SAND2017-8239C

Long Time Behavior of Time-Dependent Density Functional Theory

N.A. Modine
Sandia National Laboratories

Cheng-Wei Lee and André Schleife
University of Illinois, Urbana-Champaign

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

Motivation: Is There An Analogue Of Molecular Dynamics For Electrons?

Molecular Dynamics (MD)

- System of atoms or molecules
- Integrate classical equations of motion
- Obtain thermodynamic properties

Time-Dependent Density Functional Theory (TDDFT)[1]

- System of electrons
- Integrate the quantum equations of motion
- Can we obtain thermodynamic properties?

[1] E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).

Is There A Thermal State in TDDFT? YES!

- TDDFT gives exact evolution of density (in principle…)
- Gedanken Experiment:
  - Start from electronic ground state with frozen ions
  - Excite the system with a time-dependent potential
  - Propagate the system in time with the potential off
- System should equilibrate and density should change!
- Experimental example: The two-temperature-model is widely used to explain fs to ps behavior of metals

Evaluating Thermodynamic Expectations

Molecular Dynamics (MD)

- Initialize in approximate thermal state ✔
- Propagate for an “equilibration period” ✔
- Average over system snapshots ✔

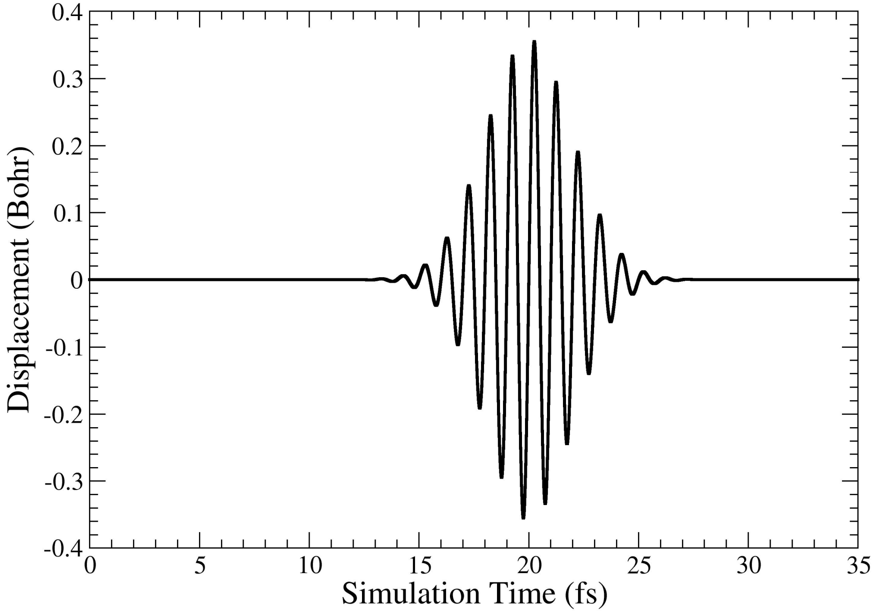
Time-Dependent Density Functional Theory (TDDFT)

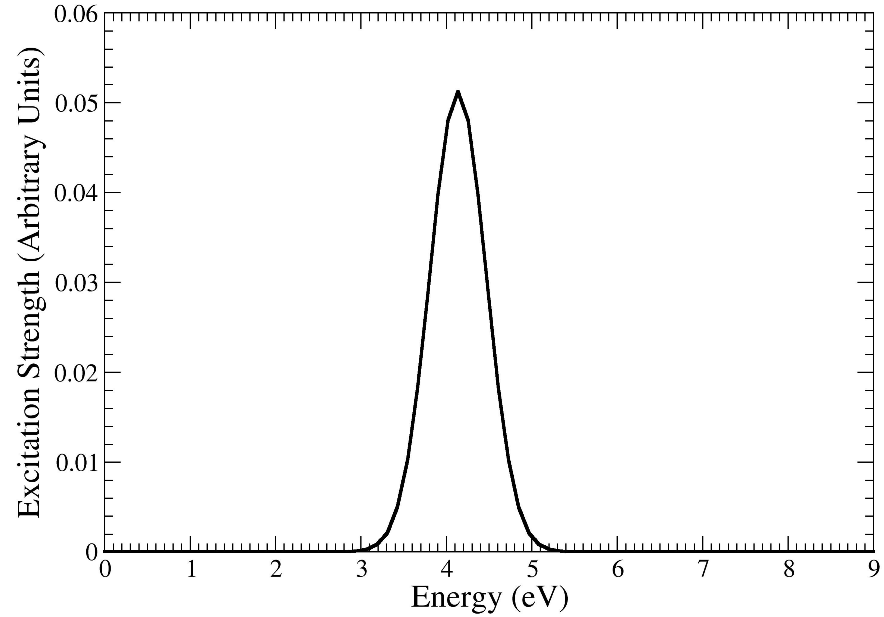
- Initialize in approximate thermal state ? ← (3)
- Propagate for an “equilibration period” ? ← (1,4)
- Average over system snapshots ? ← (2)

Does Standard TDDFT Equilibrate?

