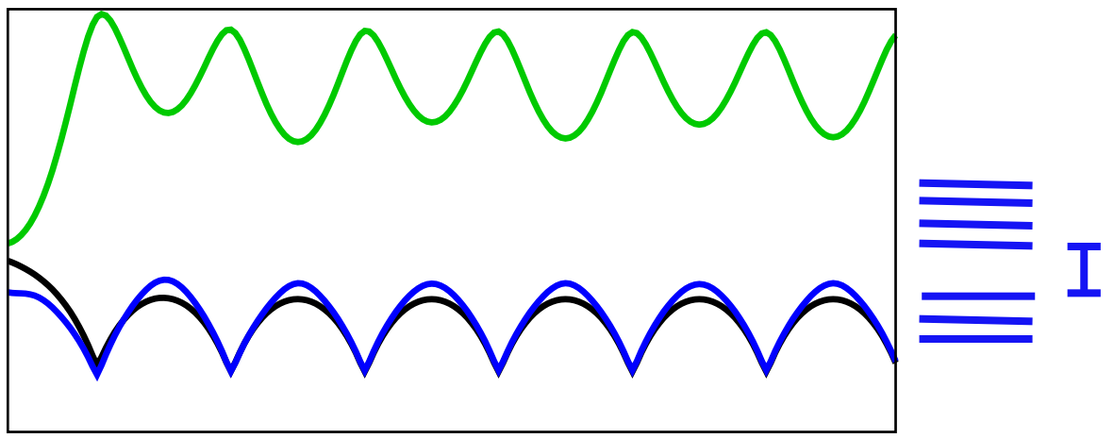
What would you do with the Exact Functional? Probing the limits of density functional theory (DFT)

E. Miles Stoudenmire
Perimeter Institute for Theoretical Physics



University of Virginia, January 2014

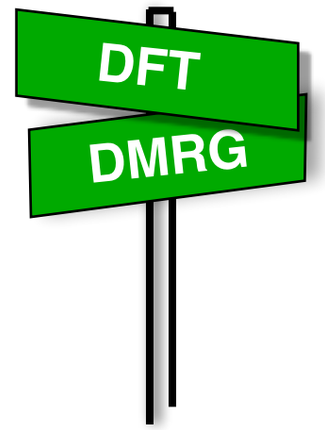
Collaborators:

Lucas O. Wagner, UC Irvine
(⟶ Amsterdam)

Kieron Burke, UC Irvine

Steve White, UC Irvine

U.S. DEPARTMENT OF ENERGY



In this talk:

We have extended the powerful density matrix renormalization group (DMRG) to solve continuum electronic systems in 1d.

One key application is studying density functional theory (DFT)—we can compute the exact functional.

Which limitations of DFT come from approximations?

Which are fundamental?

Outline:

- DMRG for continuum systems
- Exact density functional theory with DMRG
- Applications:
  - Gaps in DFT
  - Convergence of the Kohn-Sham equations

What is DMRG?

"It is at the moment the closest to an ultimate weapon as one can dream of." — T. Giamarchi


Controlled, essentially exact results


Linear scaling with system size (in 1d)


Full access to wavefunction

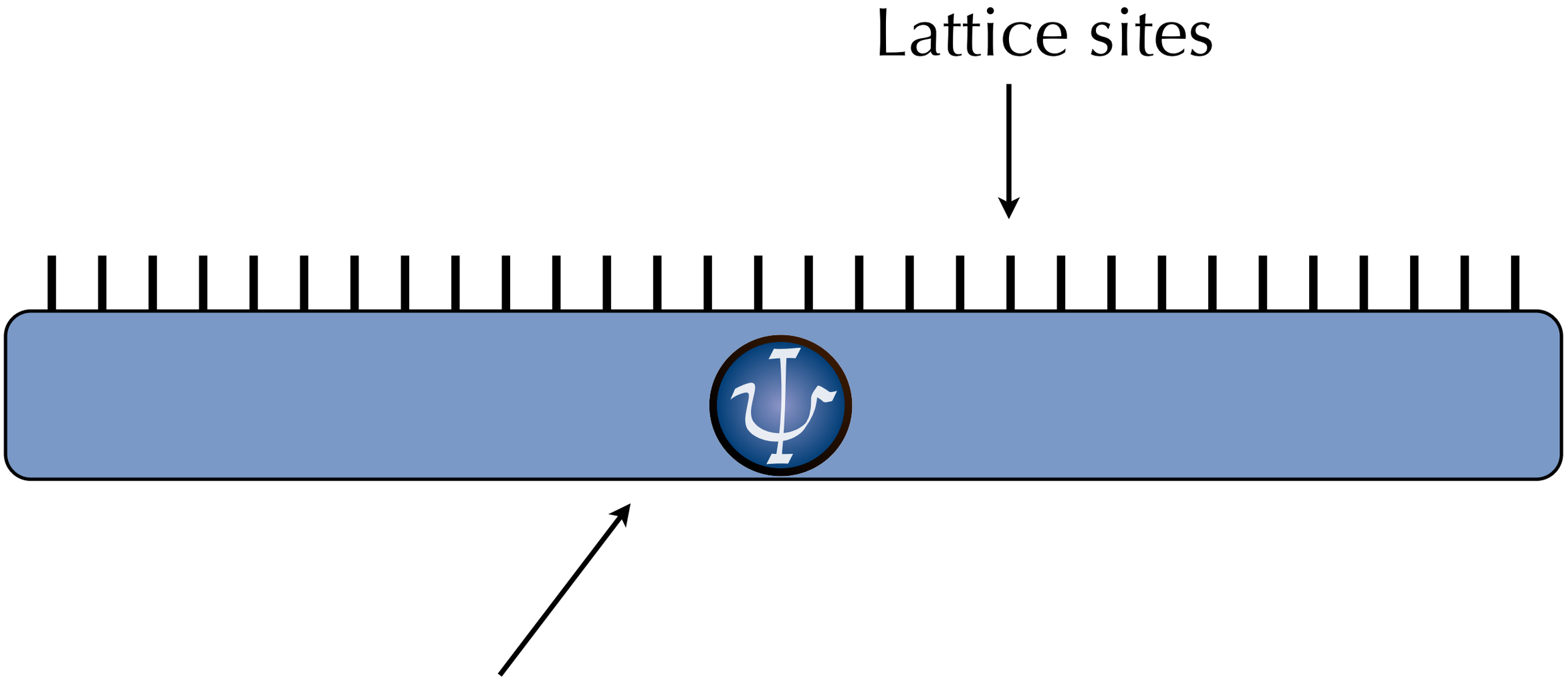

Dynamics, finite temperature


Parallelizable*


1d and narrow 2d systems

*Stoudenmire, White, PRB **87** 155137, (2013)

How does DMRG work?



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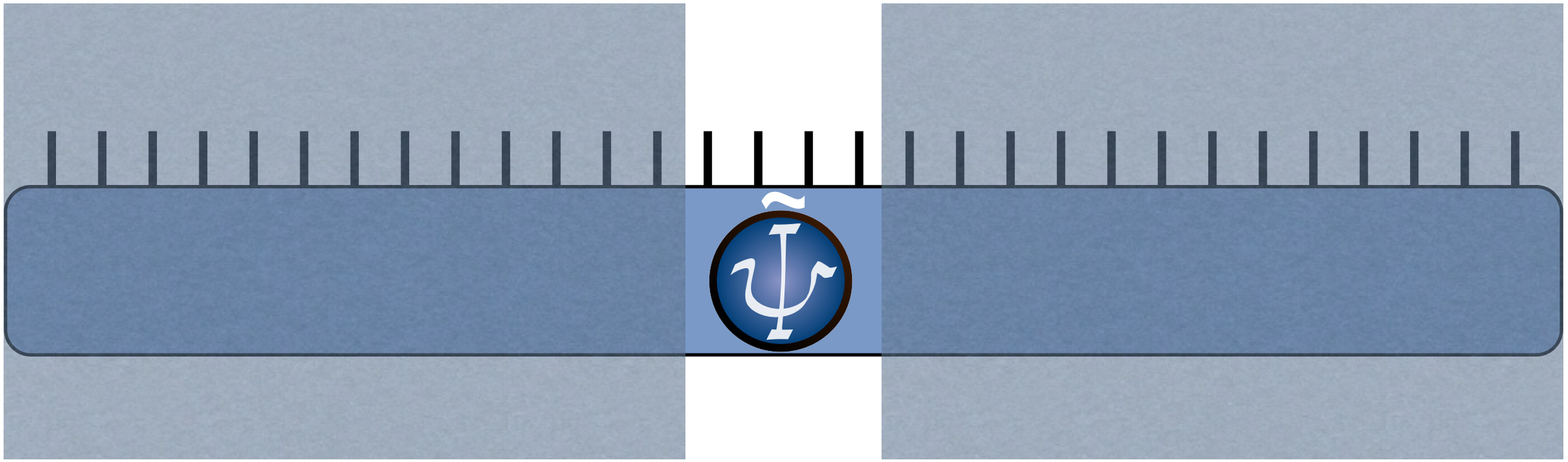
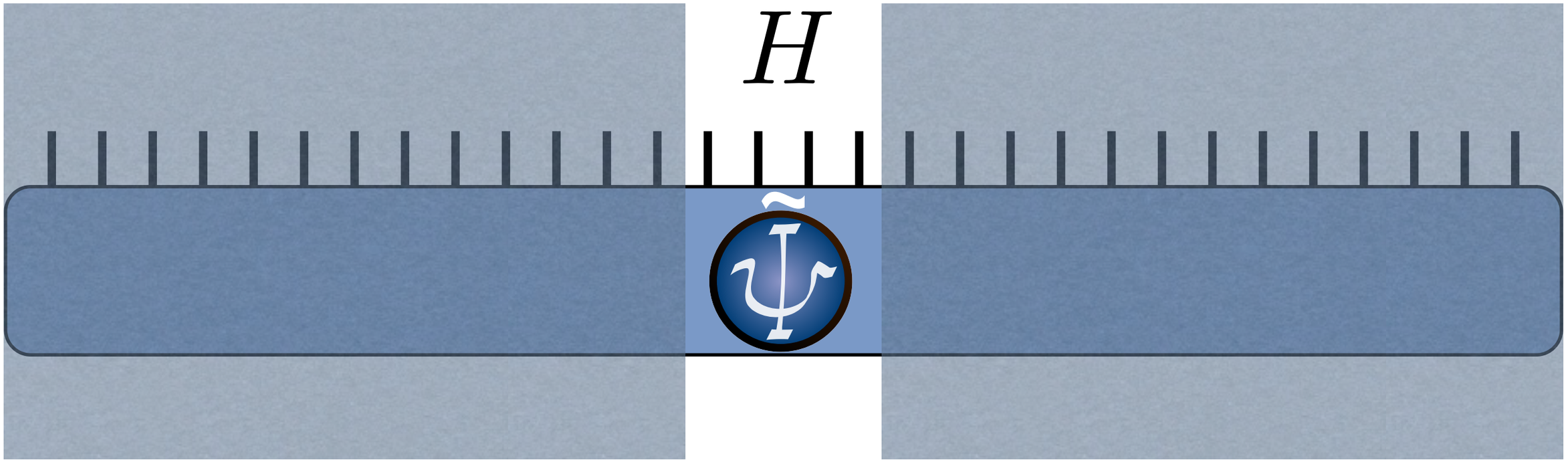


Freeze out all but a small piece of wavefunction

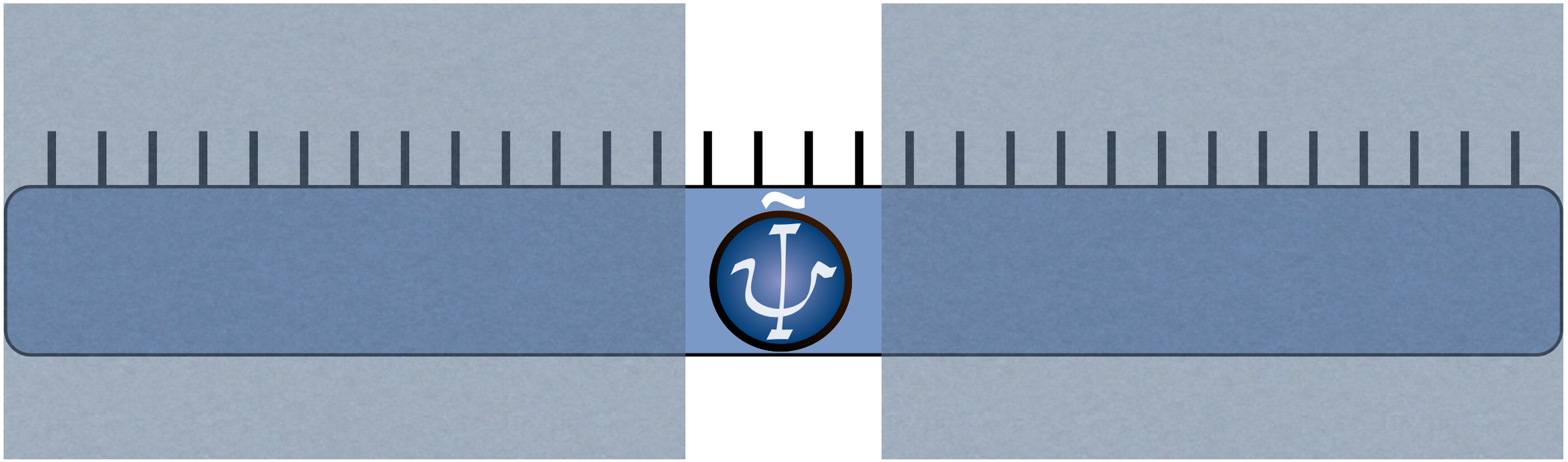
How does DMRG work?



