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Long Time Behavior of Time-Dependent Density Functional Theory

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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 ?
- Propagate for an “equilibration period” ?
- Average over system snapshots ?

Key Problem: How Does TDDFT Represent The Thermal State?

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

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

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

Reformulate Statistical Mechanics: Evaluate Expectations As Averages

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

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

Reformulating Statistical Mechanics: Evaluate Expectations As Averages

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

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

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

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

$|\Psi_i\rangle$ **is normalized on average and can be made individually normalized**

Construct TDDFT States that Approximate these Many-Body Thermal States

Start with independent particle approximation

Modine and Hatcher, JCP 142, 204111 (2014)

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

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

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

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

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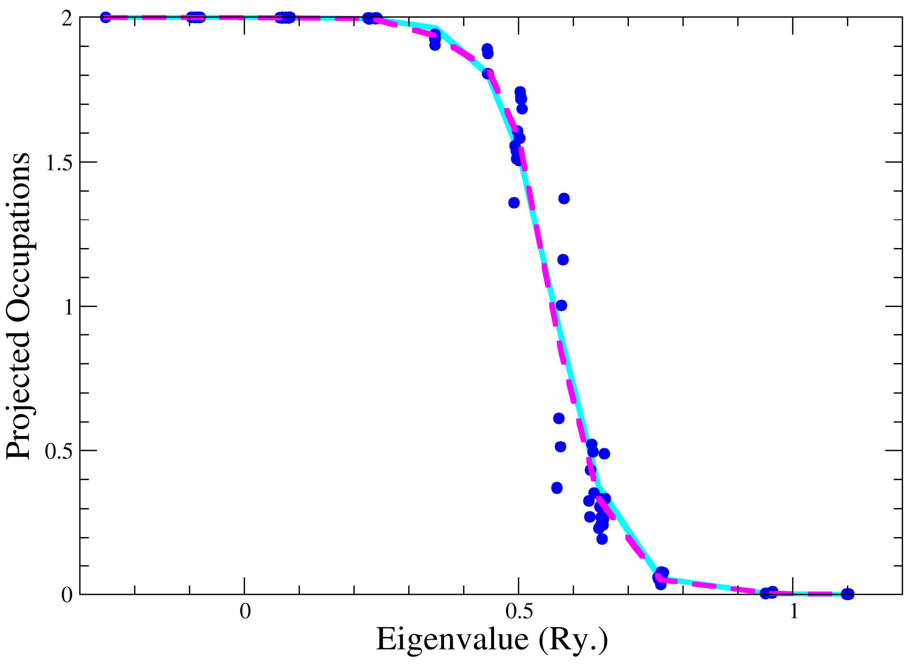
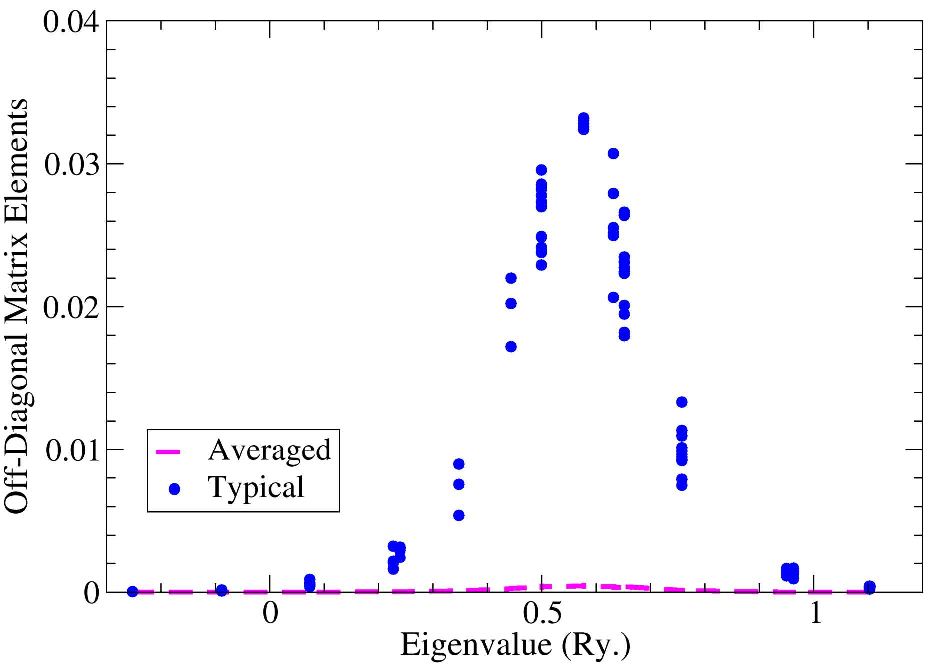
Computational Test of Approximate TDDFT Thermal States - 32 Atoms of Al at 7900 K