Start in the ground state of 32 atoms of Al and excite by pulsing the positions of some of the atoms

Atoms return to original positions and are then fixed





How Will We Detect Equilibration?

Consider a DFT reference Hamiltonian H

H could be ground state or Mermin Hamiltonian

Let $\left|\phi_\eta\right\rangle$ **be the eigenvectors of the ground state H**

Plot $f_{\eta\eta} = \sum_{b=1}^{n} \langle \psi_b | \phi_\eta \rangle \langle \phi_\eta | \psi_b \rangle$ **versus eigenvalues** ε_η

To the movies…

Los Alamos NATIONAL LABORATORY

Sandia National Laboratories

Intermission! The Plot Thickens…

Excitations clearly decay into other excitations

No signs of oscillatory return to initial state

The distribution becomes more "Fermi-like"

But, is it really going to a Fermi distribution?

What if we start with a Fermi distribution?

Key Problem: Evaluating Thermodynamic Expectations as Averages over Pure States?

(Original) TDDFT is a pure state theory

Many-Body | **Non-interacting**

$$|\Psi(R_1, \ldots, R_n; t)\rangle \longleftrightarrow |\psi_1(R_1, t)\rangle, \ldots, |\psi_n(R_n, t)\rangle$$

Statistical mechanics is a mixed state theory

$$\mathcal{Z} = \mathrm{Tr}\left(\exp\left(-\beta\hat{\mathcal{H}}\right)\right) \qquad \hat{\mathcal{P}} = \mathcal{Z}^{-1}\exp\left(-\beta\hat{\mathcal{H}}\right)$$

$$\langle\hat{\mathcal{O}}\rangle = \mathrm{Tr}\left(\hat{\mathcal{P}}\hat{\mathcal{O}}\right) = \mathcal{Z}^{-1}\sum_{\alpha}\exp(-\beta E^{\alpha})\left\langle\Phi^{\alpha}\middle|\hat{\mathcal{O}}\middle|\Phi^{\alpha}\right\rangle$$

Los Alamos NATIONAL LABORATORY
Sandia National Laboratories

The "Stochastic" Trace to the Rescue

Introduce random complex numbers z_i^α

- **Some distribution of magnitudes such that** $|z_i^\alpha|^2 = 1$
- **Random phase** $z_i^\alpha = |z_i^\alpha| \mathrm{e}^{-\mathrm{i}\theta}$

Average over M samples: $\langle f_i \rangle_M \equiv \frac{1}{M} \sum_{i=1}^{M} f_i$

Then, $\lim_{M\to\infty} \langle \overline{z_i^\alpha} z_i^\beta \rangle_M = \delta^{\alpha\beta}$

Defining $|\Theta_i\rangle = \sum_\alpha z_i^\alpha |\Phi^\alpha\rangle$

$$\lim_{M\to\infty} \langle\langle \Theta_i | \hat{A} | \Theta_i \rangle\rangle_M = \sum_{\alpha,\beta} \langle \Phi^\alpha | \hat{A} | \Phi^\beta \rangle \lim_{M\to\infty} \langle \overline{z_i^\alpha} z_i^\beta \rangle_M = \mathrm{Tr}(\hat{A})$$

Evaluate Expectations As Averages Over Correlated (Non-Stationary) States

Define "Many-Body Thermal States" $|\Psi_i\rangle = \hat{\mathcal{P}}^{1/2}|\Theta_i\rangle$

$$\langle\hat{\mathcal{O}}\rangle = \mathrm{Tr}\left(\hat{\mathcal{P}}\hat{\mathcal{O}}\right) = \mathrm{Tr}\left(\hat{\mathcal{P}}^{1/2}\hat{\mathcal{O}}\hat{\mathcal{P}}^{1/2}\right)$$

$$= \lim_{M\to\infty}\langle\langle\Theta_i|\hat{\mathcal{P}}^{1/2}\hat{\mathcal{O}}\hat{\mathcal{P}}^{1/2}|\Theta_i\rangle\rangle_M$$

$$= \lim_{M\to\infty}\langle\langle\Psi_i|\hat{\mathcal{O}}|\Psi_i\rangle\rangle_M$$

$|\Psi_i\rangle$ **is normalized on average and can be made individually normalized (Modine and Hatcher, JCP 142, 204111 (2014))**

Mapping Many-Body To TDDFT: The Independent Particle Approximation

MB quasiparticles ⟷ TDDFT eigenvectors

$$\phi_\eta^\dagger, E_\eta \longleftrightarrow |\phi_\eta\rangle, \varepsilon_\eta$$