Solve Schrodinger equation exactly for remaining piece

$$\tilde{H}|\tilde{\Psi}\rangle = \tilde{E}|\tilde{\Psi}\rangle$$

How does DMRG work?



Shift exposed region, keeping only
the most important states in the basis

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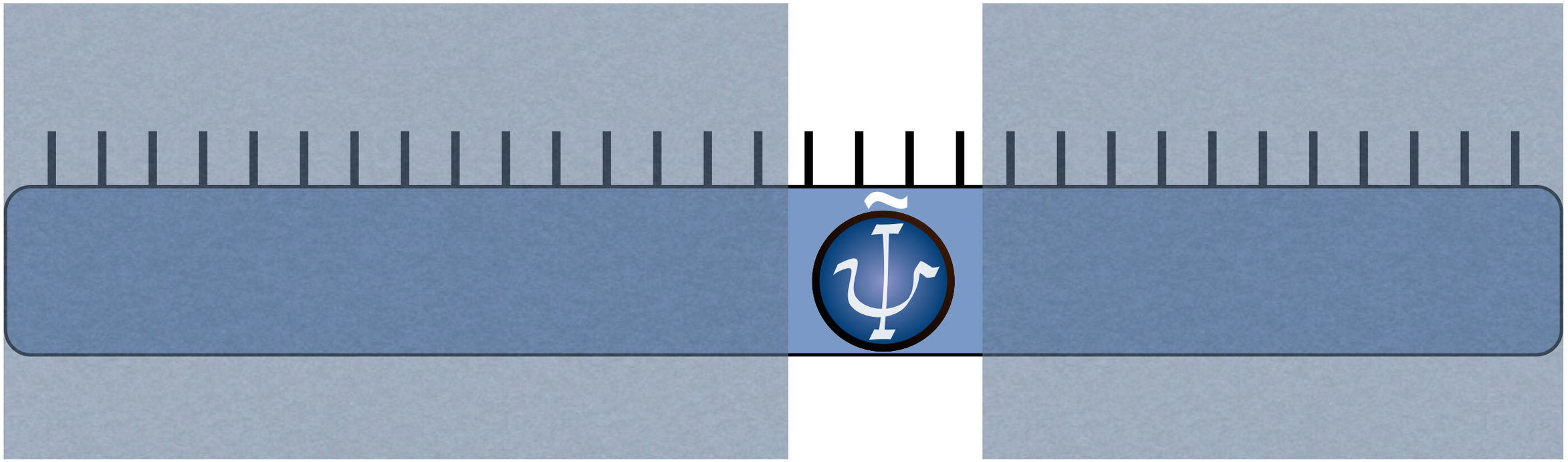

Shift exposed region, keeping only
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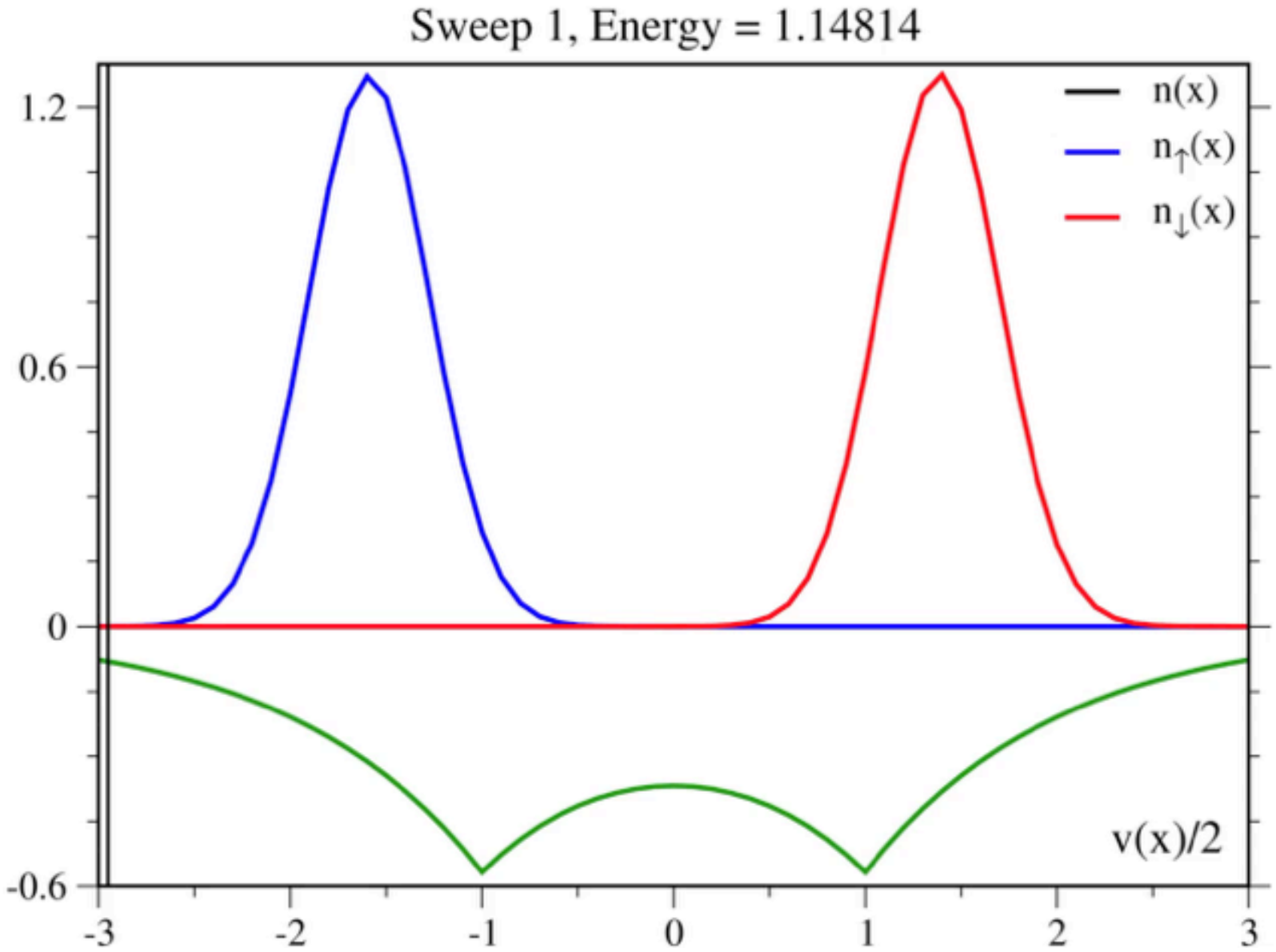
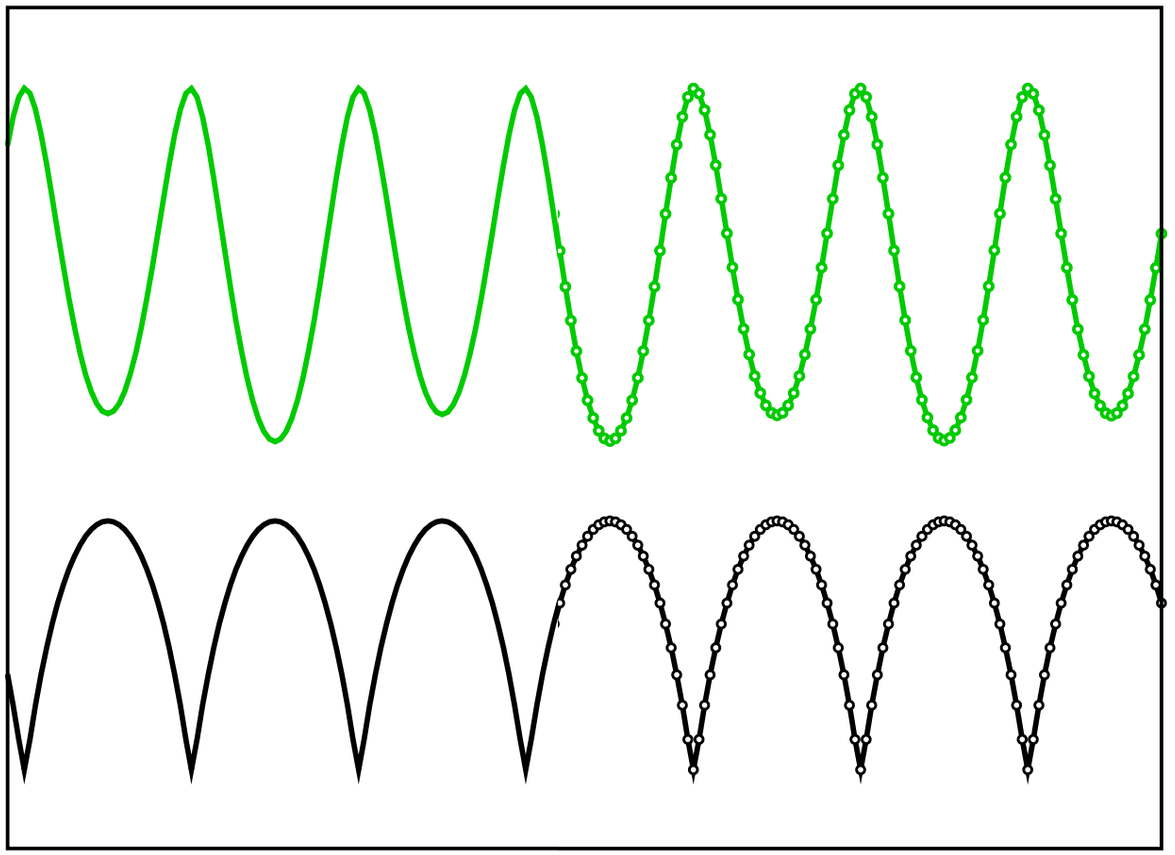
Example DMRG Calculation

Video available online: http://youtu.be/0zi4qUnSqe0



DMRG for continuum systems



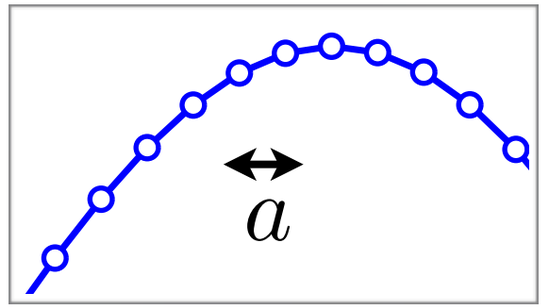
Grid basis

Need discrete degrees of freedom

Simplest approach is discretize real space:

$$T = -\frac{1}{2}\int_x c^\dagger(x)\frac{\partial^2}{\partial x^2}c(x)$$

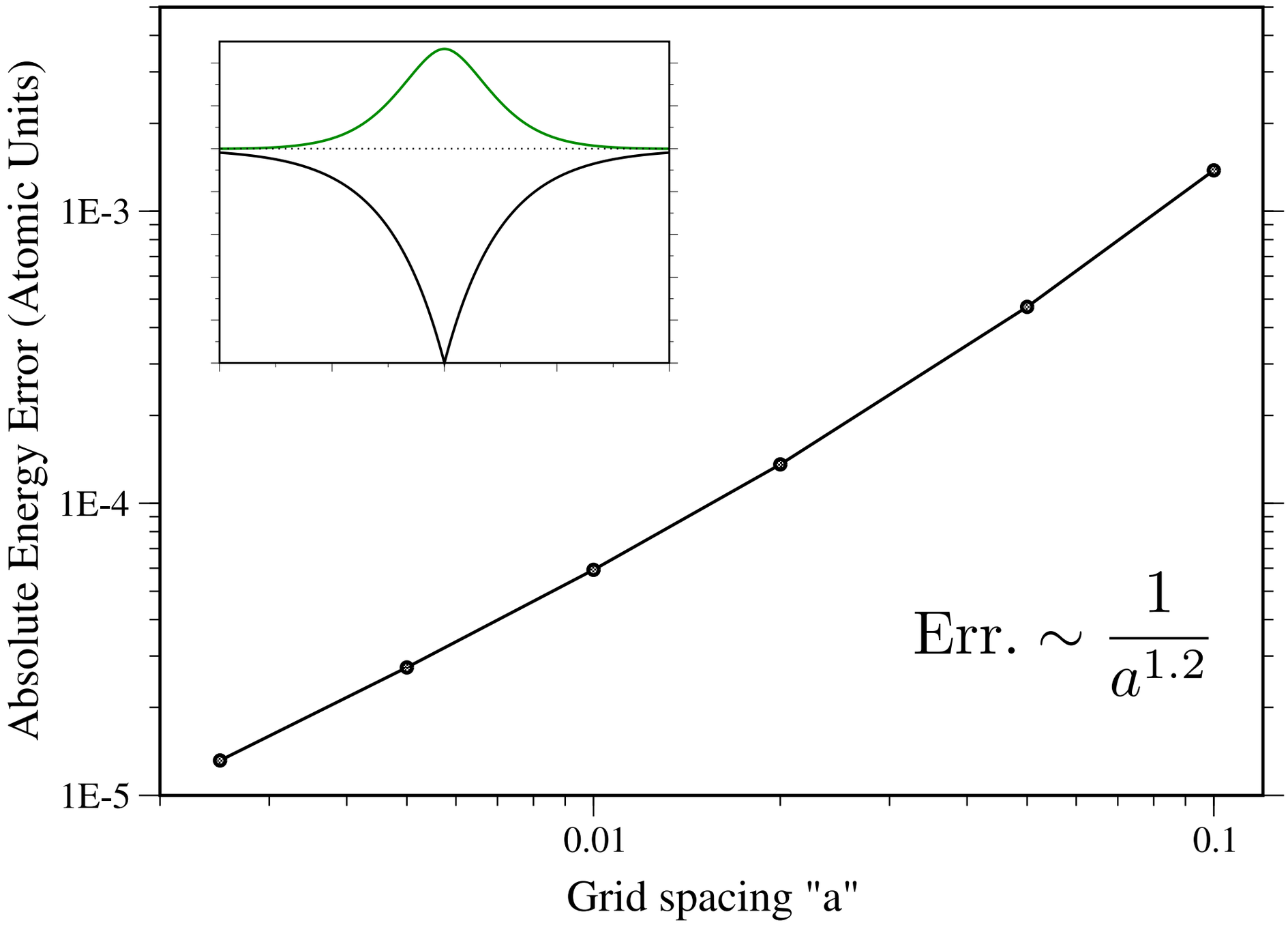
$$\simeq -\frac{1}{2a^2}\sum_j (c_j^\dagger c_{j+1} - 2n_j + c_{j+1}^\dagger c_j)$$



Not atomic lattice sites, but “grid sites”

Converge results to $a \to 0$ limit...