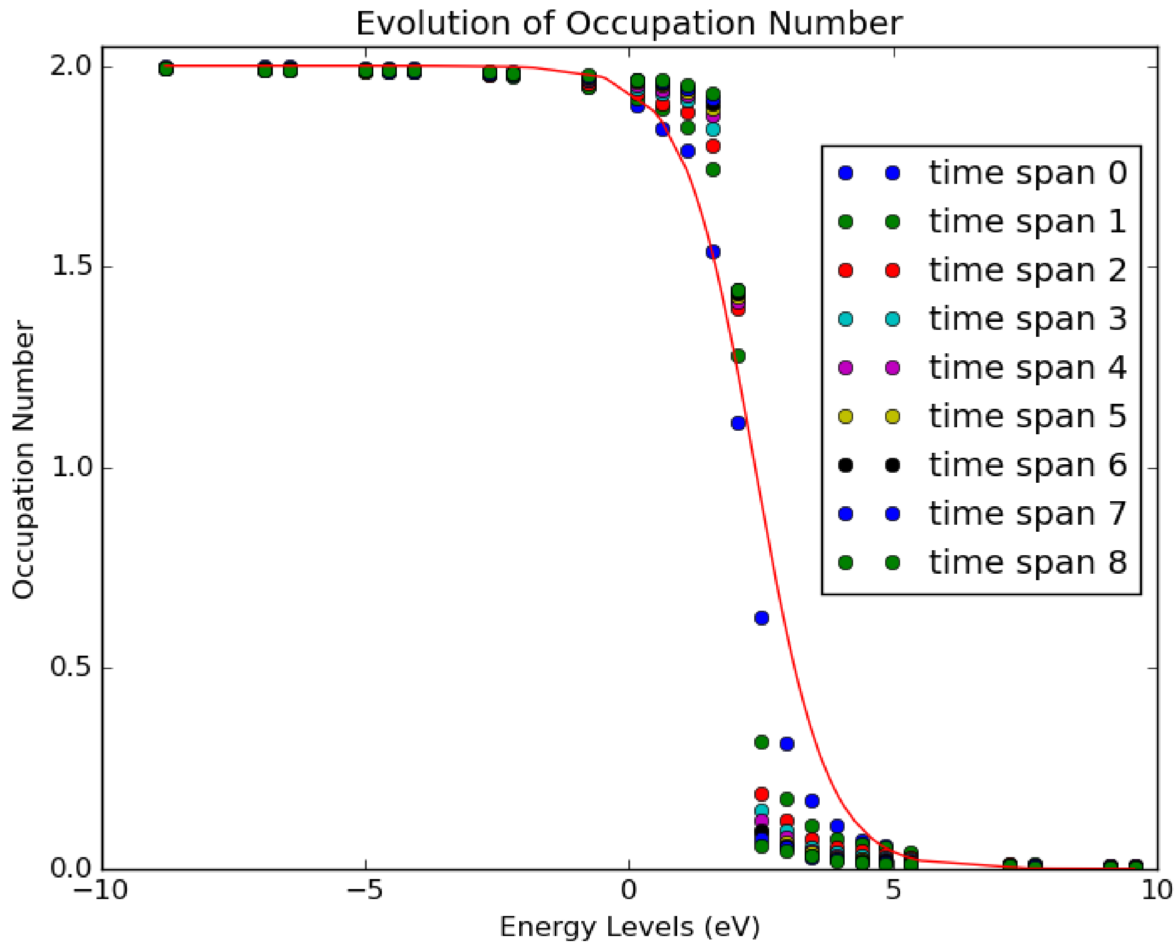
$$f_{\eta\nu} = \sum_{b=1}^{n} \langle \psi_b | \phi_\eta \rangle \langle \phi_\nu | \psi_b \rangle$$





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

What Happens When We Run TDDFT?