Quasiparticles do not interact

$$|\Phi^\alpha\rangle = \phi^\dagger_{\eta_1^\alpha} \ldots \phi^\dagger_{\eta_n^\alpha} |0\rangle$$

$$E^\alpha = \varepsilon_{\eta_1^\alpha} + \cdots + \varepsilon_{\eta_n^\alpha}$$

Construct TDDFT States that Approximate the "Many-Body Thermal States"

If n is the number of electrons, a TDDFT state is a set of n orthornormal wavefunctions

Use non-orthogonal representation $|\tilde{\psi}_1\rangle, \ldots, |\tilde{\psi}_n\rangle$

$$O_{ab} = \langle \tilde{\psi}_a | \tilde{\psi}_b \rangle \qquad |\psi_a\rangle = \sum_{b=1}^{n} O_{ab}^{-1/2} |\tilde{\psi}_b\rangle$$

Ansatz for $|\tilde{\psi}_1\rangle, \ldots, |\tilde{\psi}_n\rangle$

$$|\tilde{\psi}_a\rangle = \sum_{\eta=1}^{N_b} z_a^{\eta} \exp\left(-\tfrac{1}{2}\beta\varepsilon_\eta\right) |\phi_\eta\rangle$$

Constructing Approximate TDDFT Thermal States

Many-body state corresponding to TDDFT state

$$|\Psi\rangle = \gamma^{-\frac{1}{2}} \prod_{a=1}^{n} \left[\sum_{\eta=1}^{N_b} z_a^{\eta} \exp\left(-\tfrac{1}{2}\beta \varepsilon_{\eta}\right) \phi_{\eta}^{\dagger} \right] |0\rangle$$

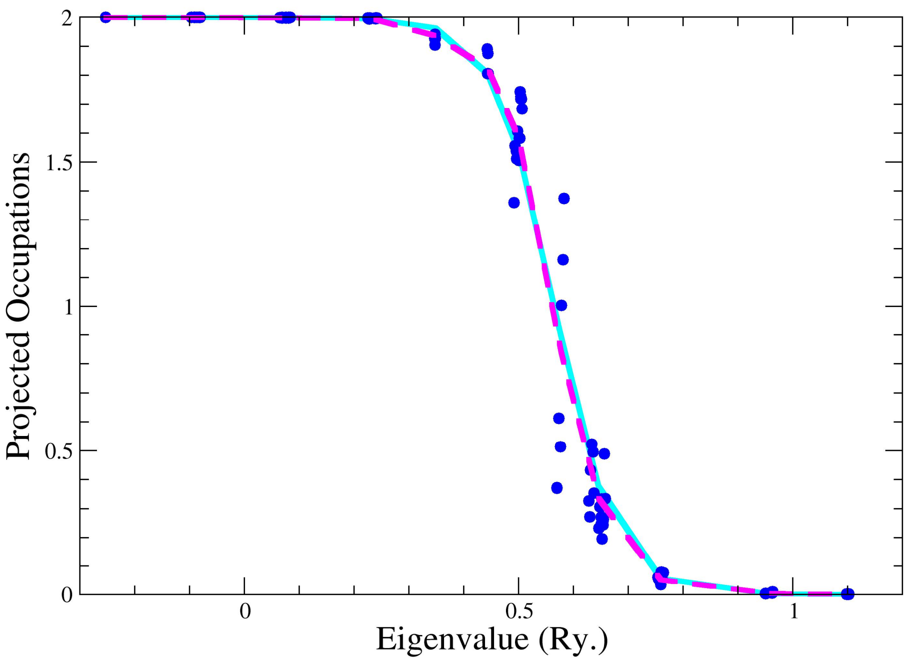
$$= \gamma^{-\frac{1}{2}} \sum_{\alpha} y^{\alpha} \exp\left(-\tfrac{1}{2}\beta\left(\varepsilon_{\eta_1^{\alpha}} + \cdots + \varepsilon_{\eta_n^{\alpha}}\right)\right) \phi_{\eta_1^{\alpha}}^{\dagger} \ldots \phi_{\eta_n^{\alpha}}^{\dagger} |0\rangle$$