Grid error—1d hydrogen atom:



Hamiltonian

Want to study ‘uncontrived’ 1d physics

$$\hat{H} = -\frac{1}{2}\sum_{\sigma}\int_{x}\psi_{\sigma}^{\dagger}(x)\frac{\partial^2}{\partial x^2}\psi_{\sigma}(x)$$

$$+\frac{1}{2}\int_{x,x'} v_{\mathrm{ee}}(x-x')\,\hat{n}(x)\,\hat{n}(x')$$

$$+\int_{x} v(x)\,\hat{n}(x)$$

Hamiltonian

Want to study ‘uncontrived’ 1d physics

$$\hat{H} = -\frac{1}{2a^2}\sum_{\sigma,j}(c^{\dagger}_{\sigma j}c_{\sigma j+1} - 2n_{\sigma j} + c^{\dagger}_{\sigma j+1}c_{\sigma j})$$

$$+\frac{1}{2}\sum_{i,j} v^{ij}_{\mathrm{ee}}\, n_i\,(n_j - \delta_{ij})$$

$$+\sum_{j} v^{j}\, n_j$$

Hamiltonian

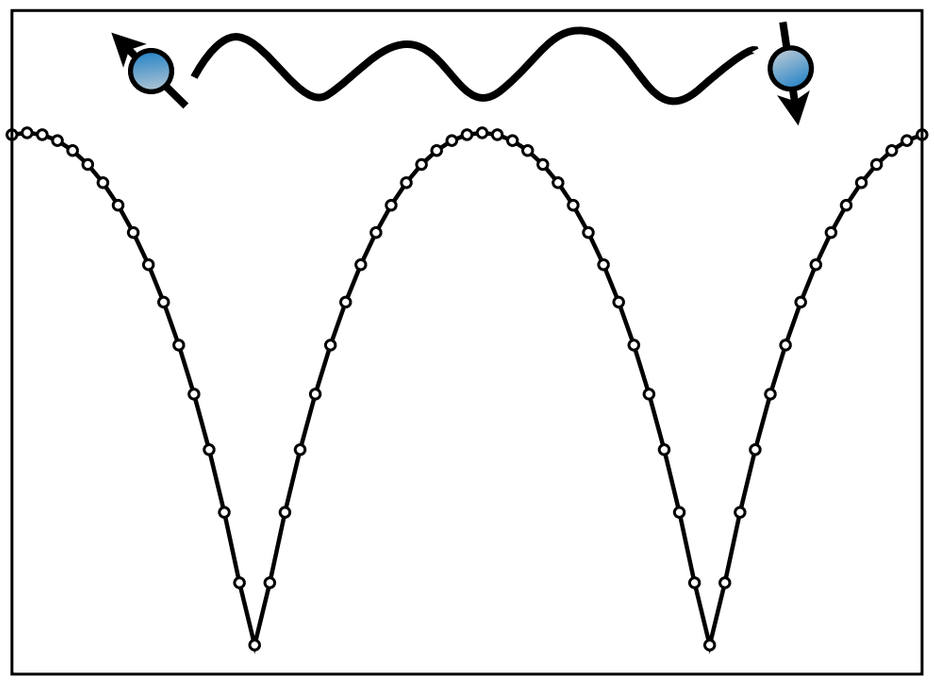
What to choose for $v(x)$, $v_{\mathrm{ee}}(x-x')$?

1d matter:

$$v(x) = \sum_a v_a(x - x_a) = \sum_a -Z v_{\mathrm{ee}}(x - x_a)$$

Also we choose:

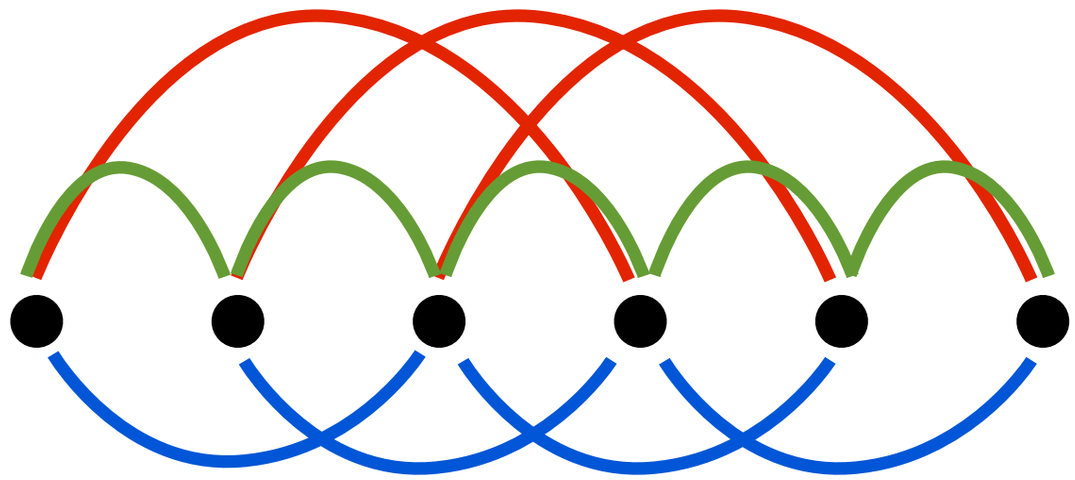
$$v_{\mathrm{ee}}(x - x') = e^{-|x-x'|}$$



Why hasn't DMRG been applied to these systems before?

- Cost of long-range interactions
- Poor convergence—separation of energy scales

- Cost of long-range interactions



Normally DMRG scales $\propto N$,

with this approach $\propto N^2 \times N = N^3$

Disaster for the continuum! $(N \sim 1000)$

- Cost of long-range interactions

Fortunately solution recently proposed:

By writing Hamiltonian as a product of "transfer matrices"* at each site, can represent arbitrary strings of operators.

Choosing strings of operator $\lambda \hat{I}$ produces exponentially decaying interactions.

* a matrix product operator (MPO)

McCulloch, arxiv:0804.2509 (2008)

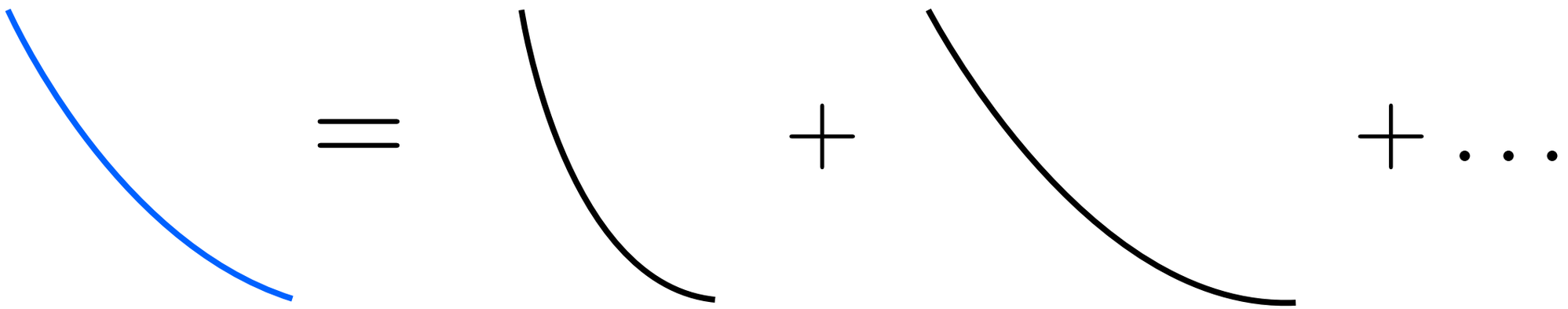
- Cost of long-range interactions

Bottom line:

Cost of exponential interactions can be made same as next-neighbor

Can approximate power-laws as sum of exponentials:

$$\frac{1}{|i-j|^{\alpha}} \simeq \sum_p \chi_p \ \lambda_p^{i-j}$$



Crosswhite, Doherty, Vidal, PRB **78** 035116, (2008)

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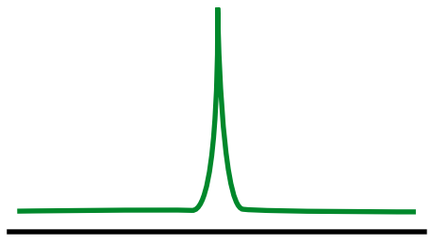
At least 3 widely varying energy scales in our systems:

Grid kinetic energy ($\sim 1/a^2$)



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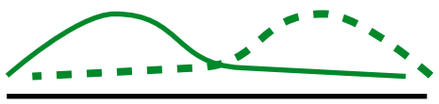
Density fluctuation (U)



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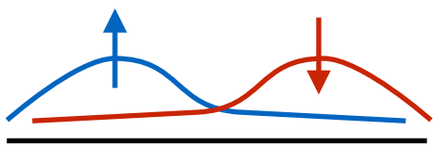
Spin fluctuation (t^2/U)



- Poor convergence—separation of energy scales

Unusual situation for DMRG:

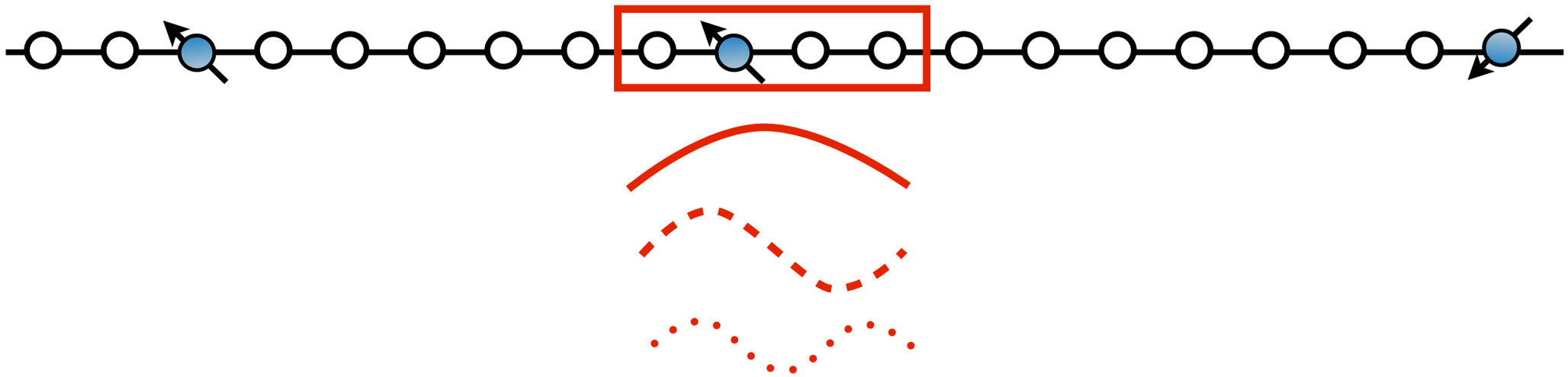
Typically concerned about cost of “keeping enough states” for good accuracy.

Here number of states ~100 (small) but number of sweeps needed can be ~1000 or more.

- Poor convergence—separation of energy scales

Solution: make better initial state.

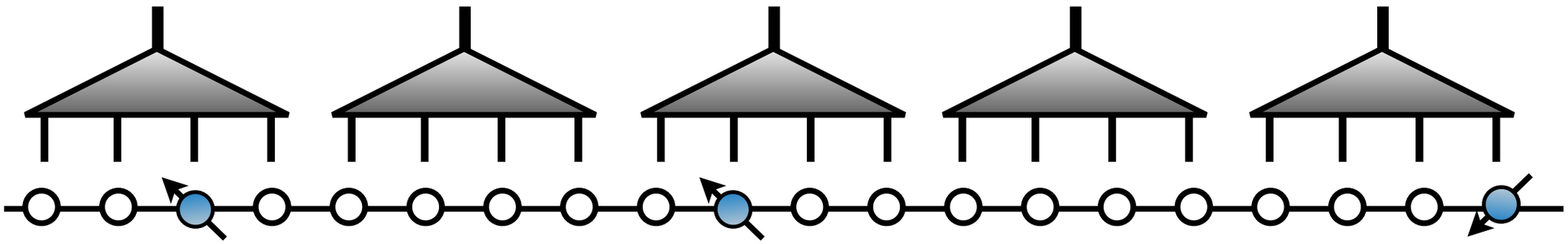
From grid point of view, system very dilute:



For small region, only handful of orbitals contribute to wavefunction.

