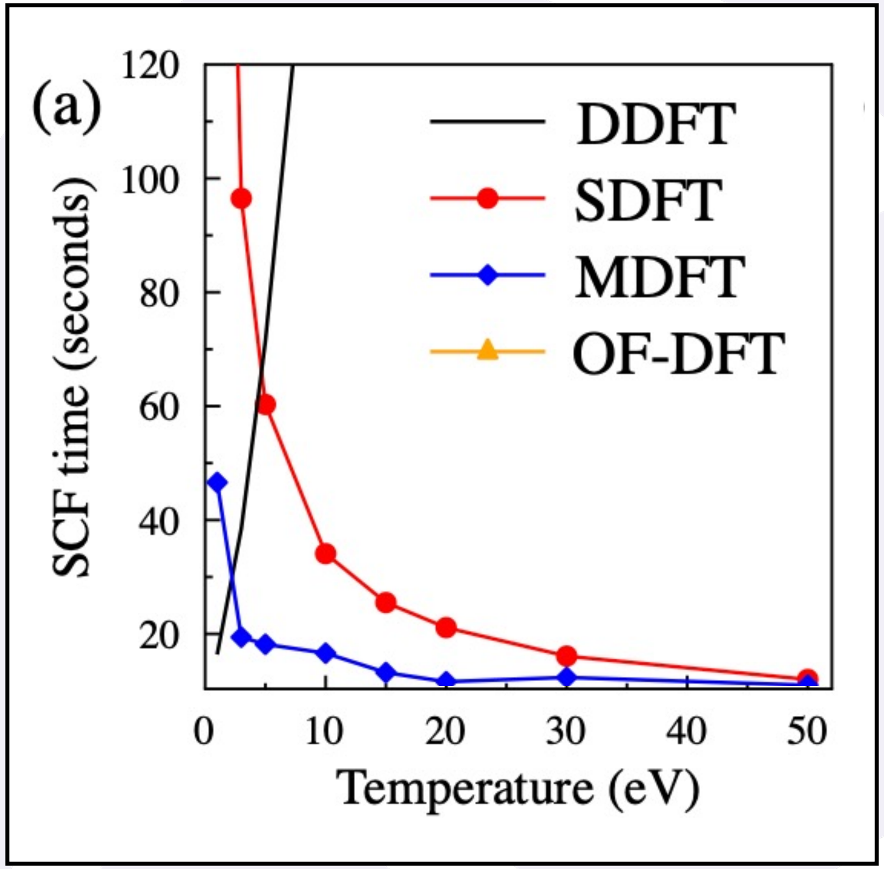

White and Collins *Phys. Rev. Lett.*, 125, 055002 (2020)

A step towards excited states – electron exchange

$$\hat{H} = \left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}[\rho(\mathbf{r})] + e^2 \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[\rho(\mathbf{r})] \right)$$

Kinetic Energy Operator

External potential
(Coulomb potentials from nucleus)

Hartree-Potential
Classical potential between single electron charge distributions

APPROXIMATED!
Exchange-Correlation Functional
all the quantum effects

Kohn and Sham, *Phys. Rev.,* 140, A1133 (1965)

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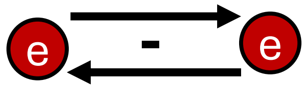
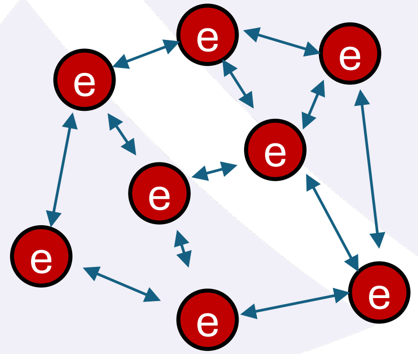
$$v_{\text{xc}}[\rho(\mathbf{r})] = v_{\text{x}}[\rho(\mathbf{r})] + v_{\text{c}}[\rho(\mathbf{r})]$$

X: Electron Exchange
Anti-symmetry of Fermions



C: Coulomb Correlation
Complex and Dynamic Coulomb Interactions



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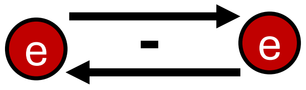

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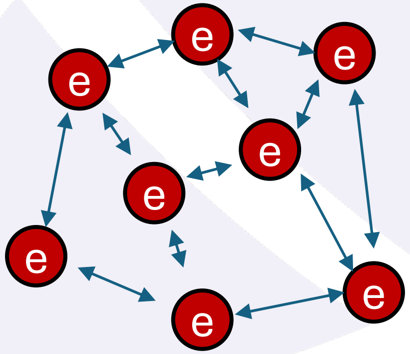

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Compressing the exchange operator

Hybrid exchange – replace a fraction of exchange density functional with Fock exchange energy

$$E_X[\rho(\mathbf{r})] \rightarrow (1-\alpha)E_X[\rho(\mathbf{r})] + \alpha E_x^F$$

$$V_X[\rho(\mathbf{r})] \rightarrow (1-\alpha)V_X[\rho(\mathbf{r})] + \alpha V_x^F$$

Perdew *et al*., *J. Chem. Phys*., 105, 22 (1996)
Adamo *et al*., *J. Chem. Phys*., 110, 13 (1999)
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Exact exchange operator is a functional of single-particle eigen-states → computationally demanding

$$E_x^F = \sum_a \int d\mathbf{r} \sum_b \int d\mathbf{r}' \frac{\phi_a^*(\mathbf{r})\phi_a(\mathbf{r}')\phi_b^*(\mathbf{r})\phi_b(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$V_x^F(\mathbf{r},\mathbf{r}') = \sum_b \frac{\phi_b^*(\mathbf{r})\phi_b(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Perdew *et al*., *J. Chem. Phys.*, 105, 22 (1996)
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$$V_x^F(\mathbf{r},\mathbf{r}') = \sum_b \frac{\phi_b^*(\mathbf{r})\phi_b(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