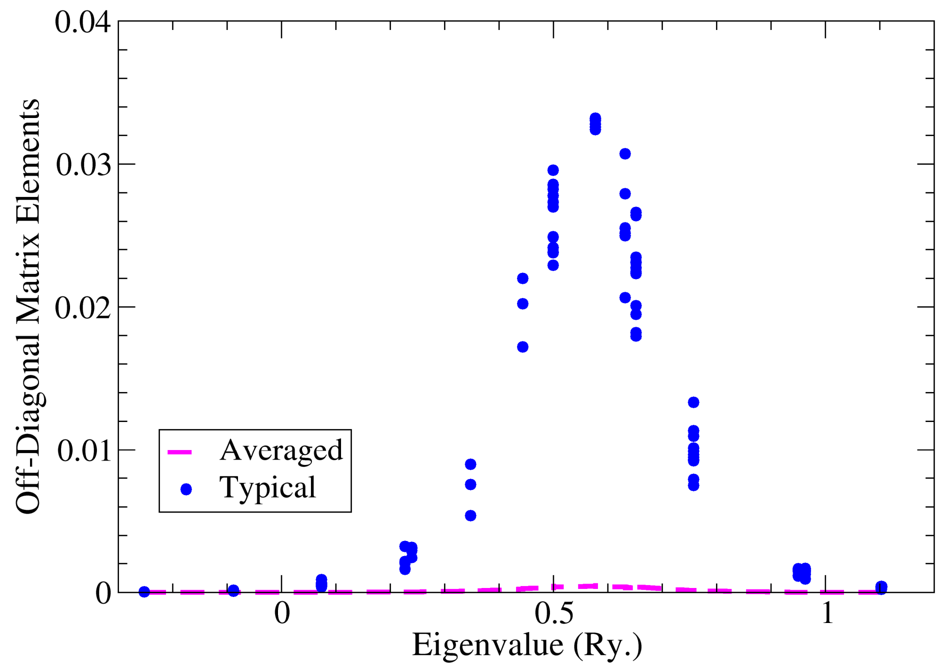
$$= \mathcal{Z}^{-\frac{1}{2}} \sum_{\alpha} x^{\alpha} \exp\left(-\tfrac{1}{2}\beta E^{\alpha}\right) |\Phi^{\alpha}\rangle = |\Psi_i\rangle$$

Where $\lim_{M\to\infty} \langle \overline{x^{\alpha}} x^{\beta} \rangle_M = \delta^{\alpha\beta}$

Computational Test of Approximate TDDFT Thermal States - 32 Atoms of Al at 7900 K

$$f_{\eta\nu} = \sum_{b=1}^{n} \langle \psi_b | \phi_\eta \rangle \langle \phi_\nu | \psi_b \rangle$$





Projected occupations average to Fermi function and off-diagonal elements average to zero

What Happens When We Run TDDFT?

Initialize with an "Approximate TDDFT Thermal State" for 32 atoms of Al at T=7900K

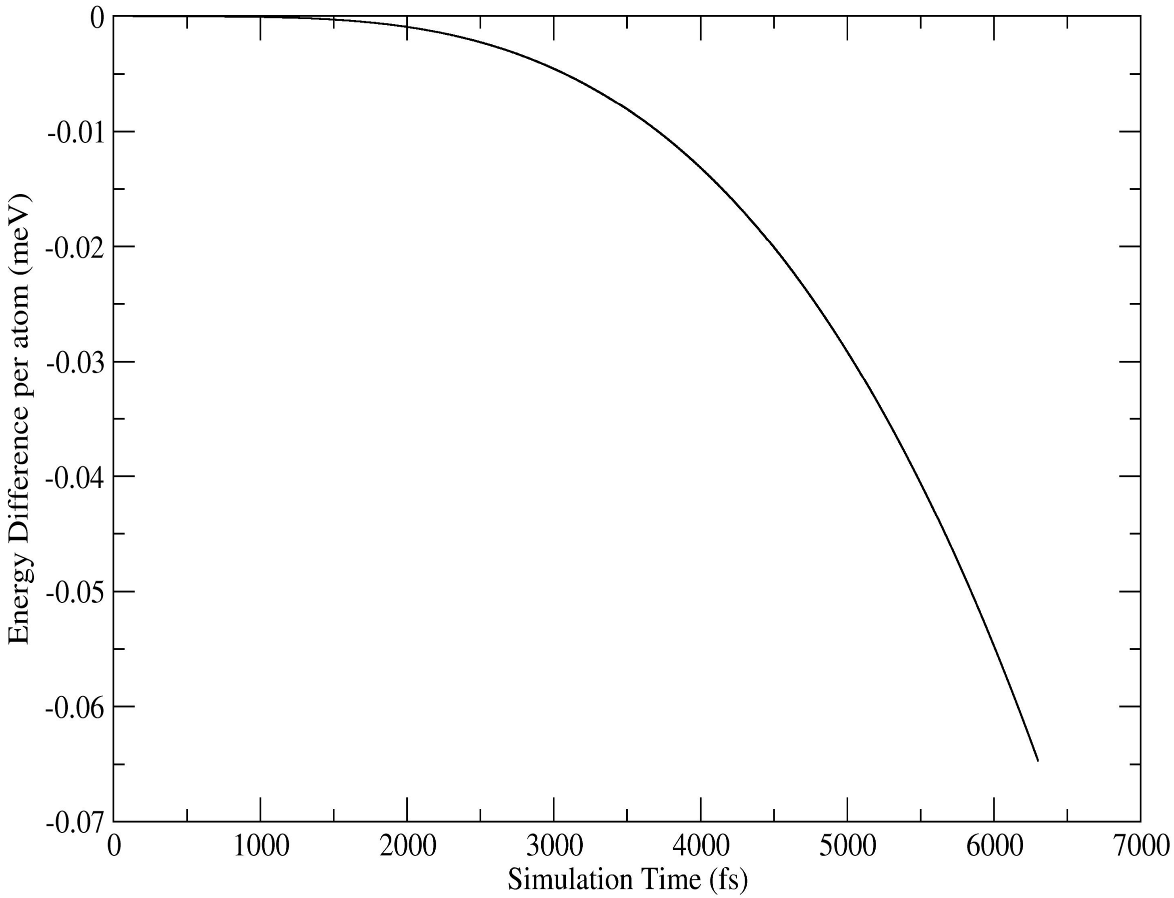
Calculate Projected Weights using 7900K Mermin DFT reference states