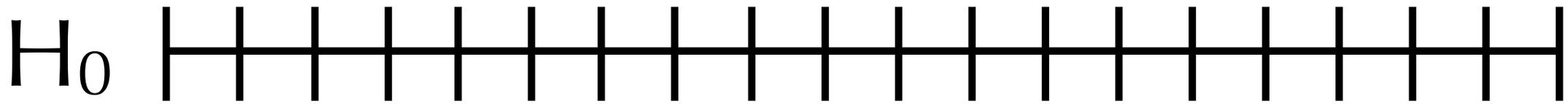
- Poor convergence—separation of energy scales

Create coarse-graining mapping that projects all but these orbitals



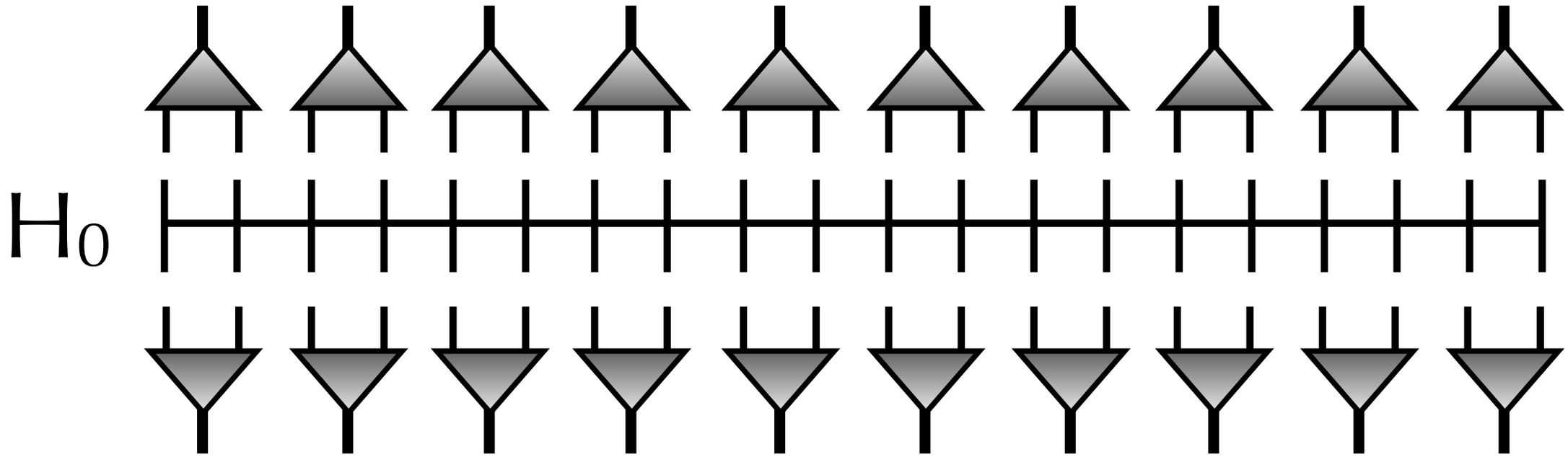
Dolfi, Bauer, et al., PRL **109** 020604 (2012)

Apply maps to Hamiltonian



Use DMRG at each scale and apply maps in reverse

Apply maps to Hamiltonian



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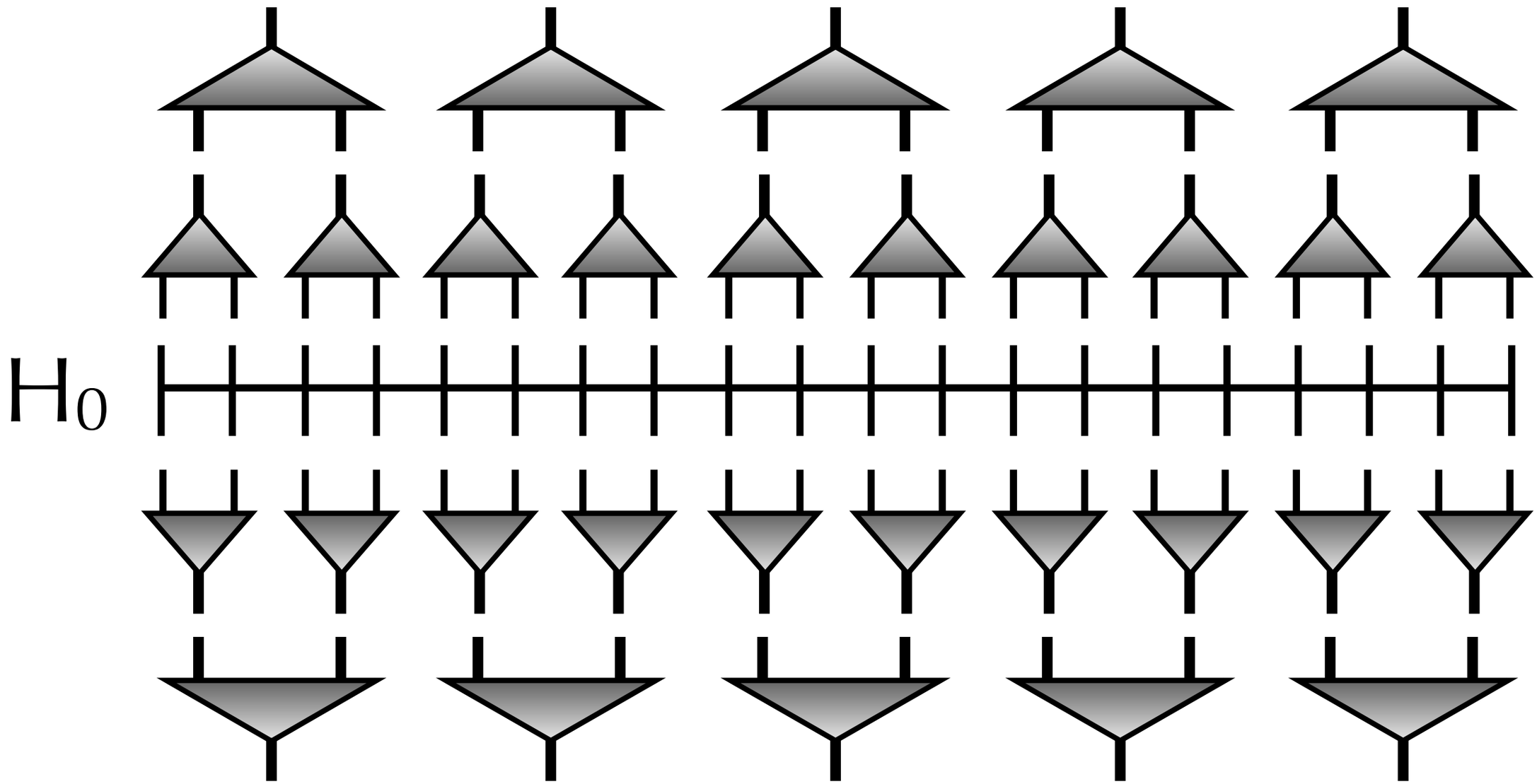

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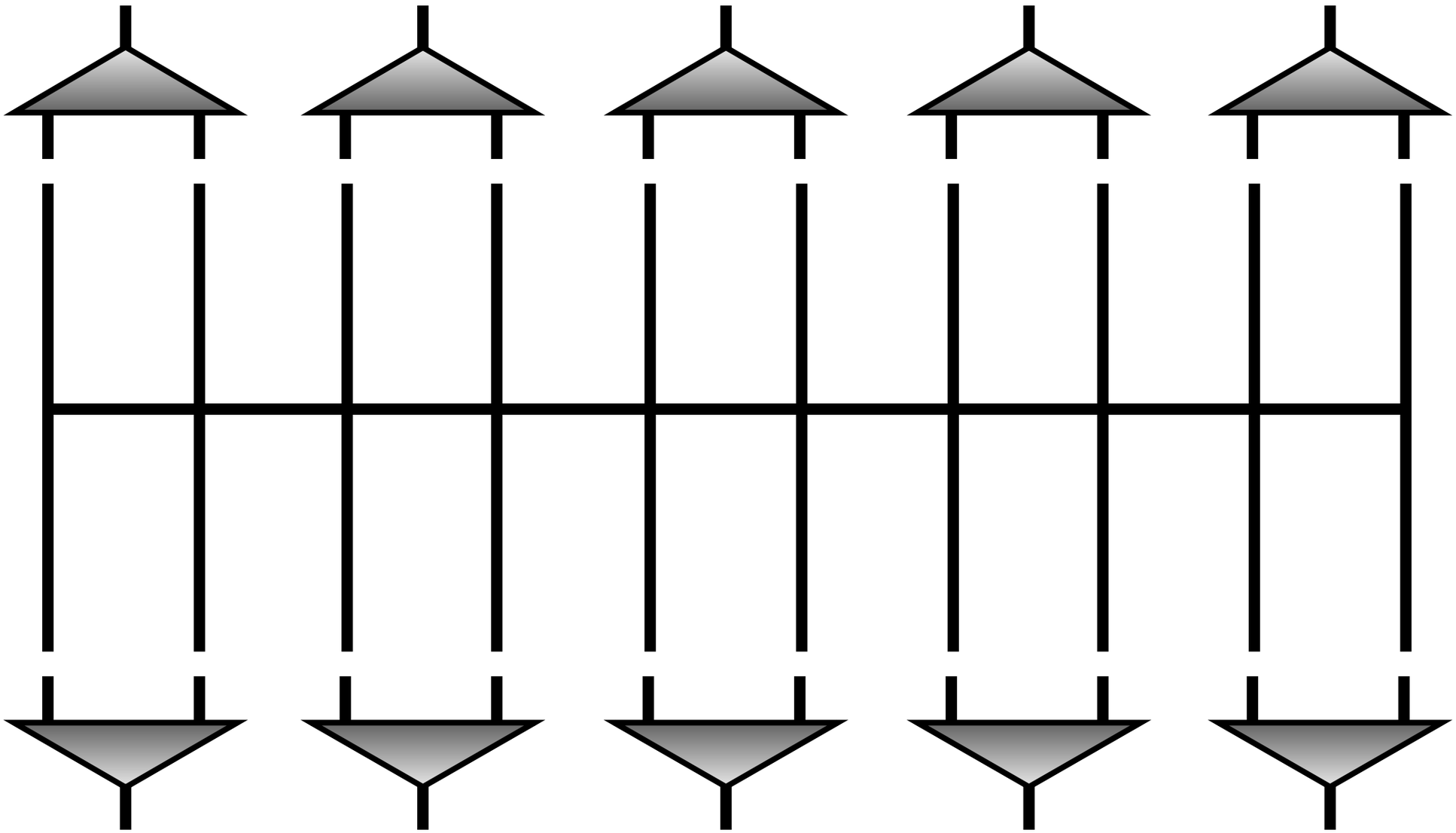