In planewave codes, we compute the action of the exchange operator on a single particle eigenstate

$$V_x^F\phi_a(\mathbf{r}) = \sum_b \int d\mathbf{r}' \frac{\phi_b^*(\mathbf{r})\phi_b(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_a(\mathbf{r})$$

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- Computing the exchange potential acting on the eigenstates is expensive

Lin., *J. Chem. Theo. Comp.*, 12, 2242 (2018)

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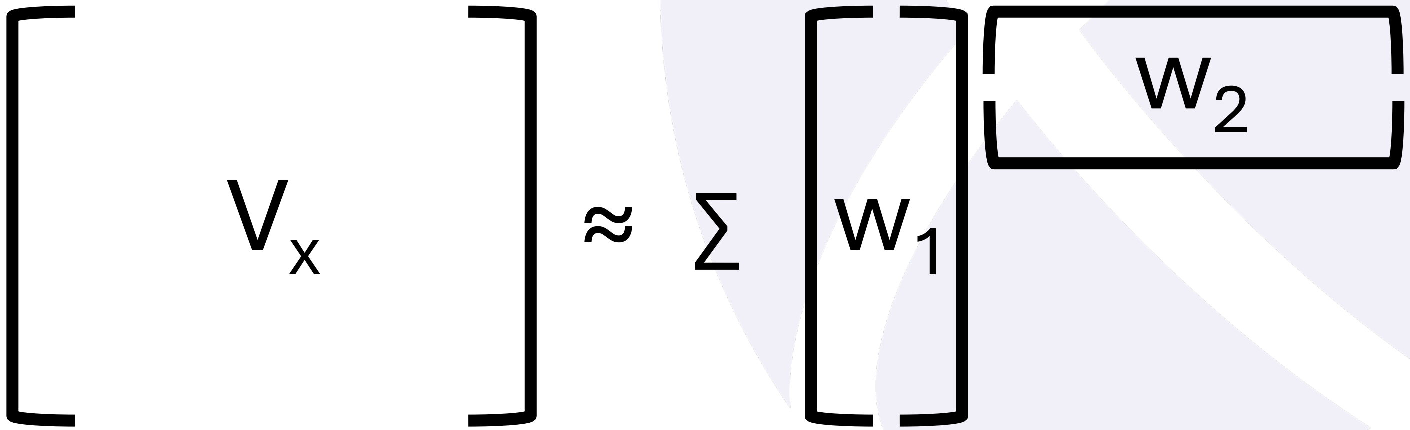
- Computing the exchange potential acting on the eigenstates is expensive

- Can we compress and low-rank approximate exchange operator that is suitable for mDFT?

$$V_x \approx \sum_a |w_{1,a}\rangle\langle w_{2,a}|$$



Lin., *J. Chem. Theo. Comp.*, 12, 2242 (2018)

Compressing the mixed exchange operator

Set of mixed deterministic and filtered stochastic vectors for the density matrix

$$\psi \subset \{\phi, \tilde{X}\}$$

$$\psi' \subset \{\phi', \tilde{\chi}'\}$$

Auxiliary set of deterministic and unfiltered stochastic vectors for exchange

Compressing the mixed exchange operator

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Auxiliary set of deterministic and unfiltered stochastic vectors for exchange

- Compute exchange operator on auxiliary vector set, which will act as our compression vectors

$$w_a(\mathbf{r}) = V_x^F \psi'_a(\mathbf{r}) = \sum_b \int d\mathbf{r}' f_b(T) \frac{\psi_b^*(\mathbf{r})\psi_b(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \psi'_a(\mathbf{r})$$

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- We develop the following compression scheme, which includes projection on deterministic and stochastic subspaces

$$V_x \approx \sum_a^{N_{\mathrm{aux.}}} \left(|\psi_a'\rangle\langle w_a| + |w_a\rangle\langle\psi_a'| \right) - \sum_b^{N_{\mathrm{d,aux.}}} |\phi_b'\rangle\langle w_b|\phi_b'\rangle\langle\phi_b'|$$

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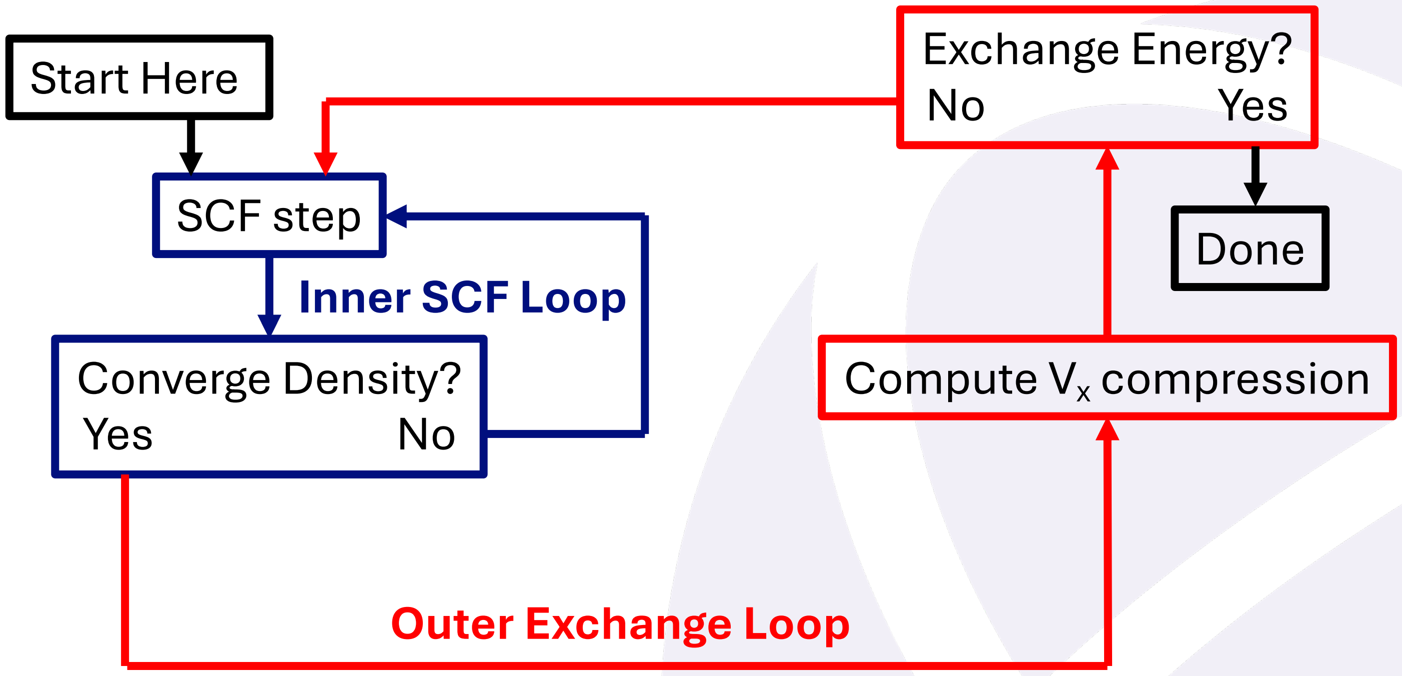
Double loop SCF scheme for compressed mixed electron exchange