Initial projected weights fluctuate around a Fermi distribution

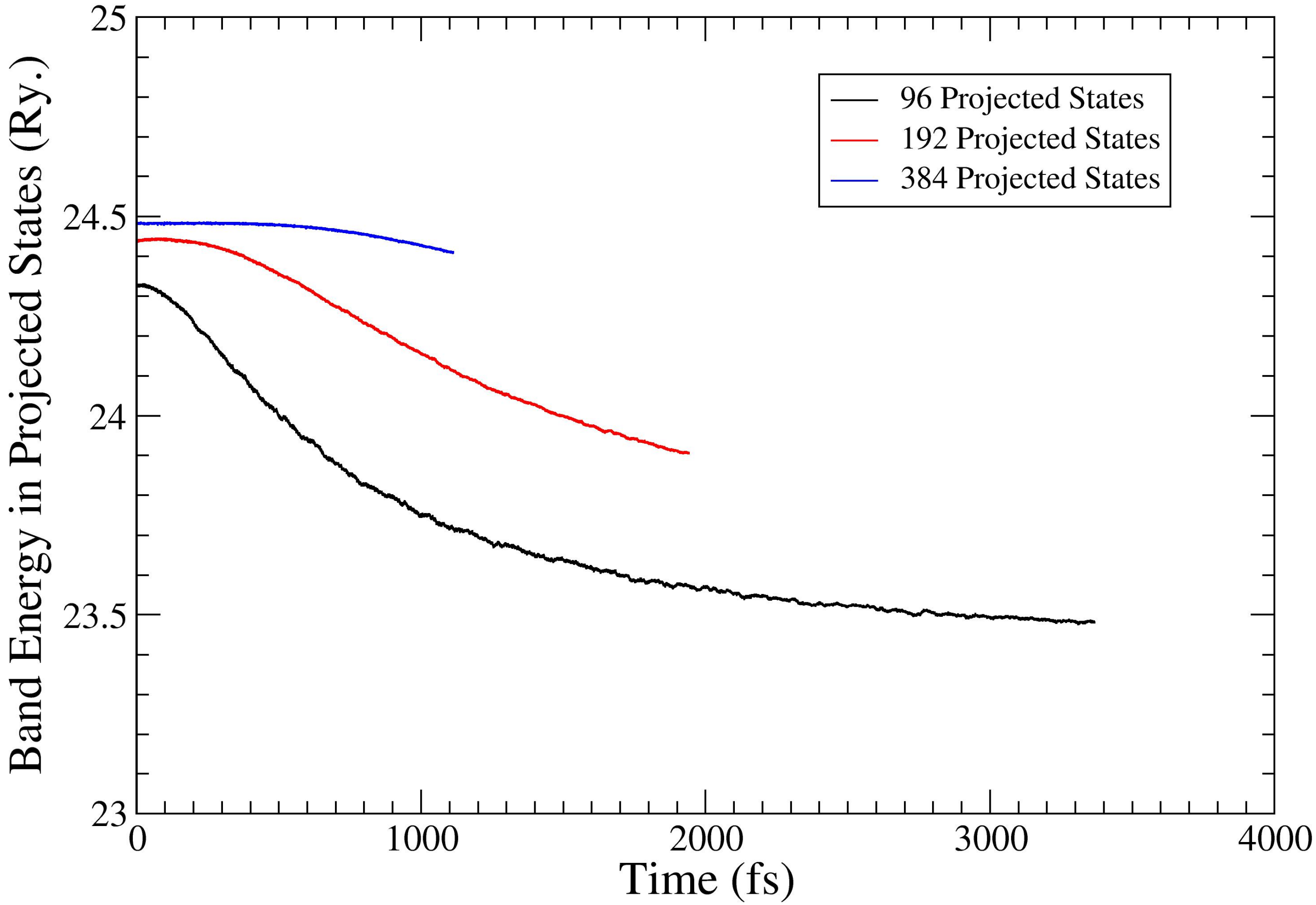
Run TDDFT – Back to the movies…

Where is the Energy Going?