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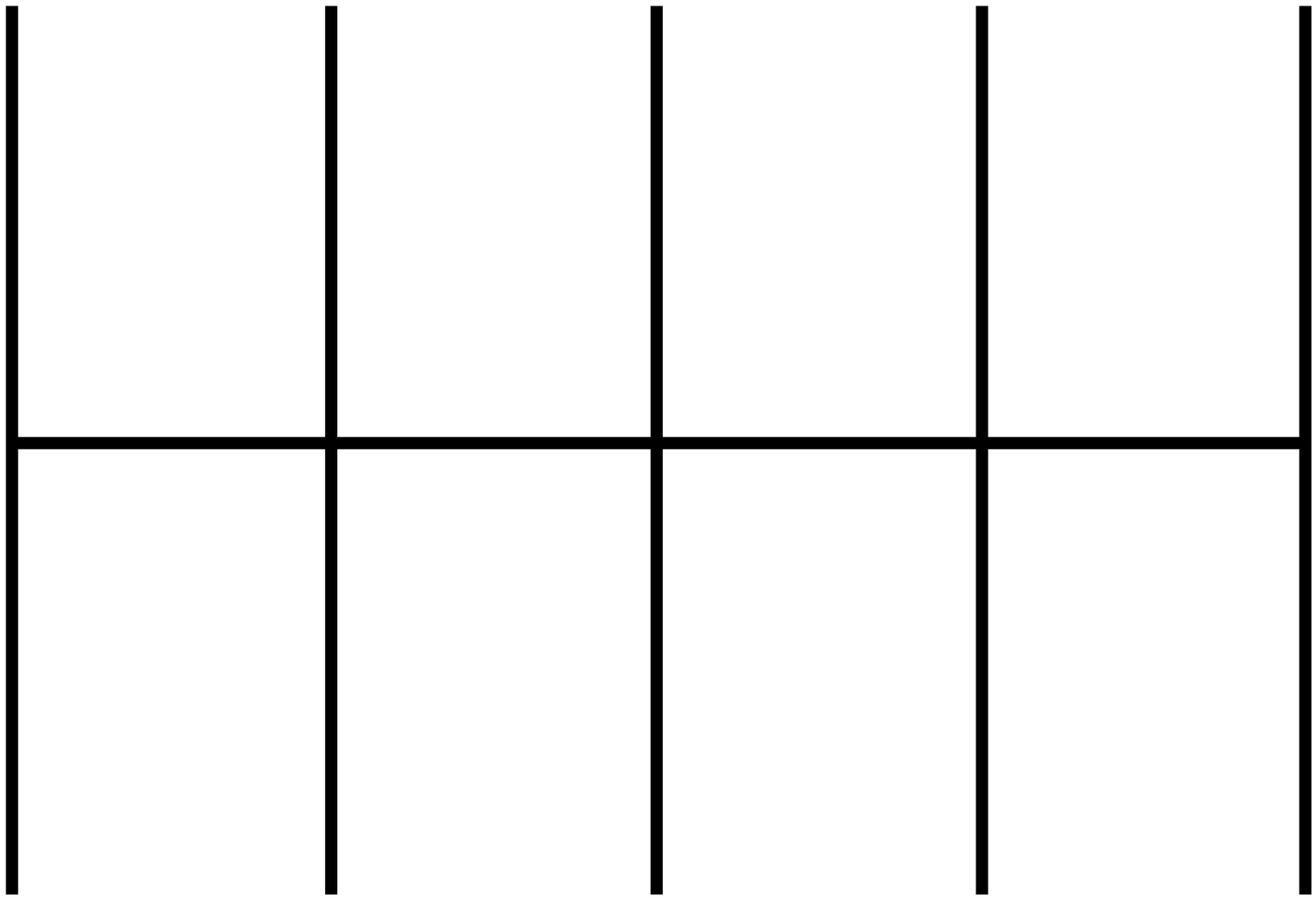
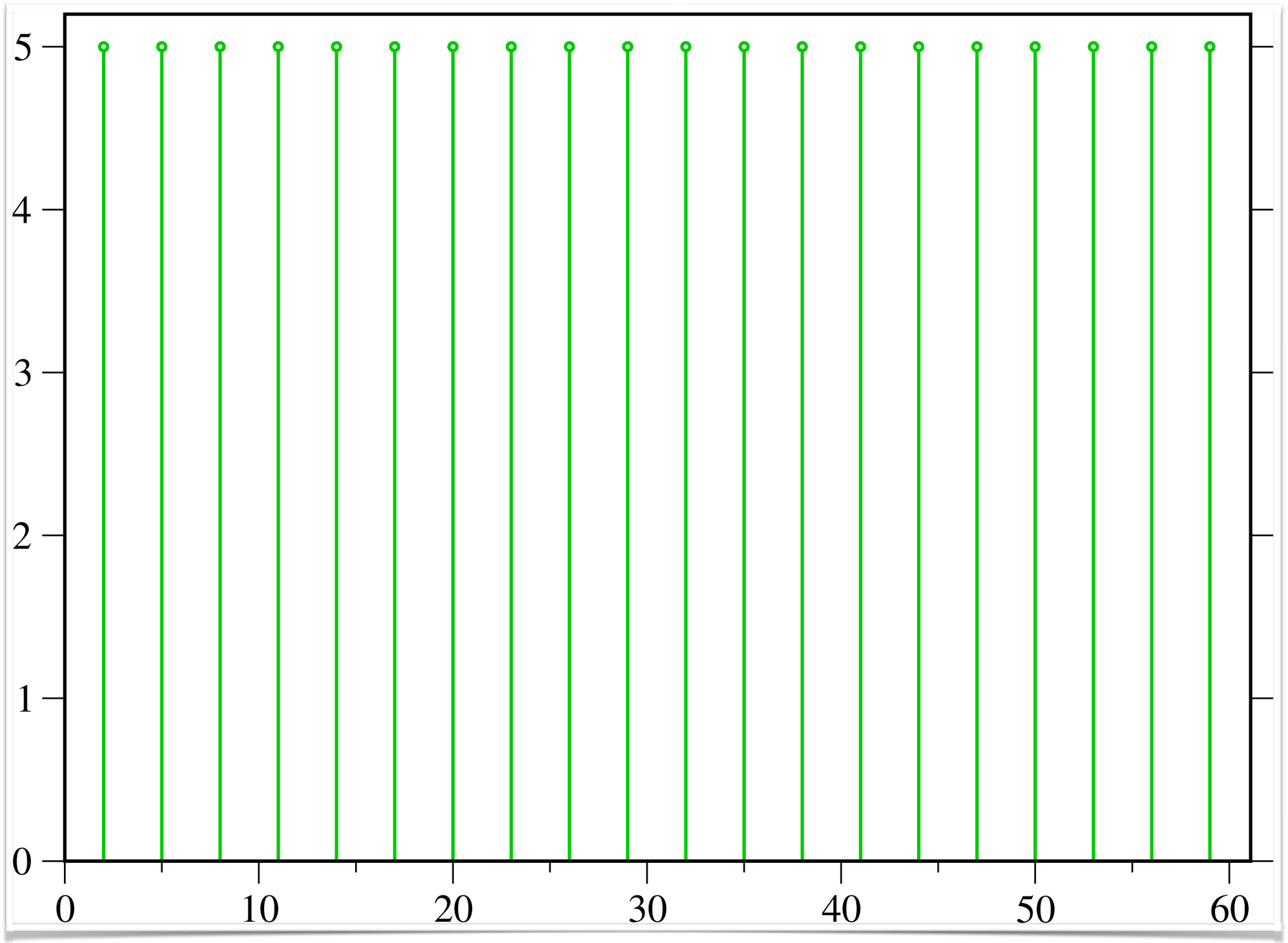


Use DMRG at each scale and apply maps in reverse

Demonstration:



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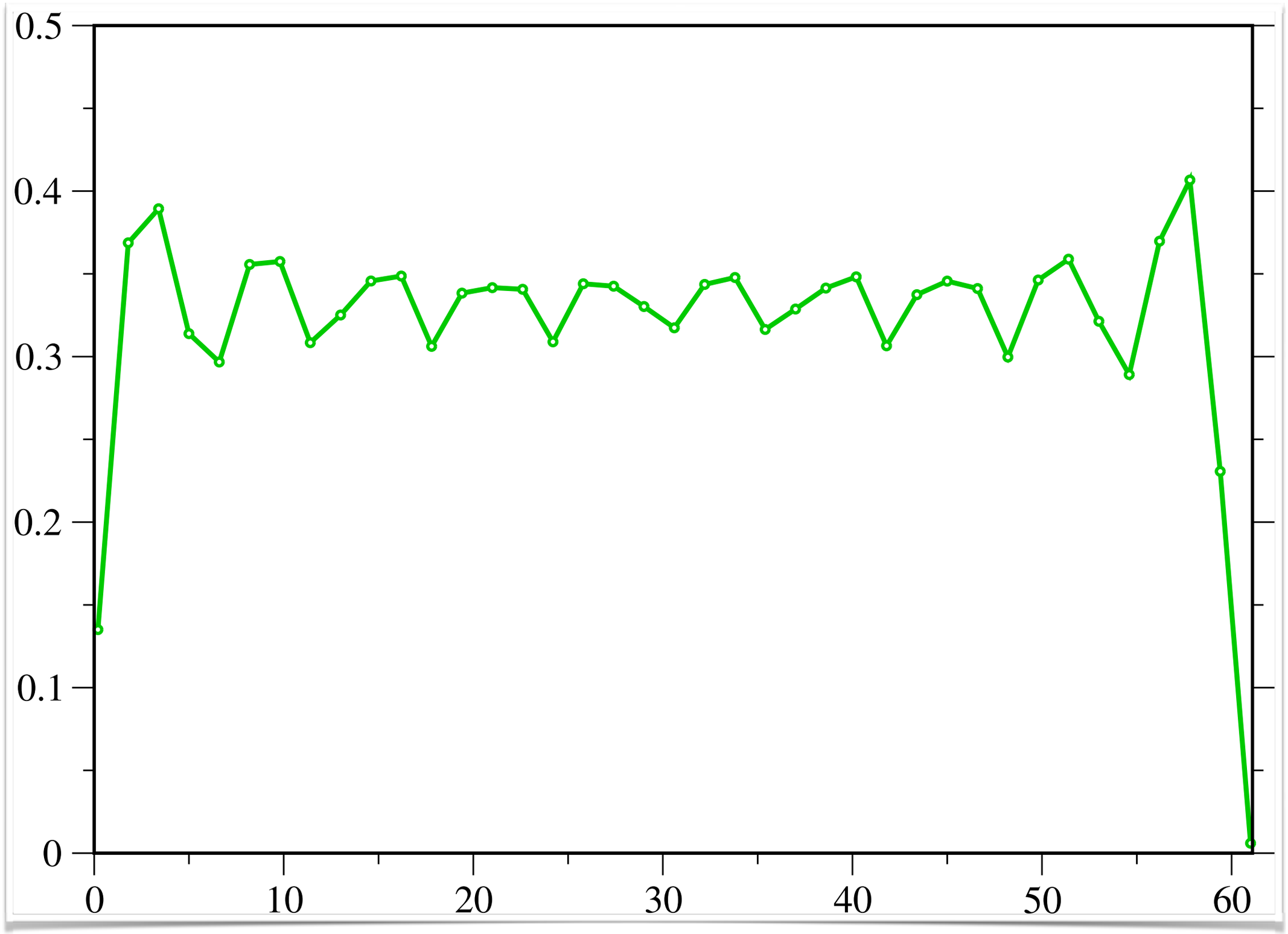

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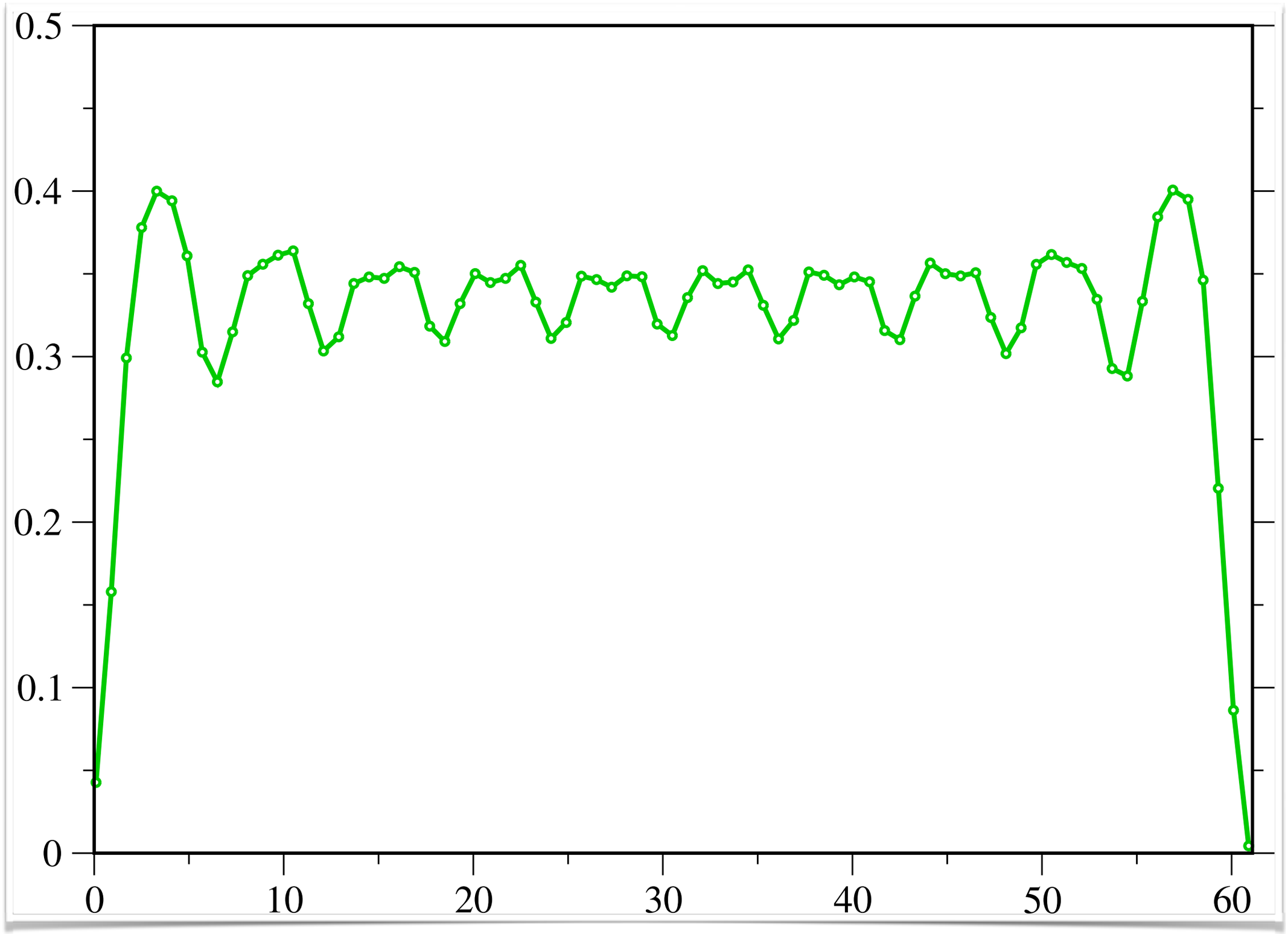