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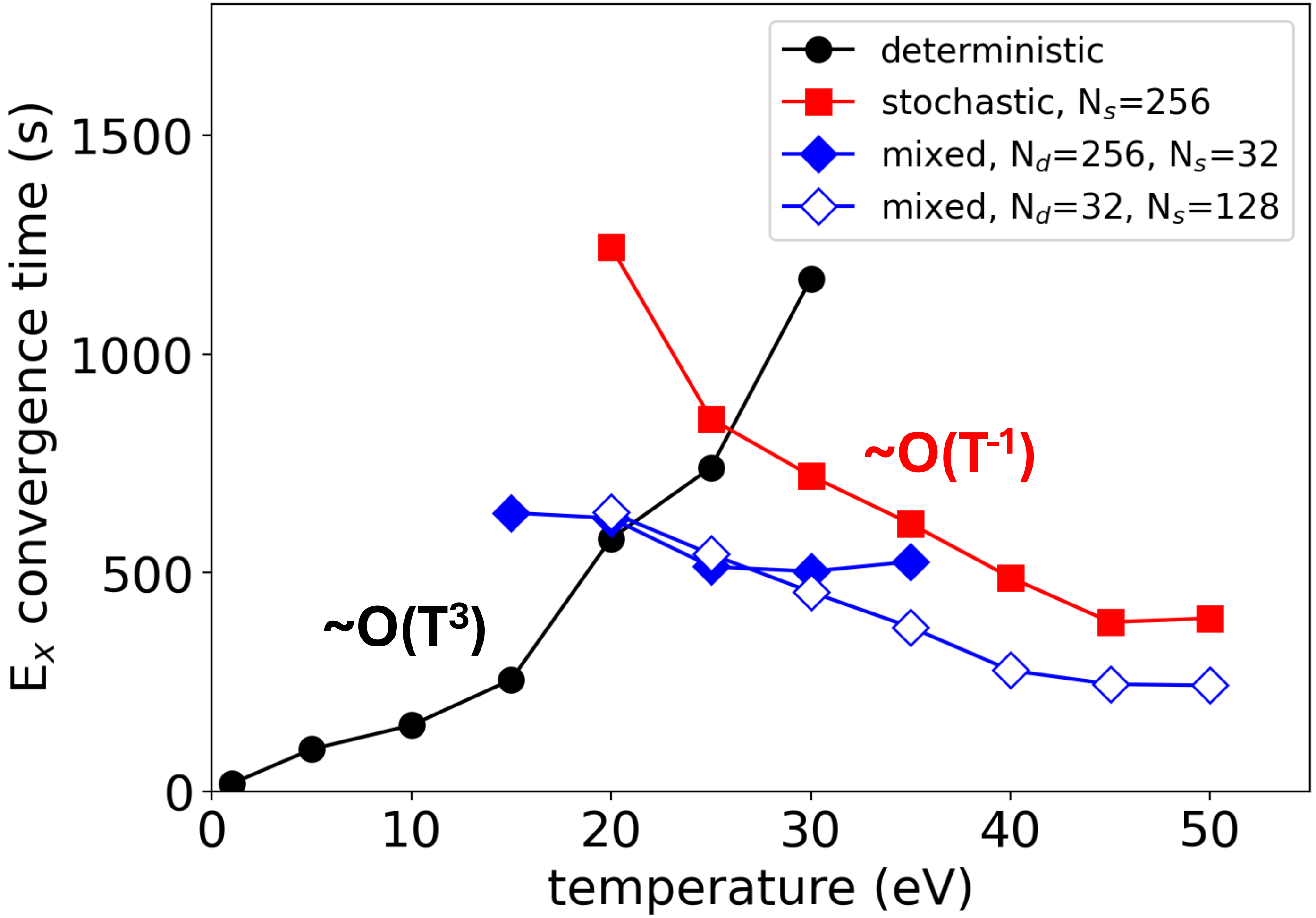
Performance of compressed + mixed exchange operator