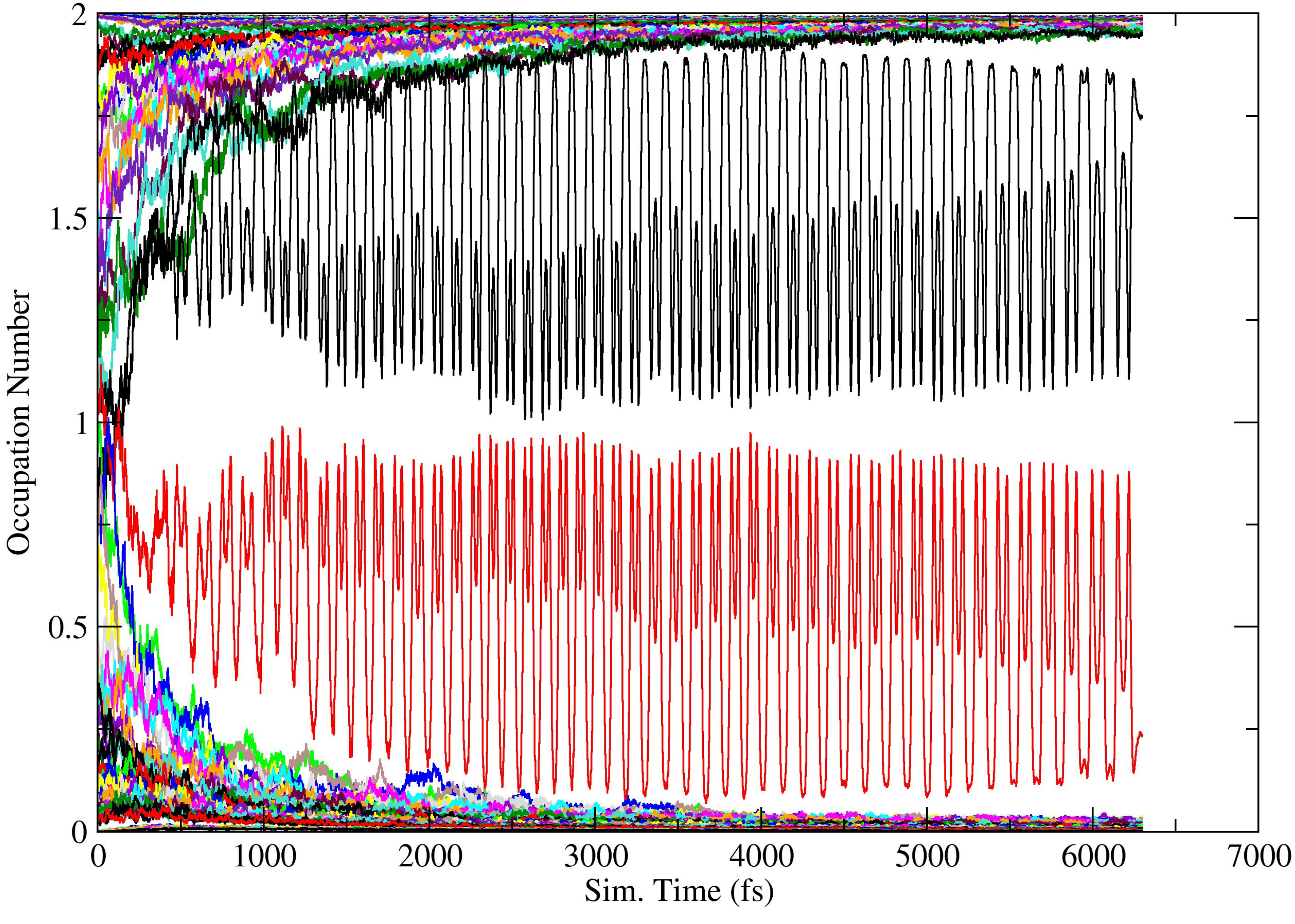
2.4 ps TDDFT run with adiabatic LDA

Starting from approximate TDDFT thermal states

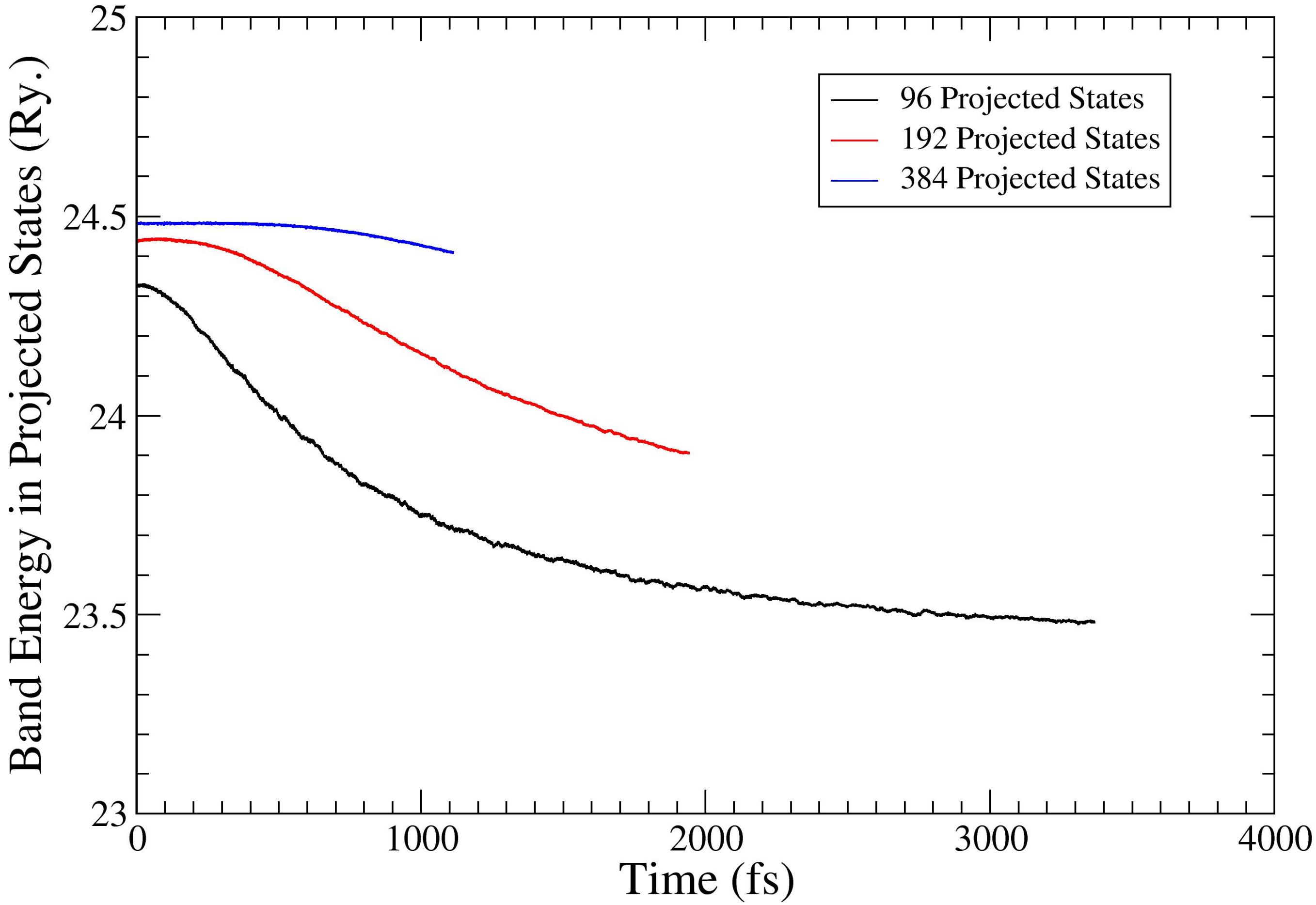
Occupations averaged in 300 fs windows

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

Projected Occupations vs. Time

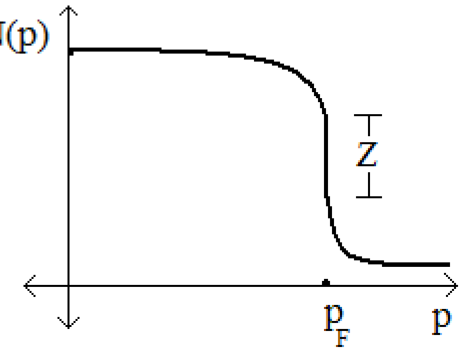


What is Causing the Slow Dynamics?



Electronic weight (and energy) is gradually redistributing (diffusing?) into higher and higher energy states

Two Arguments Why This “Weird” Behavior Might Not Be Wrong



(1) Fermi Liquid (FL) Theory

- Bare particle distribution is non-Fermi
- 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

- Thermal excitation perturbs the Hamiltonian (H_0), and thus higher energy eigenstates of H_0 get mixed in
- Dropping 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
- We argue that non-Fermi projected occupations could actually be the correct physical behavior

Constructing TDDFT Thermal States Approximations

MB quasiparticles ⟷ TDDFT eigenvectors

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

Quasiparticles do not interact

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

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

Constructing TDDFT Thermal States Approximate Correspondence

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