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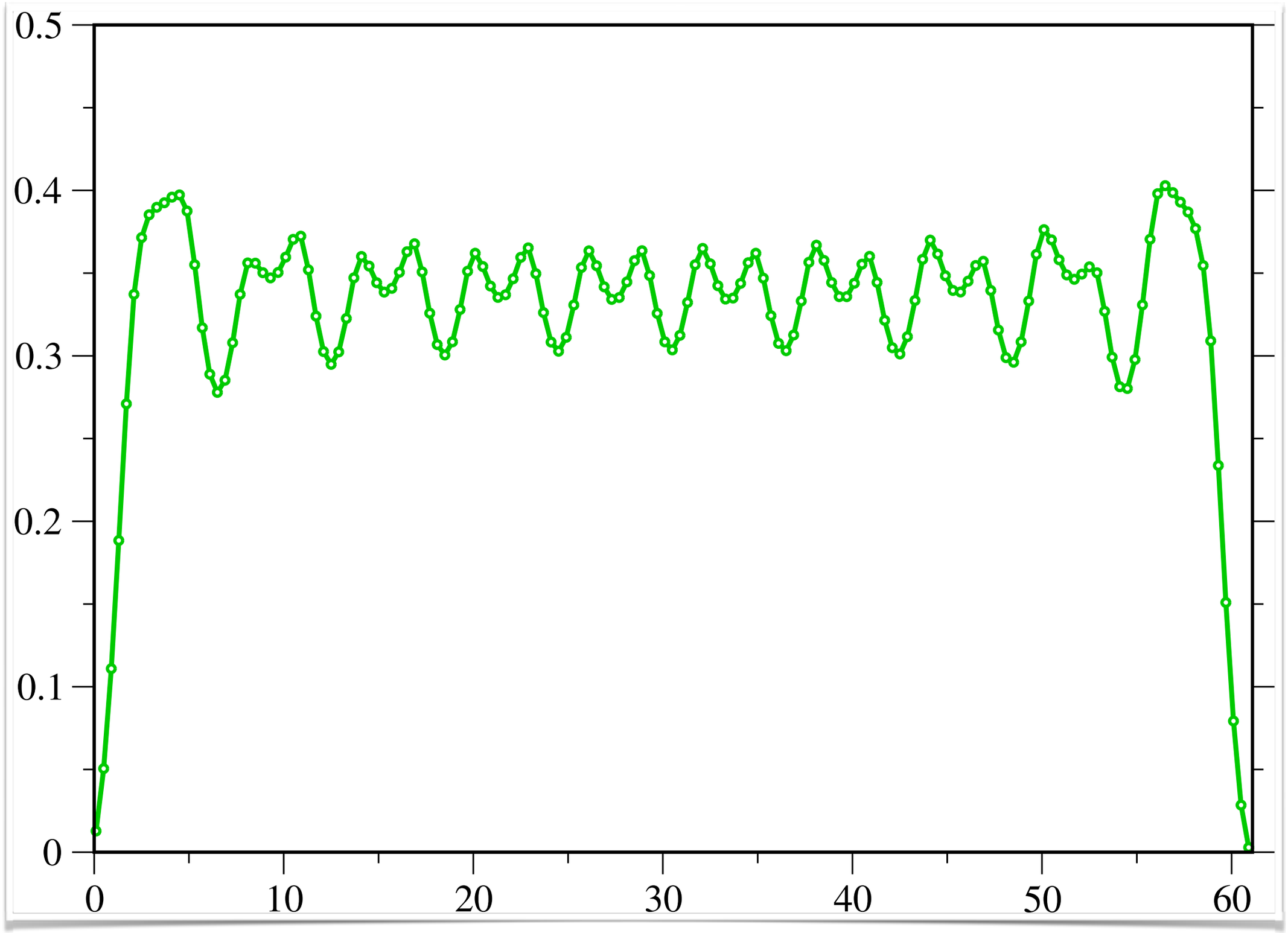

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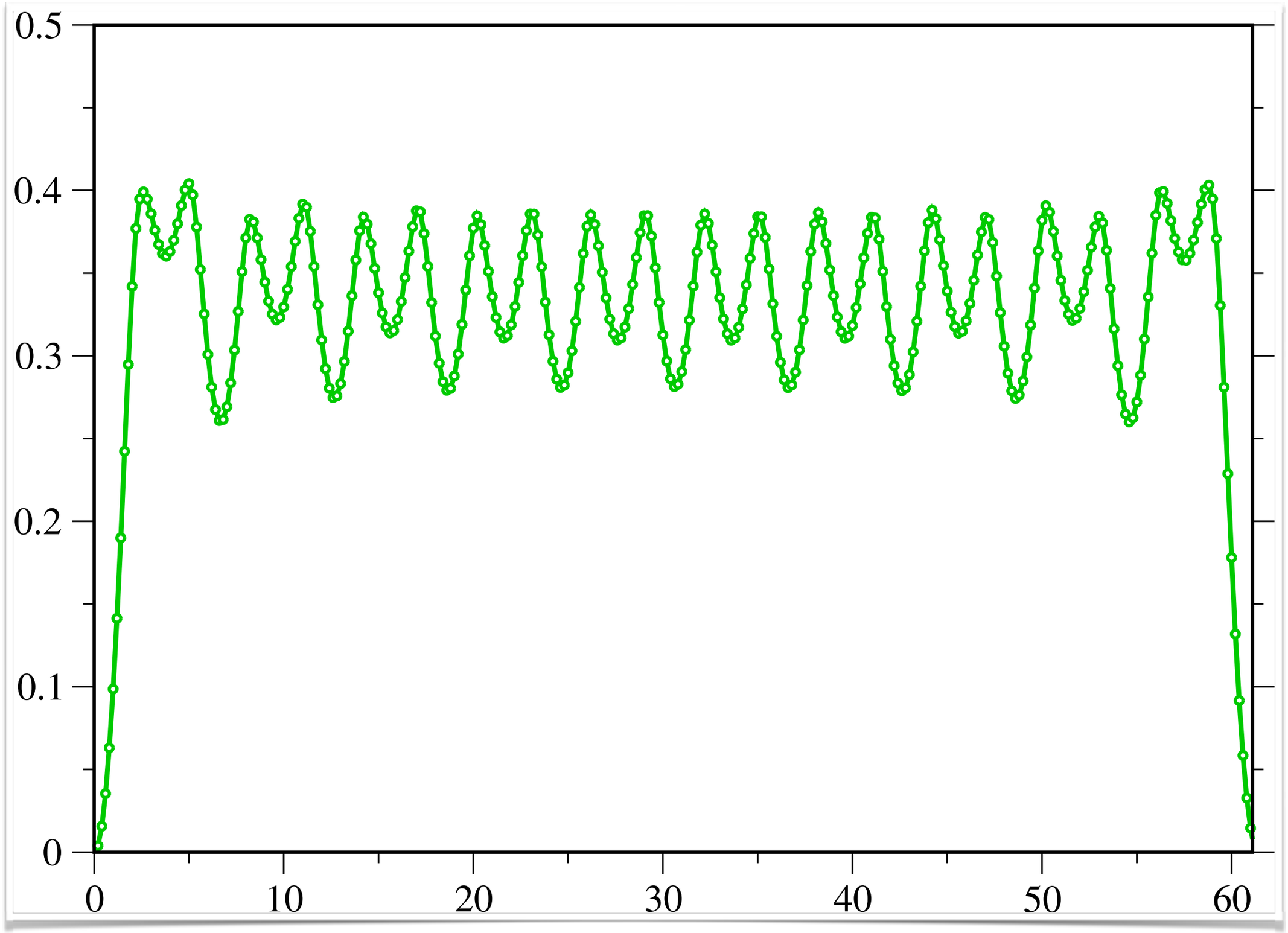

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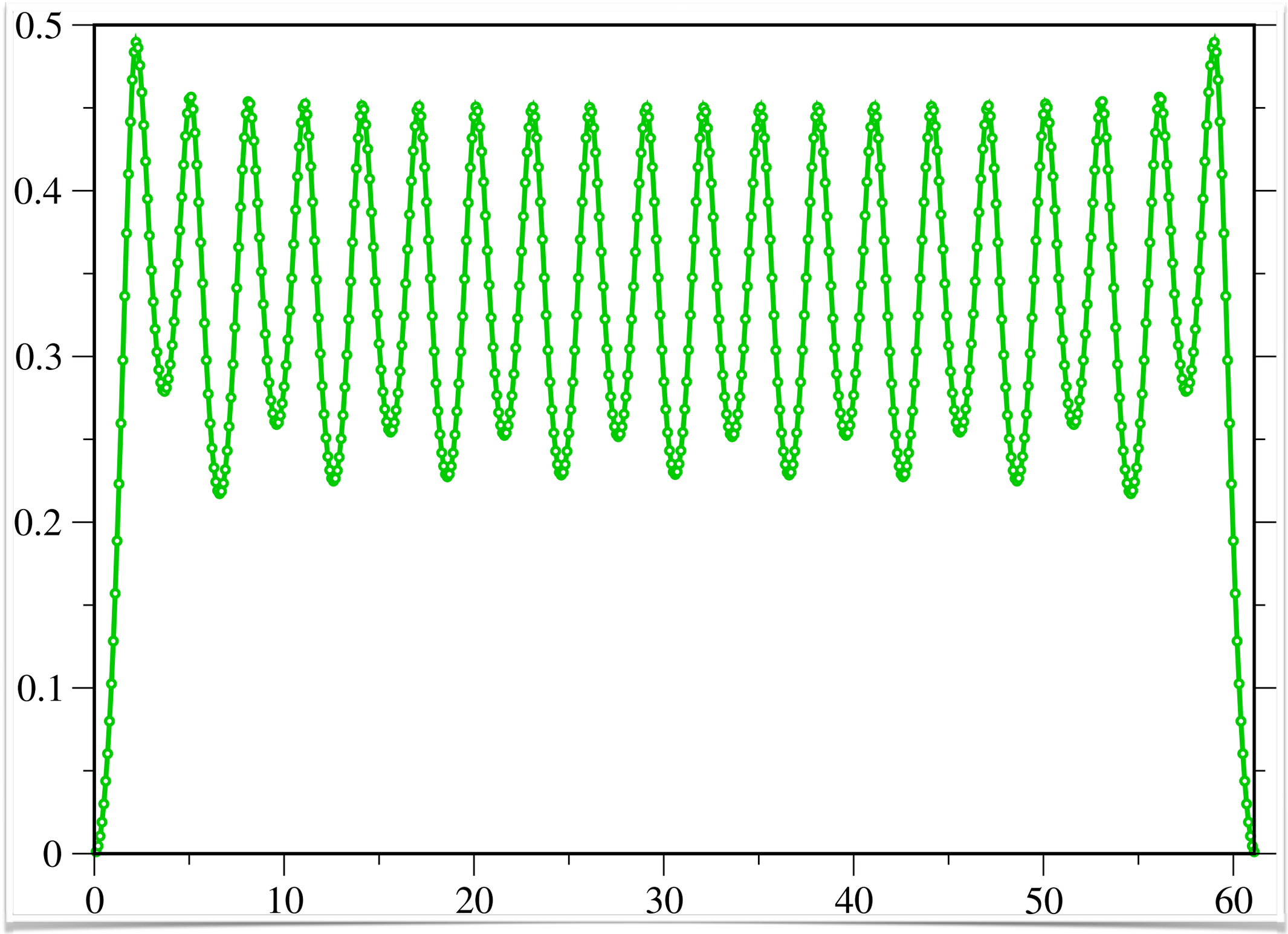


DMRG for continuum systems

Summary: powerful tool to solve broad class of continuum 1d systems essentially exactly.

Today: DFT, but exciting possible applications for 1d cold atom/molecule experiment.