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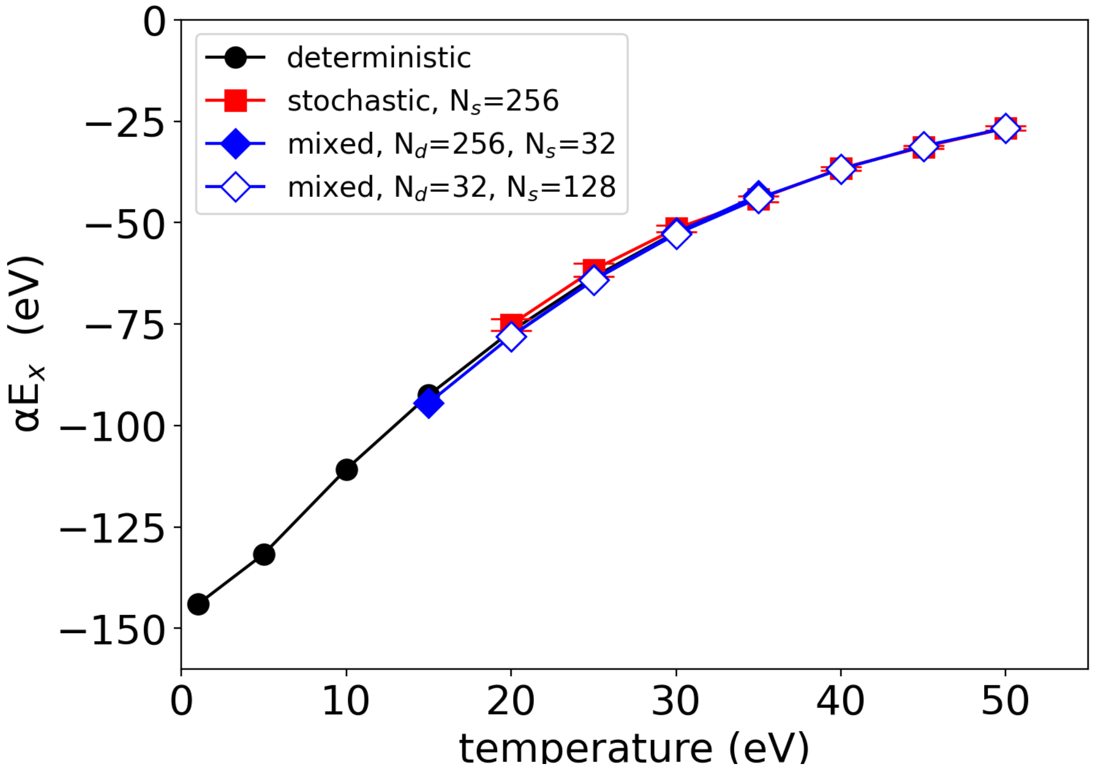

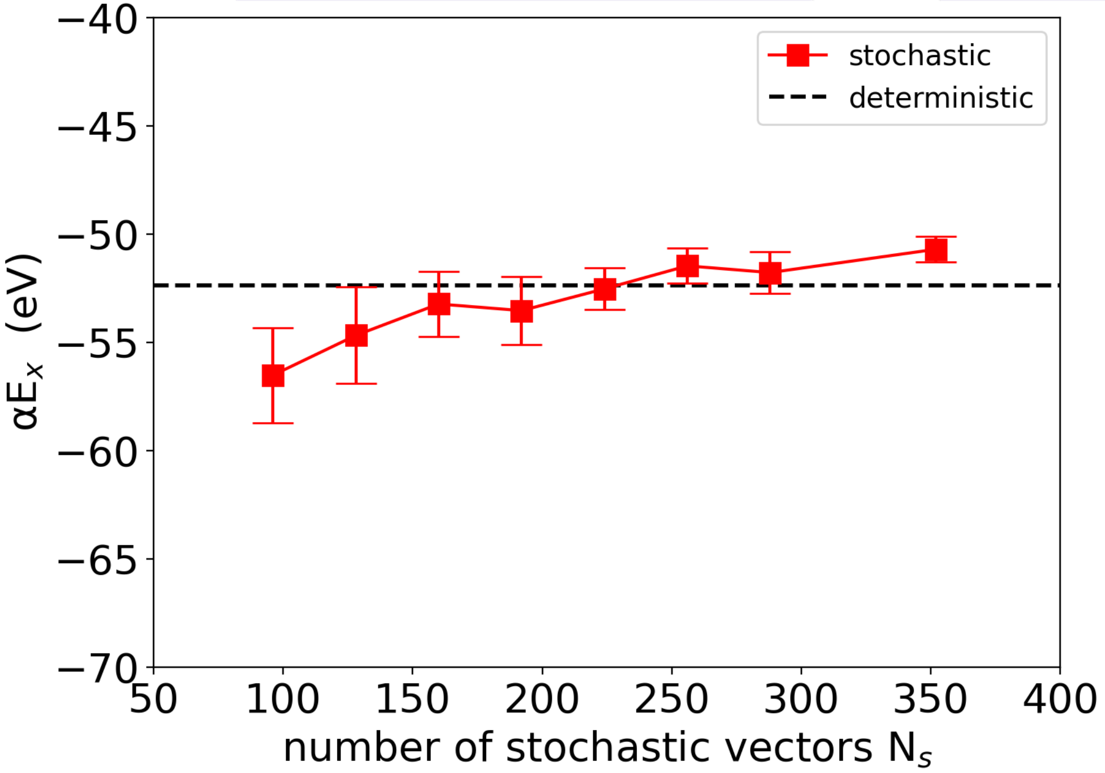

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What degree of compression is achievable