TDDFT energy is actually conserved very well: Loss of ~2 meV out of ~14 eV added to system

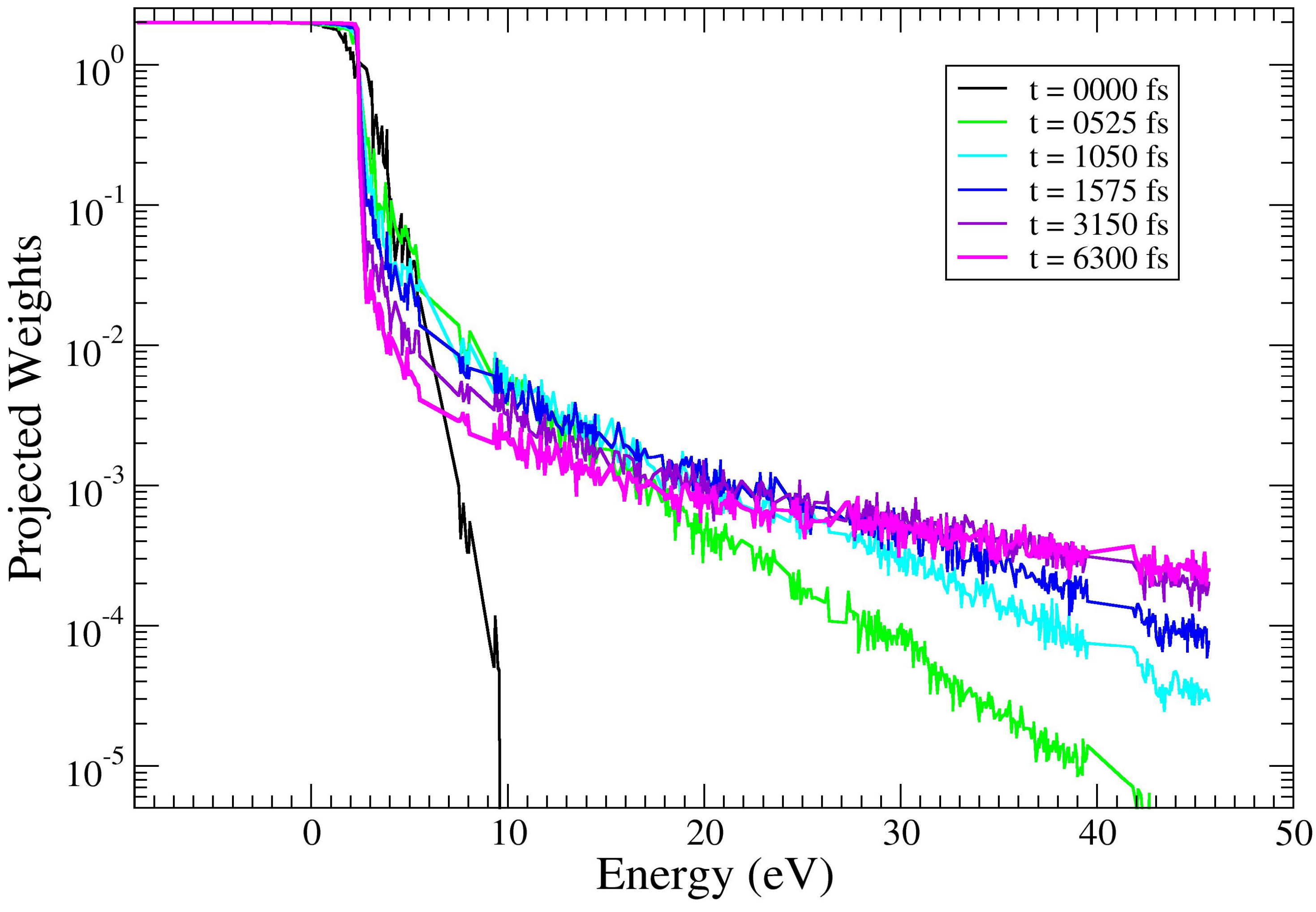


What About Band Energy?