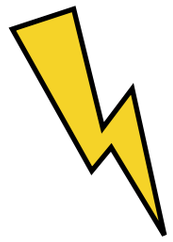
+ Minimal approximation of Hamiltonian required
+ Exploit DMRG's abilities to simulate:
  - Real-time dynamics
  - Finite T effects

Stoudenmire, Wagner, Burke, White, PRL **109**, 056402 (2012)

Application #1:

Computing Gaps in DFT

Lightning DFT overview…

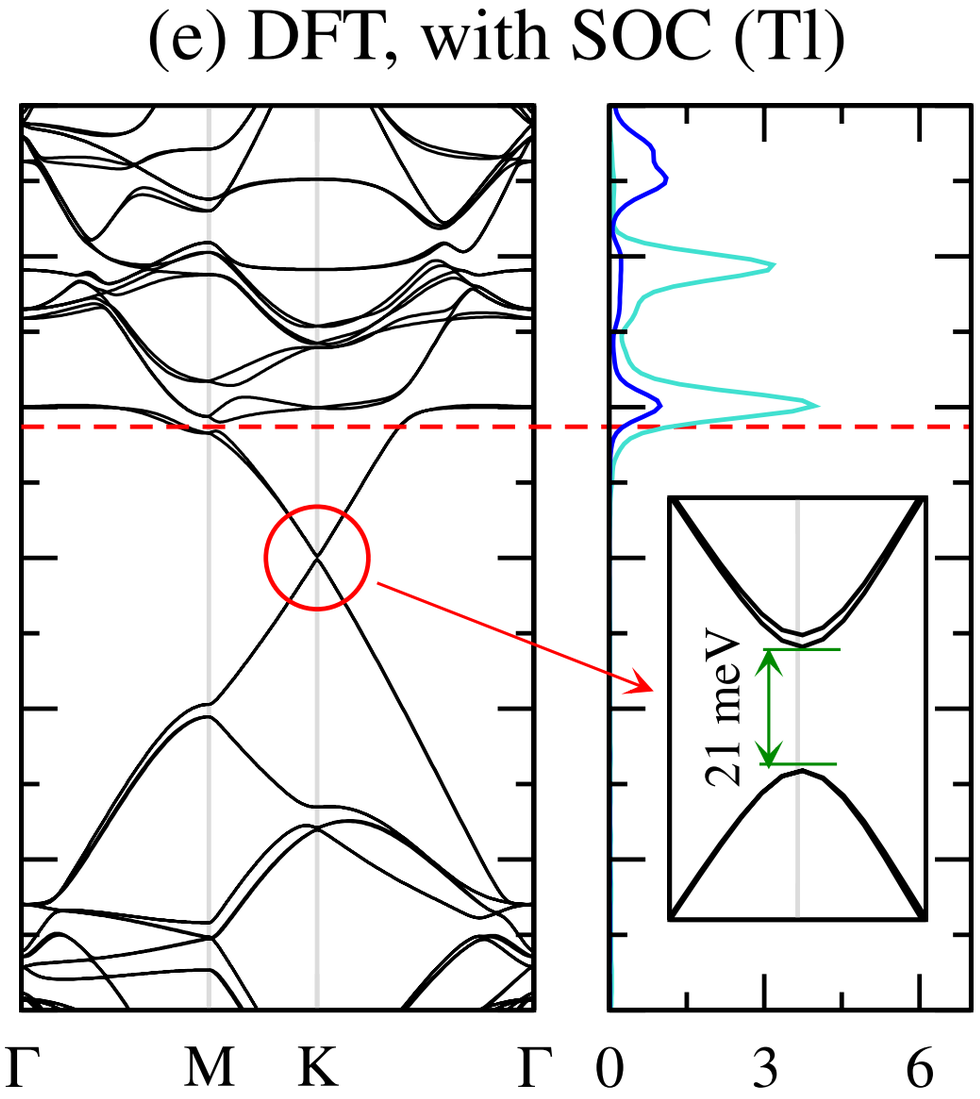


Density functional theory (DFT)

Often where “rubber meets the road” in condensed matter / materials physics / chemistry.

Recent application:

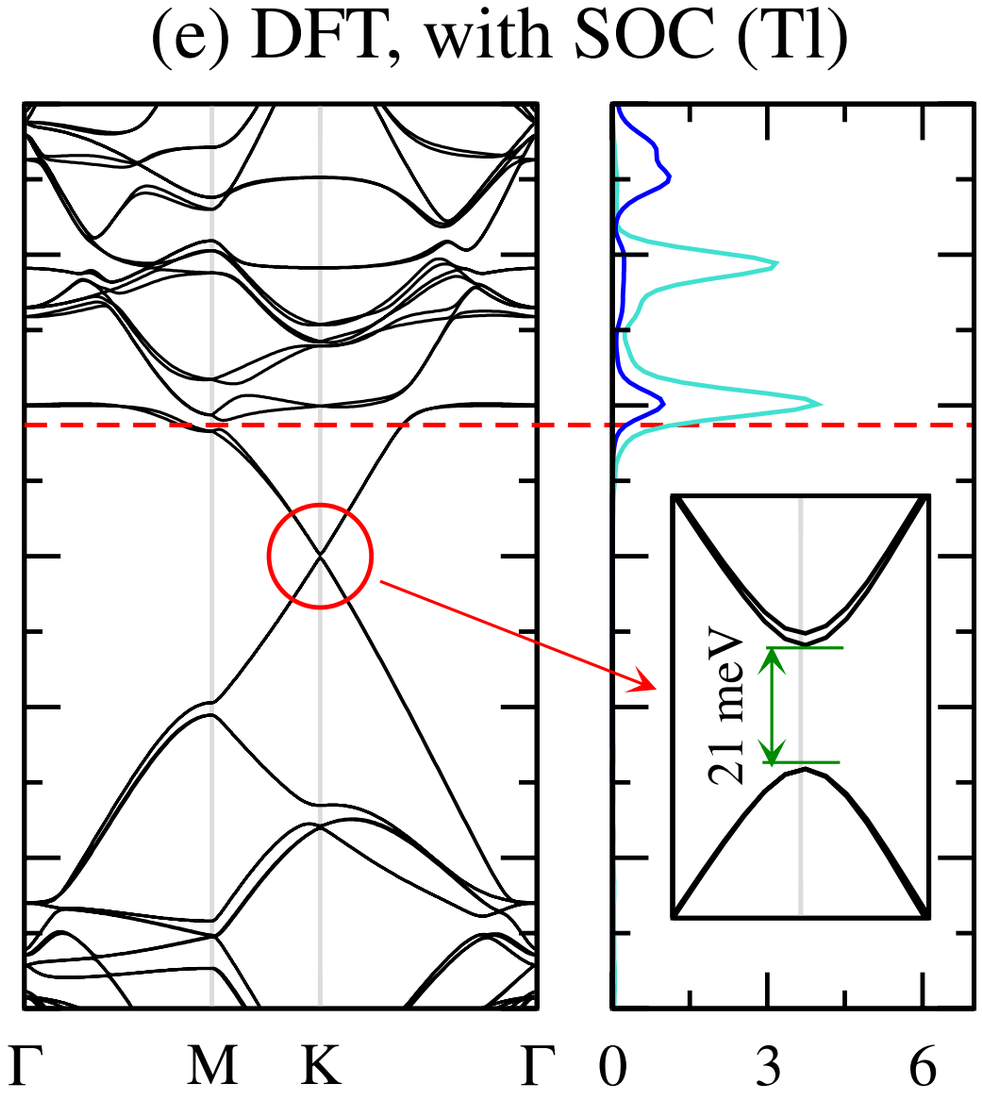
Enhanced bulk topological gap in graphene coupled to heavy adatoms



Weeks, Hu, Alicea, Franz, Wu, PRX **1**, 021001 (2011)

Density functional theory (DFT)

Outputs a band structure, but what does it mean for an interacting system?



Density functional theory (DFT)

DFT an exact reformulation of quantum mechanics using density instead of wavefunction:

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle$$

$$E[n] = \min_{\Psi \to n} \langle \Psi | \hat{H} | \Psi \rangle$$

“one of the greatest free lunches ever” — K. Burke

Density functional theory (DFT)

Rigorous foundation is the Hohenberg-Kohn theorem:

$$\hat{H} = \hat{T} + \hat{V}_{\mathrm{ee}} + \int_x v(x)\,\hat{n}(x)$$

$$v(x) \longrightarrow \psi(\{x_j\}) \longrightarrow n(x)$$

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HK '64

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HK '64

Density functional theory (DFT)

$n(x) \rightarrow v(x)$ mapping holds for *each* type of interaction, including none:

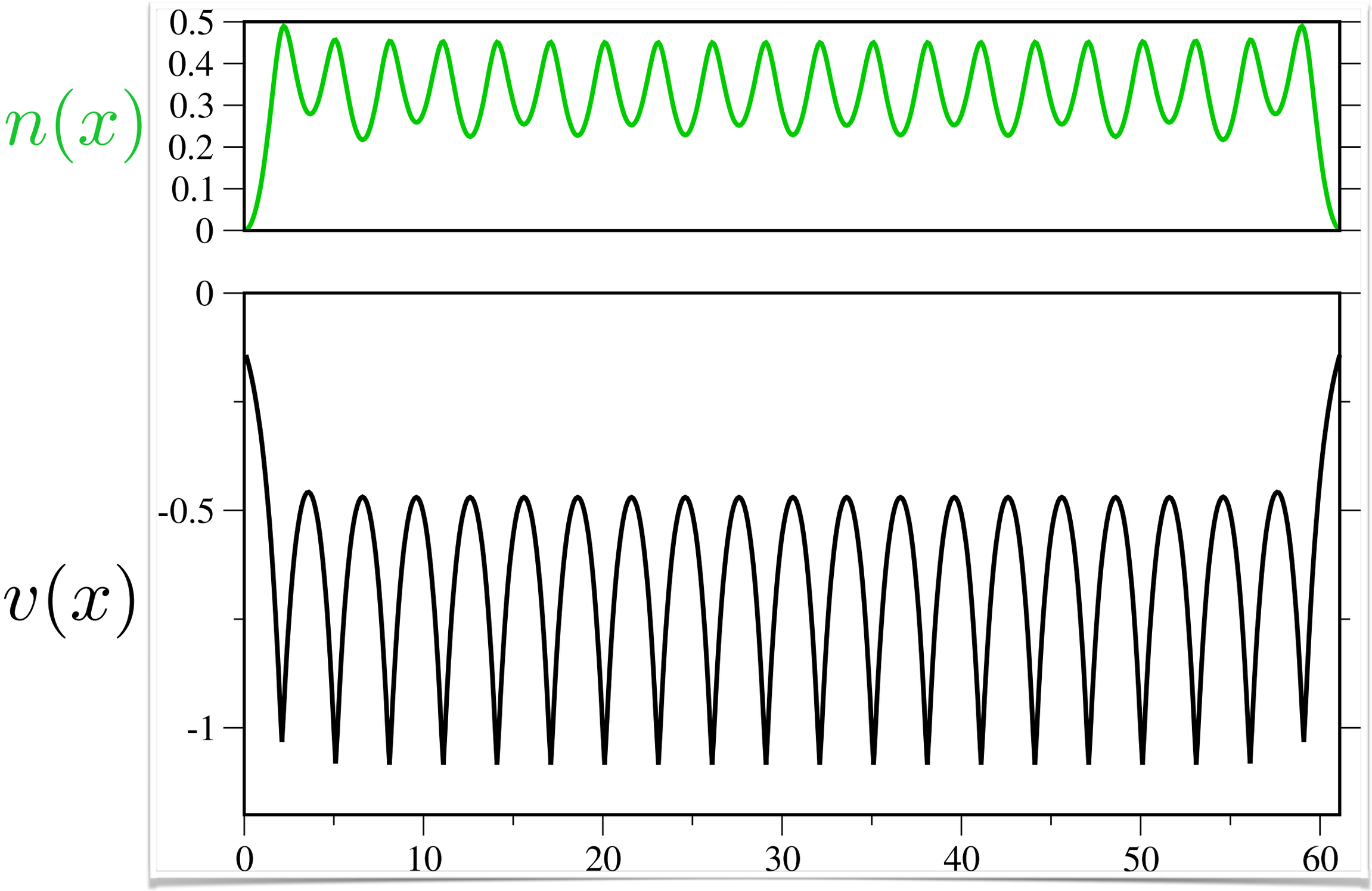
$$\hat{H} = \hat{T} + \hat{V}_{\mathrm{ee}} + \int_x v(x)\,\hat{n}(x)$$

$$\hat{H}_s = \hat{T} + \int_x v_s(x)\hat{n}(x)$$

$n(x)$

Non-interacting system called “Kohn-Sham system”. Defined to have same density as interacting one.

Easy to find *exact* Kohn-Sham potential if you have exact density already:



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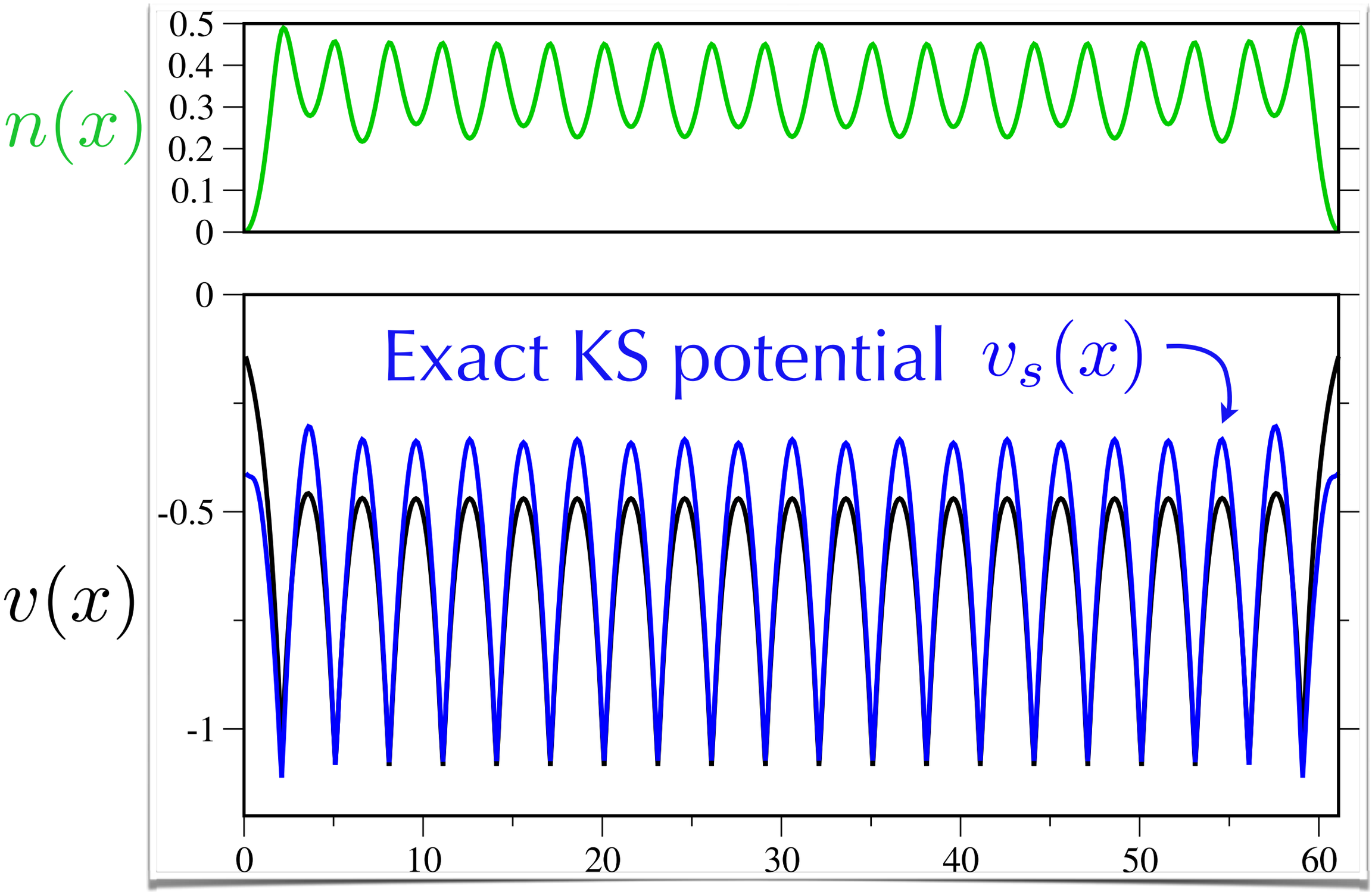