System of 32 Ne atoms

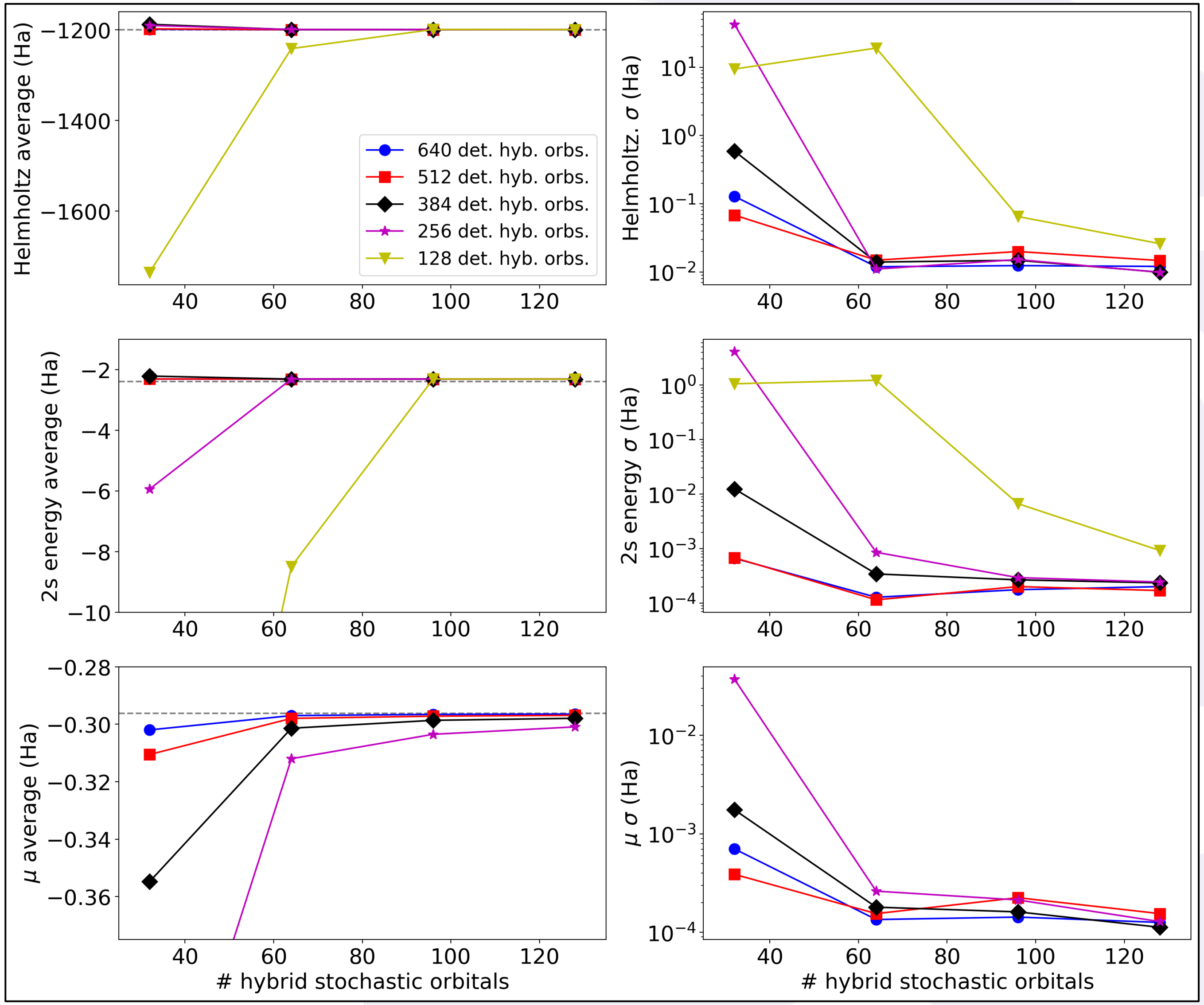
- Molecular dynamics snapshot
- **Fix orbitals to converge density matrix**
- **Reduce number of compression orbitals**

$$\psi \subset \{\phi, \tilde{X}\}$$

640 128

$$\psi' \subset \{\phi', \tilde{\chi}'\}$$

N$_{d'}$ N$_{s'}$



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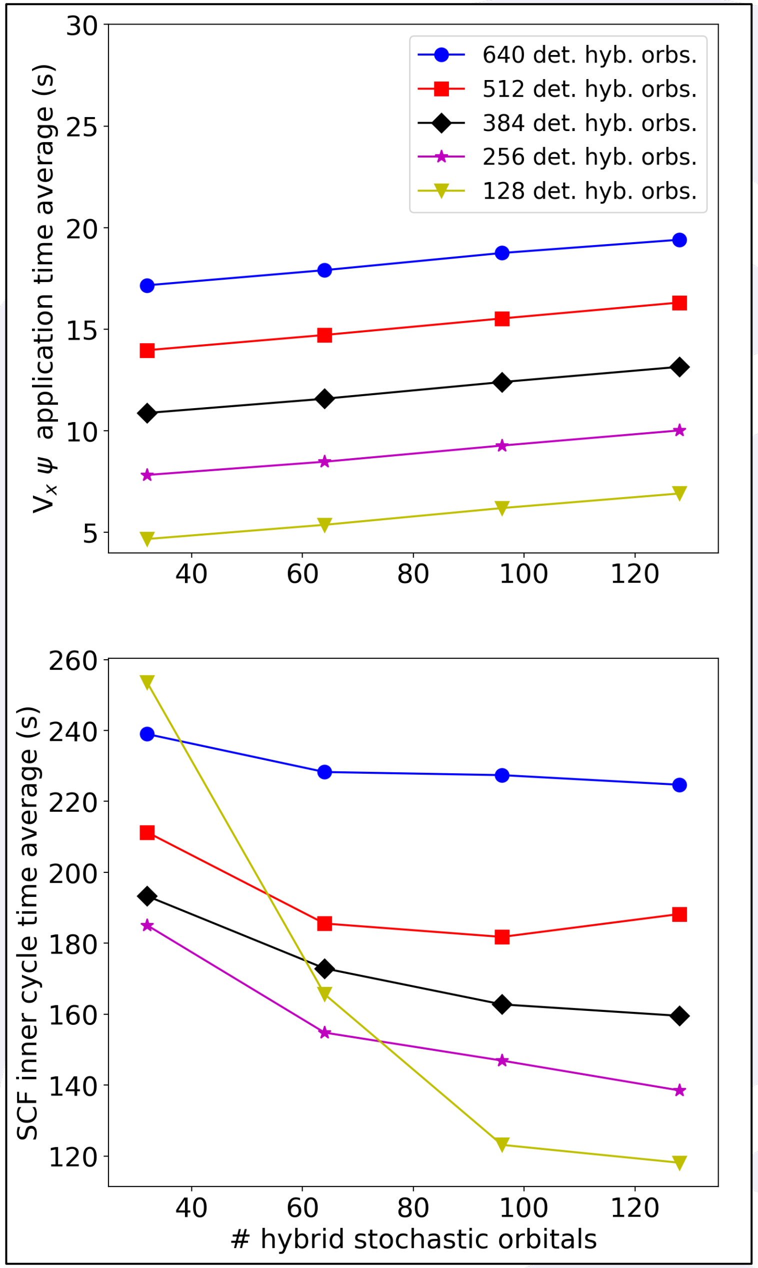