Electronic weight (and energy) is slowly moving into higher and higher energy states

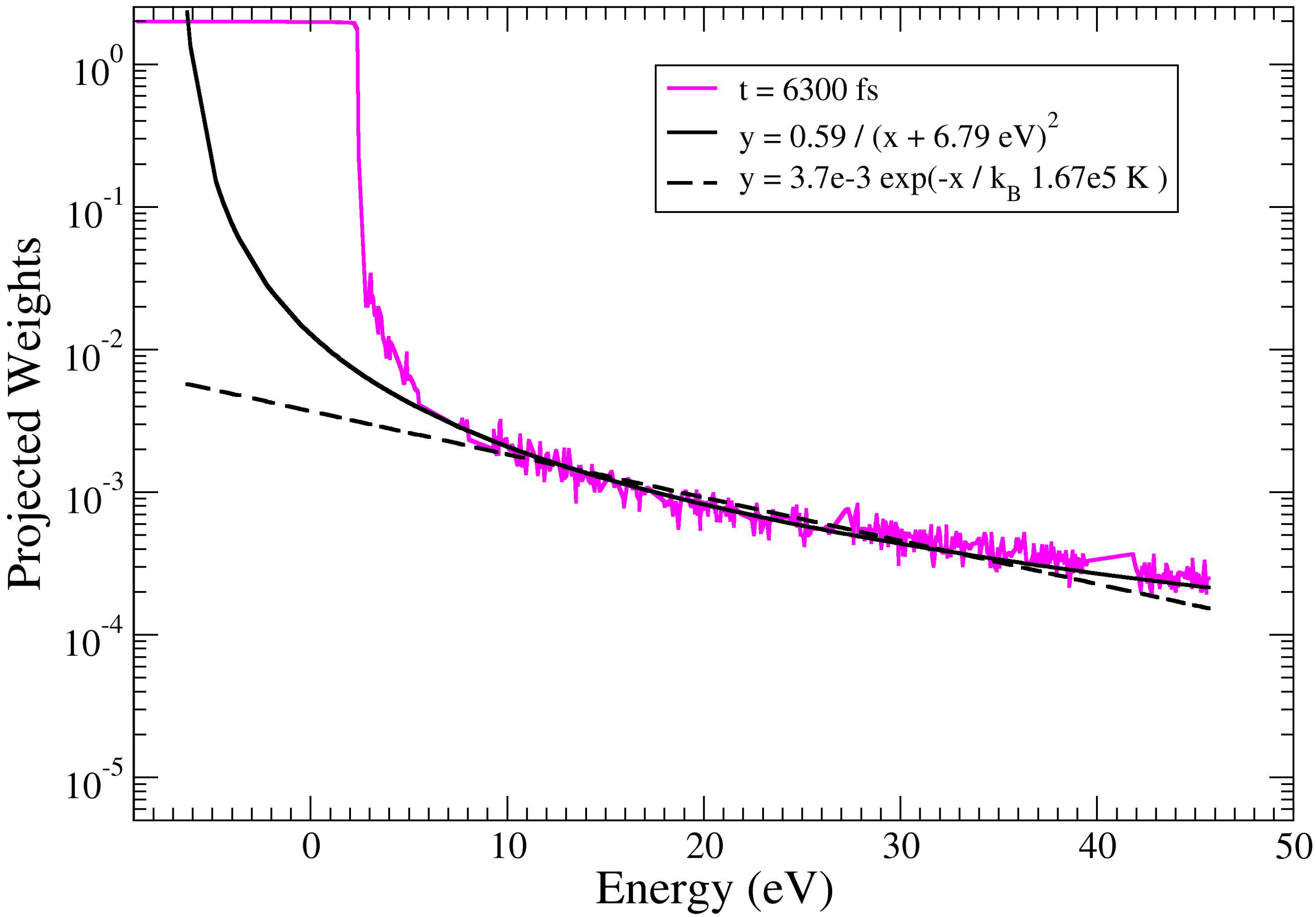
Let's Look In Detail At The Tails



Los Alamos NATIONAL LABORATORY

Sandia National Laboratories

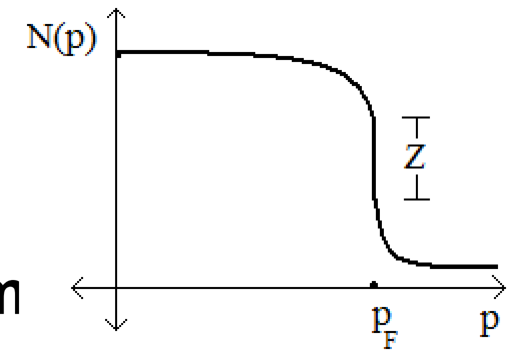
$1/E^2$ Gives Decent Fit To Tails



Los Alamos NATIONAL LABORATORY

Sandia National Laboratories

Is This Weird Behavior A Problem with Our Test Rather Than TDDFT?