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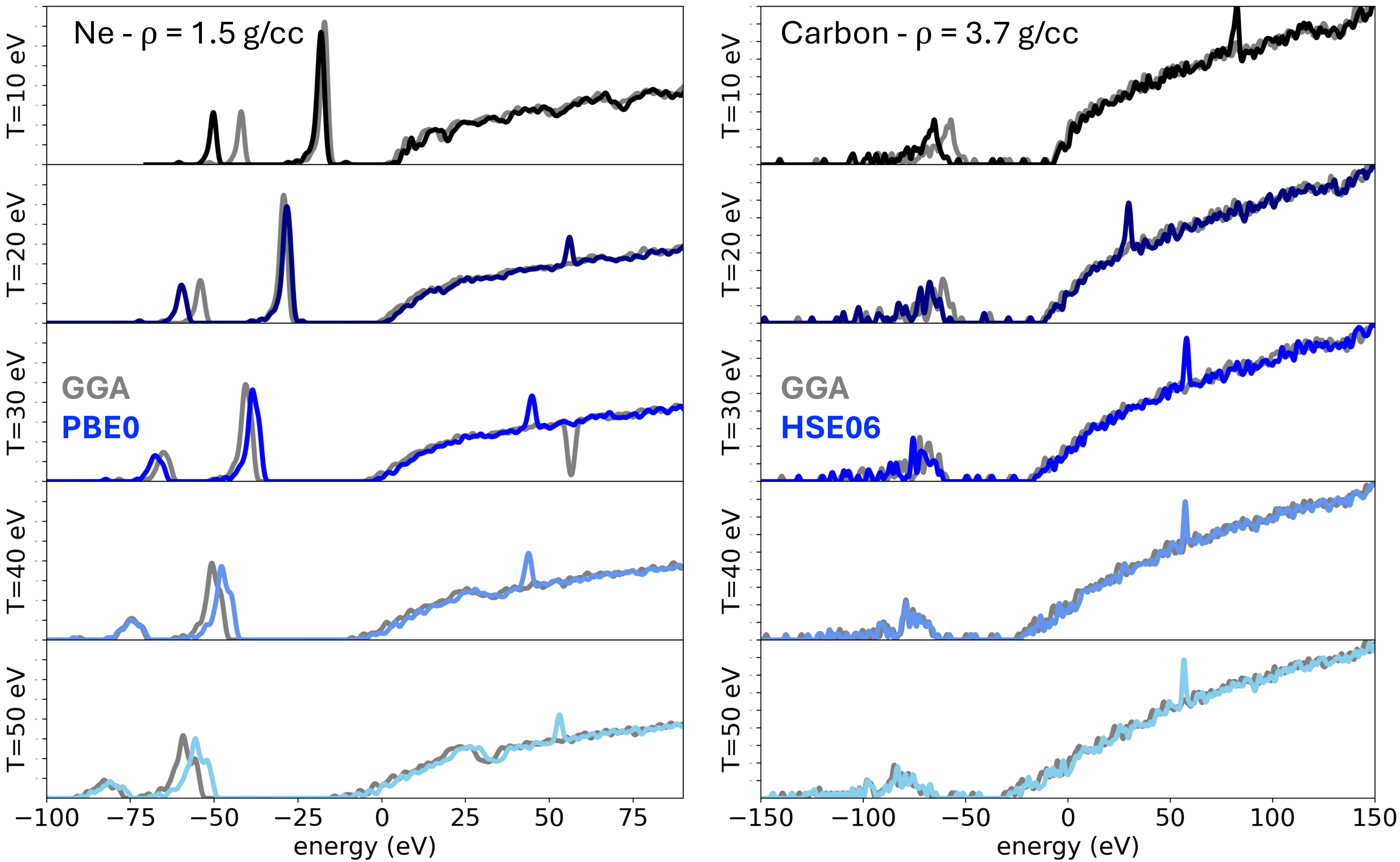
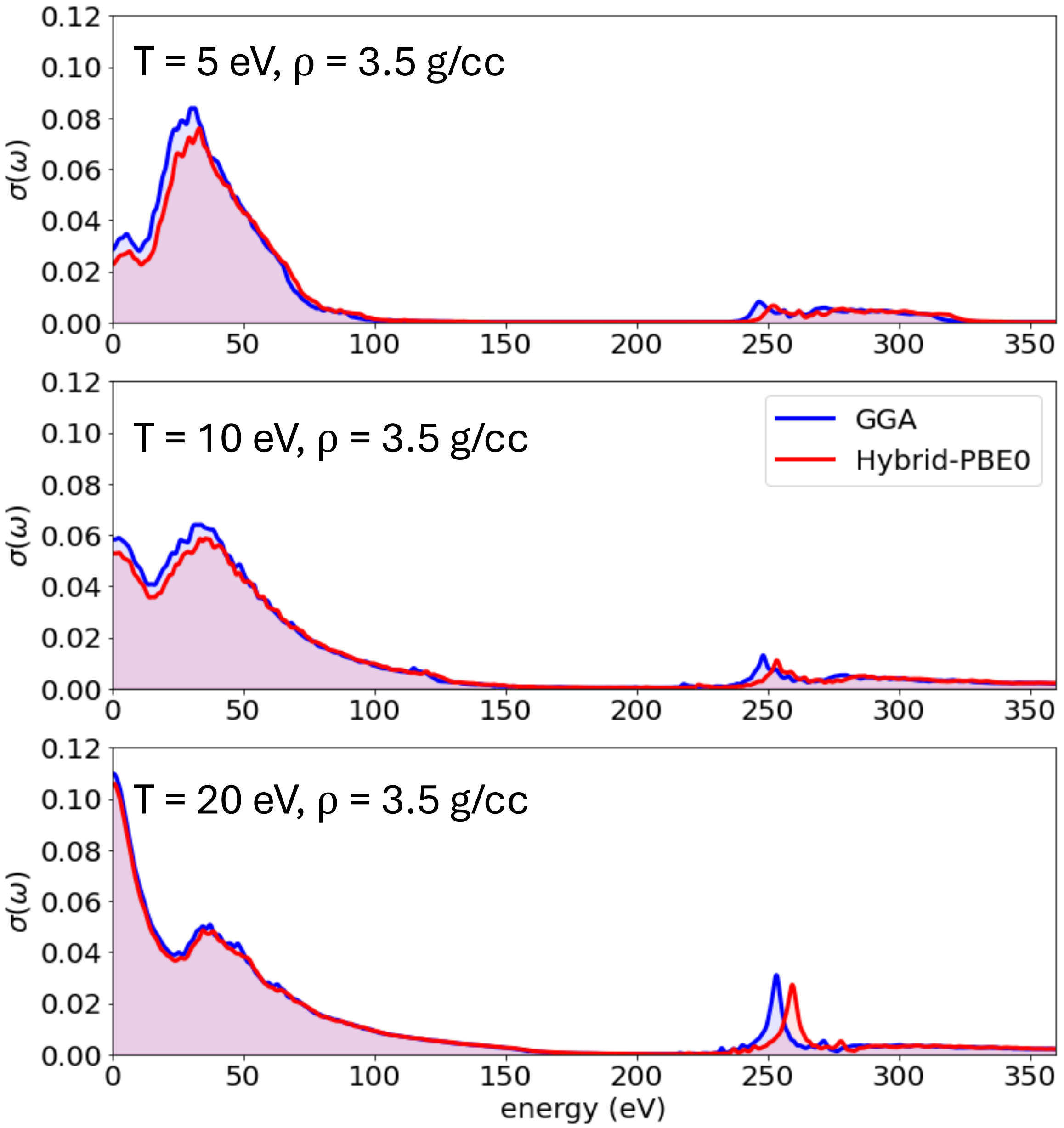
Density of states of hot Ne and Carbon gas



AC conductivity in hot + dense Neon gas (32 atoms in a cell)



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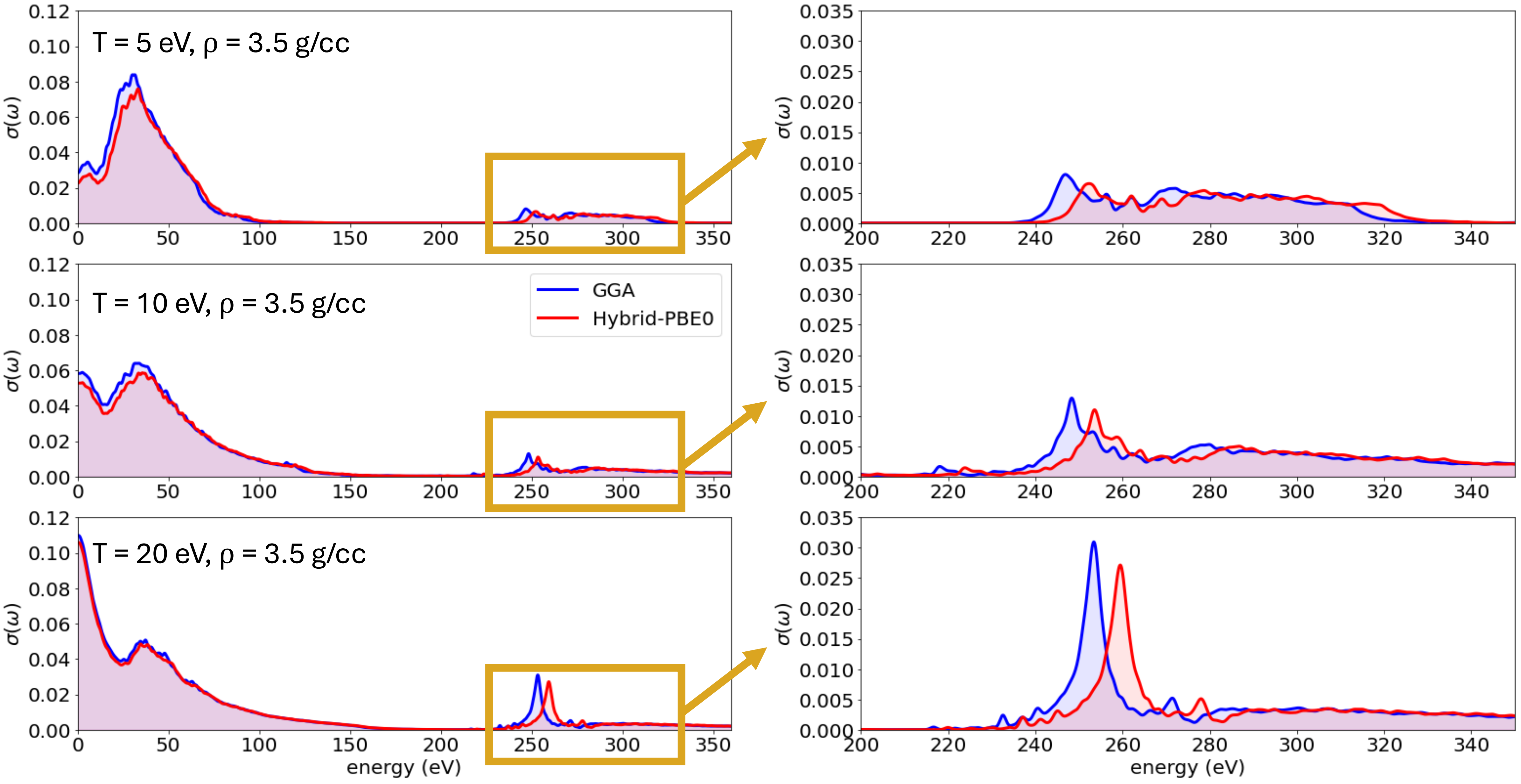
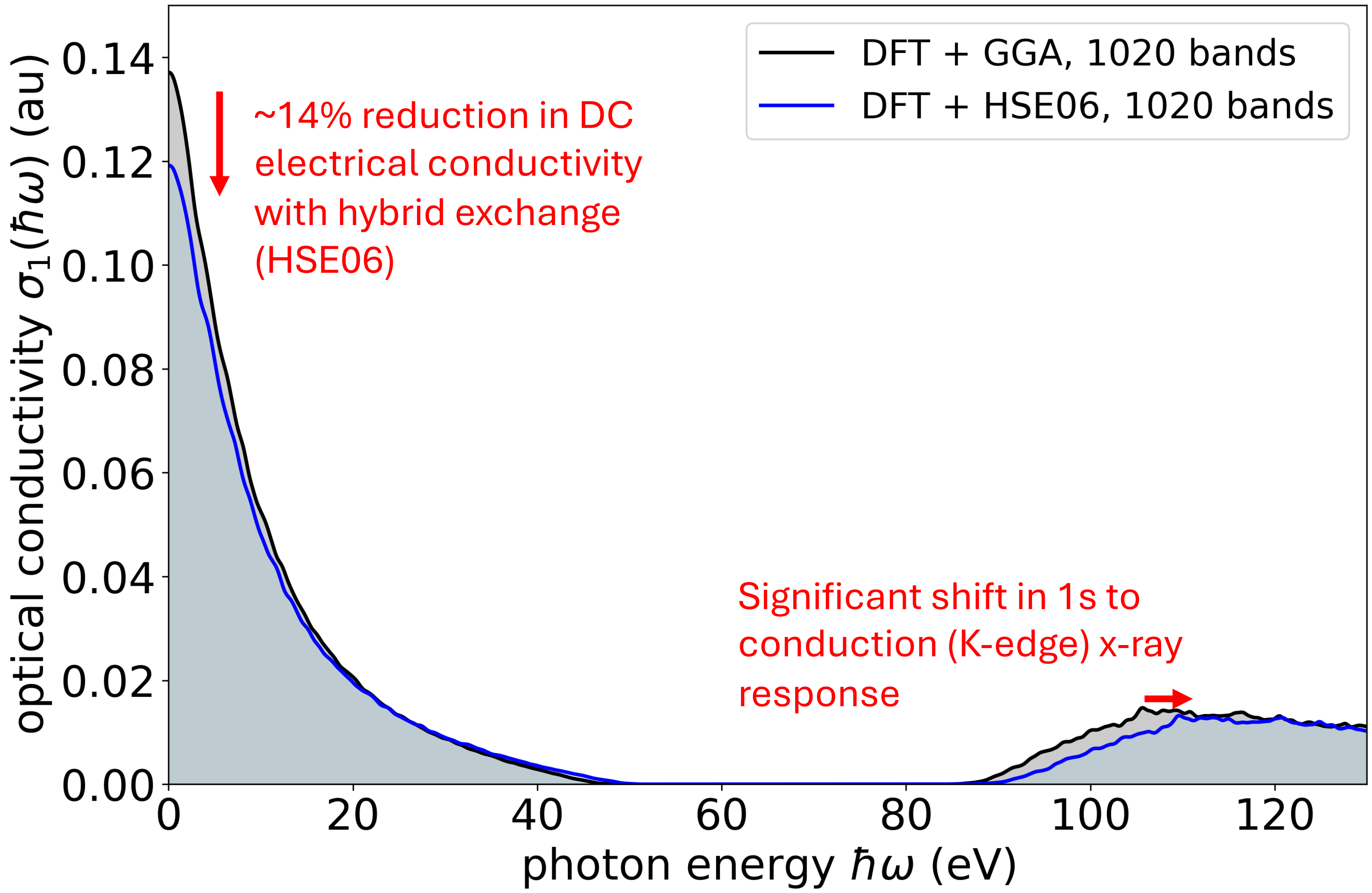