(1) Fermi Liquid (FL) Theory

⑩ Bare particle distribution is non-Ferm

⑩ TDDFT maps the FL ground state to the Fermi function, but we cannot expect this for general excited states

(2) Perturbation theory plus conservation laws

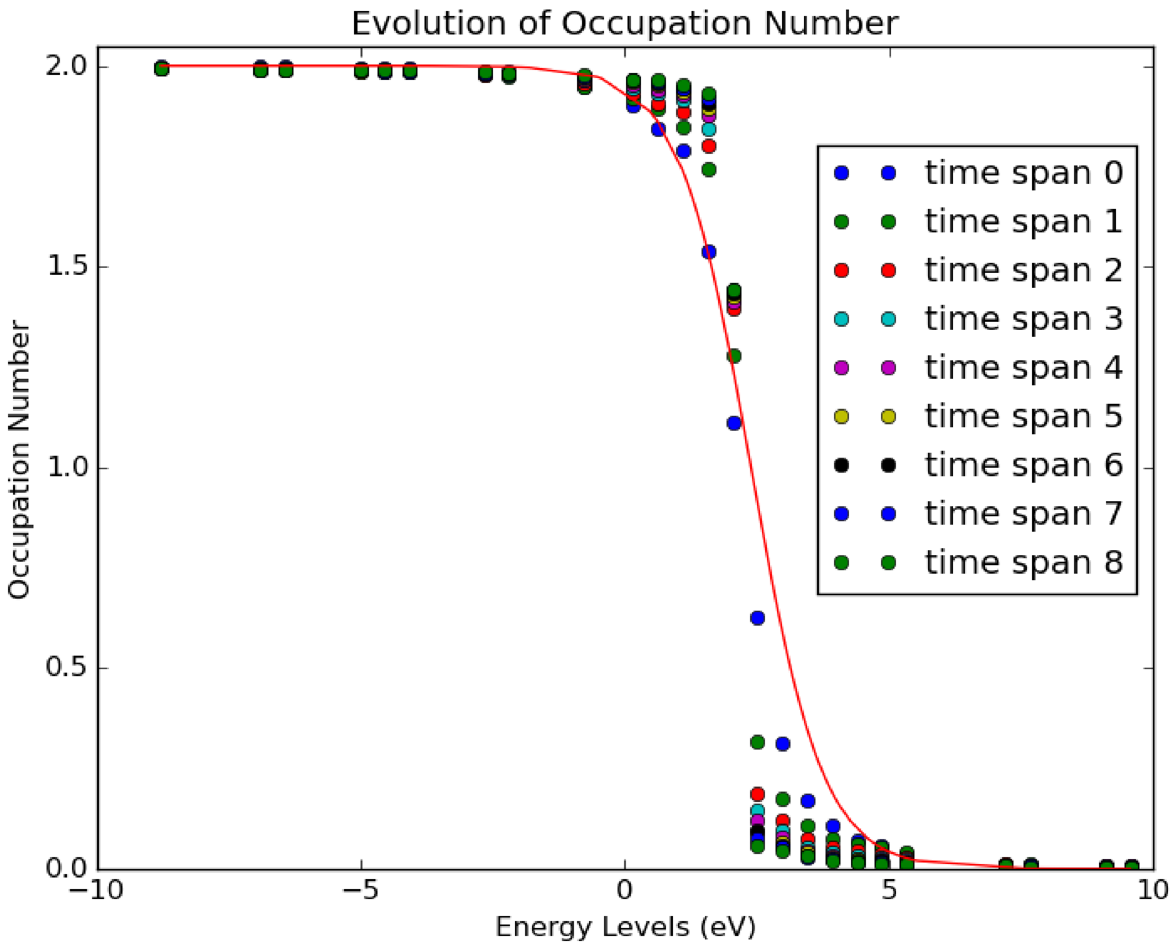
⑩ Thermal excitation perturbs the Hamiltonian (H_0), and thus higher energy eigenstates of H_0 get mixed in

⑩Dropping more quickly at the Fermi level allows for energy conservation despite tails in the distribution

Conclusions

- We investigated the long-time behavior of TDDFT
- The projected occupations evolve away from the Fermi function even when the initial state is constructed to have Fermi occupations
- The time scale for this change is long (several ps), which seems to be related to slow development of the extended high energy tail in the distribution
- This "Non-Fermi behavior" could results from:
  - (A) Problems with our analysis in terms of K-S eigenstates
  - (B) A failure of "detailed balance" in adiabatic LDA
  - (C) An issue with equilibration in closed quantum systems

What Happens When We Run TDDFT?



2.4 ps TDDFT run with adiabatic LDA

Starting from approximate TDDFT thermal states

Occupations averaged in 300 fs windows

Distribution function evolves away from Fermi function with longer tails and a sharper drop at the Fermi level!

Projected Occupations vs. Time