AC conductivity in hot + Beryllium gas (128 atoms in a cell)

- Atomic geometry courtesy of **MD calculation by Vidushi Sharma at CNLS**



Part 1: Stochastic/deterministic electron exchange at extreme temperatures

$$V_x \approx \sum_a |w_{1,a}\rangle\langle w_{2,a}|$$

The influence of hybrid exact exchange on electronic structure and conductivity are sustained to high temperature – larger influence on core states

Can be applied towards

- **Parameterizing AC conductivity for radiation flow simulations**
- **Exchange pressure corrections for equation of state (EOS)**
- **Corrected core ionization temperatures**
- ***Higher*-throughput electronic structure calculations at extreme temperature**

What's Next?

- Mixed deterministic/stochastic correlation → Green's Functions
- TD-DFT with mDFT + hybrid exact exchange

Other Current LANL Projects

EOS of Aluminum with mDFT + extended planewave method

Density matrix purification for Dirac Hamiltonians on GPUs/tensor cores

Towards efficient excited state calculations at extreme conditions with mixed deterministic-stochastic hybrid exchange

Joshua A. Leveillee
Center for Nonlinear Studies Postdoctoral Fellow
T-1 / CNLS
Wednesday June 12th, 2024

Questions?

Supplemental Slides – DOS and conductivity in mDFT

Density of states

$$D(\epsilon) = \lim_{\gamma \to 0} \mathrm{Tr}\Big[\frac{\gamma}{\pi} \frac{1}{(E - \hat{H})^2 + \gamma^2}\Big]$$

Kubo-Greenwood

$$\sigma(\omega, \Gamma) = \frac{1}{\omega} \int_0^\infty dt e^{(i\omega - \Gamma)t} \langle \hat{J}(t) \hat{J}(0) \rangle$$

$$\langle \hat{J}(t) \hat{J}_0 \rangle = \sum_d \langle \phi_d | e^{i\hat{H}t} \hat{J}_0 e^{-i\hat{H}t} \hat{J}_0 | \phi_d \rangle$$

$$\langle \hat{J}(t) \hat{J}_0 \rangle = \frac{1}{N_s} \sum_d \sum_s^{N_s} \langle \phi_d | e^{i\hat{H}t} \hat{J}_0 e^{-i\hat{H}t} | \chi_s \rangle \langle \chi_s | \hat{J}_0 | \phi_d \rangle$$