Here's how:

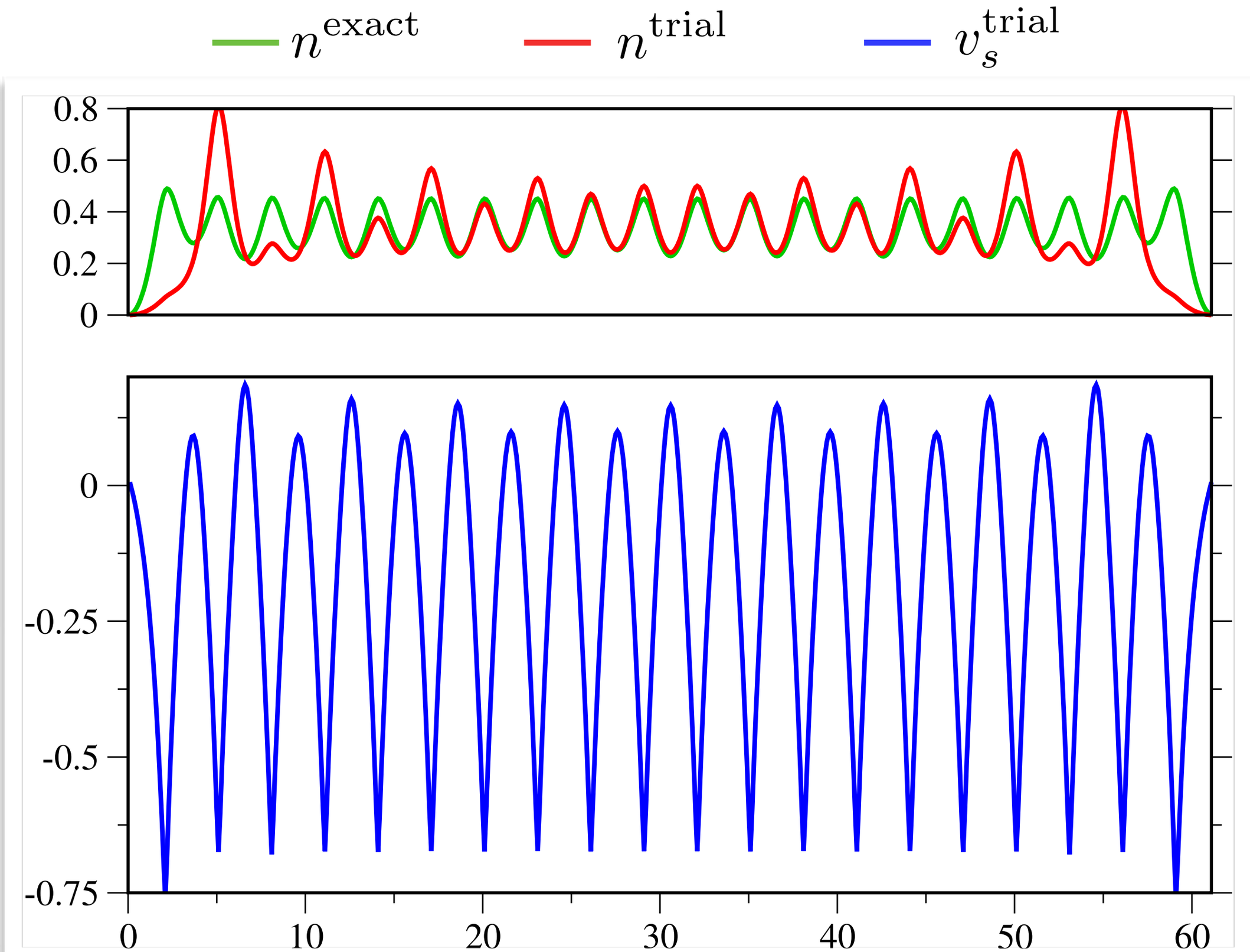
1. Start with guessed Kohn-Sham potential and solve non-interacting problem.

2. Compare resulting density to exact (interacting system) density.

3. Update potential: attempt to reduce

$$\Delta n(x) = n_{\mathrm{trial}}(x) - n(x)$$

KS Potential Demo Calculation:



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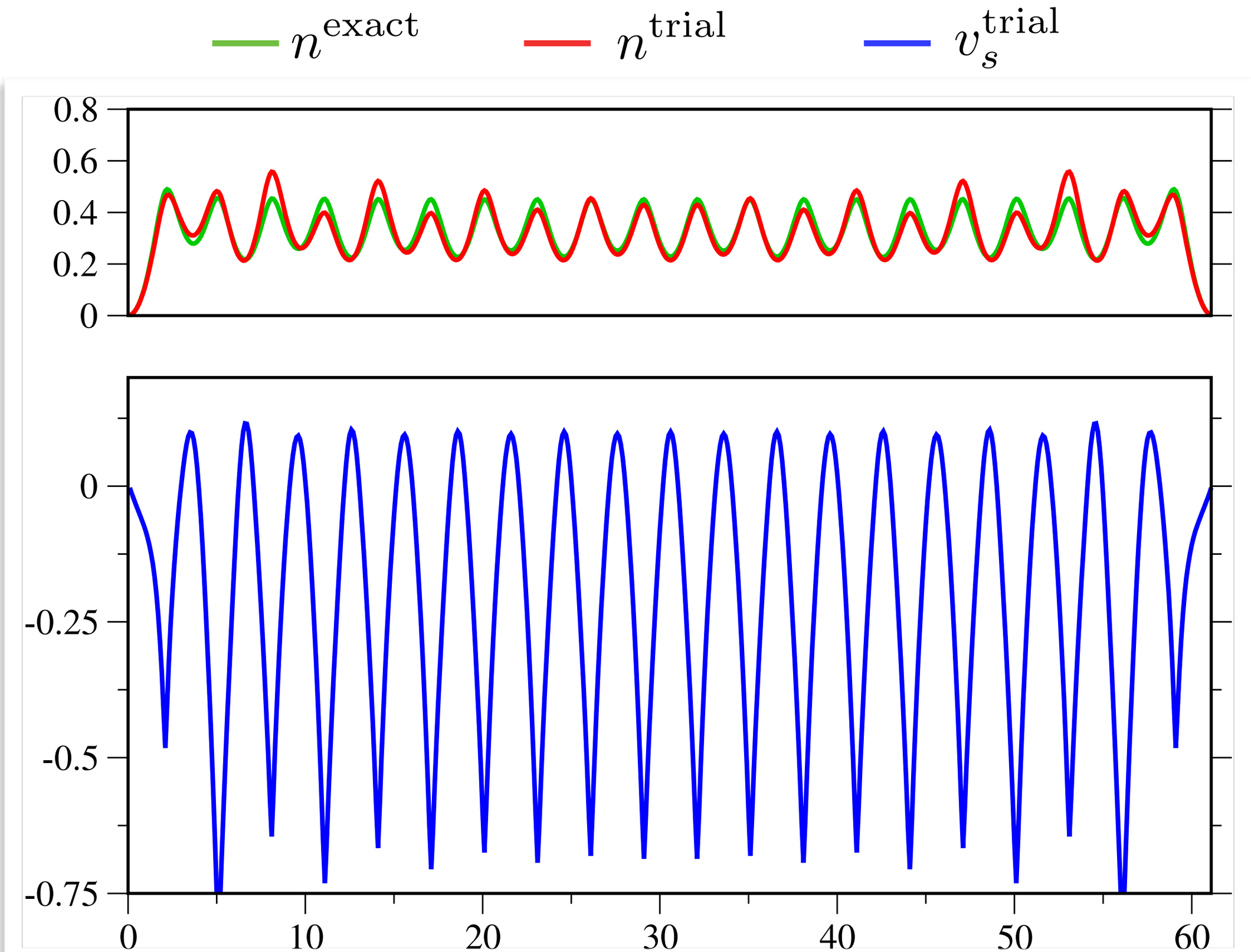

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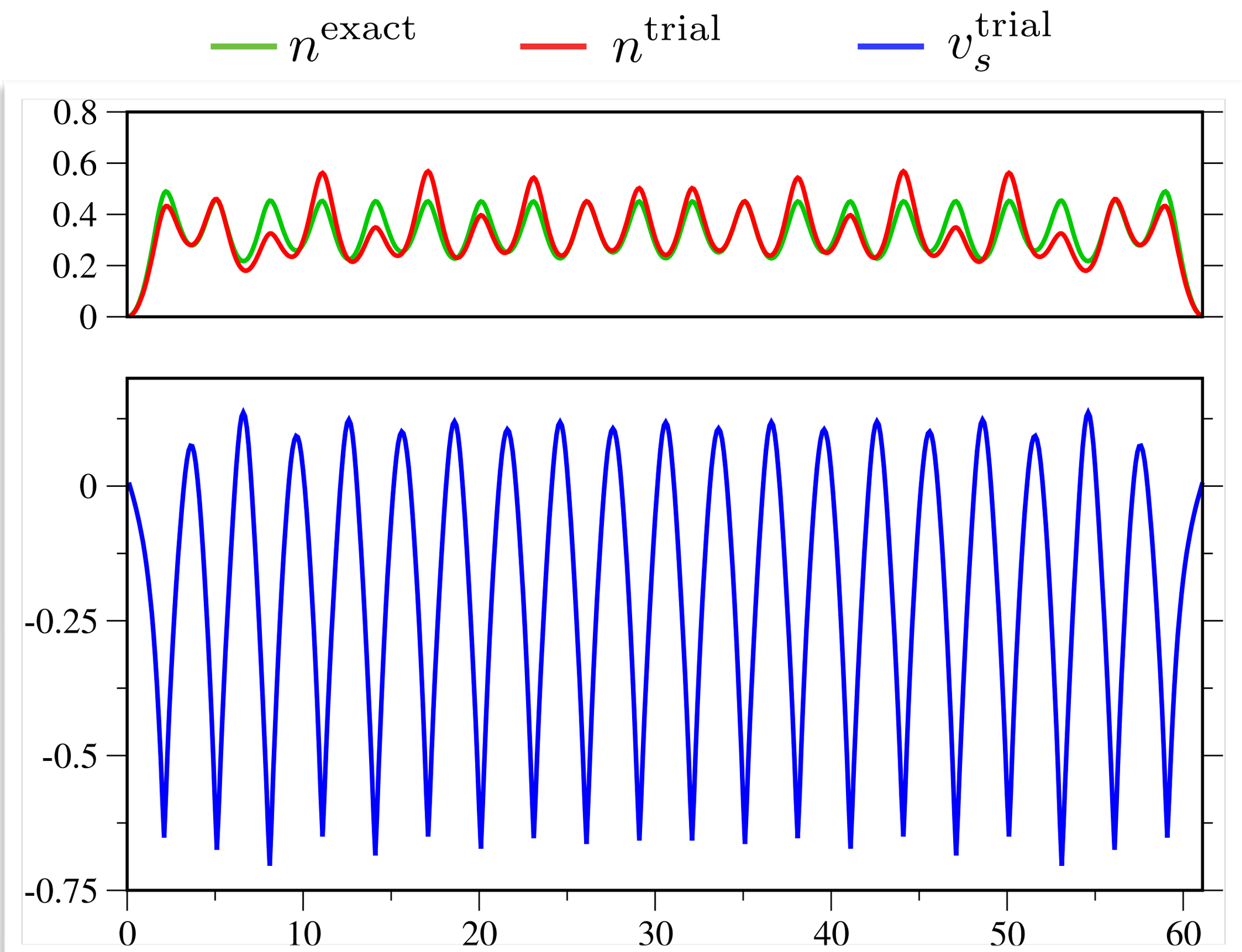

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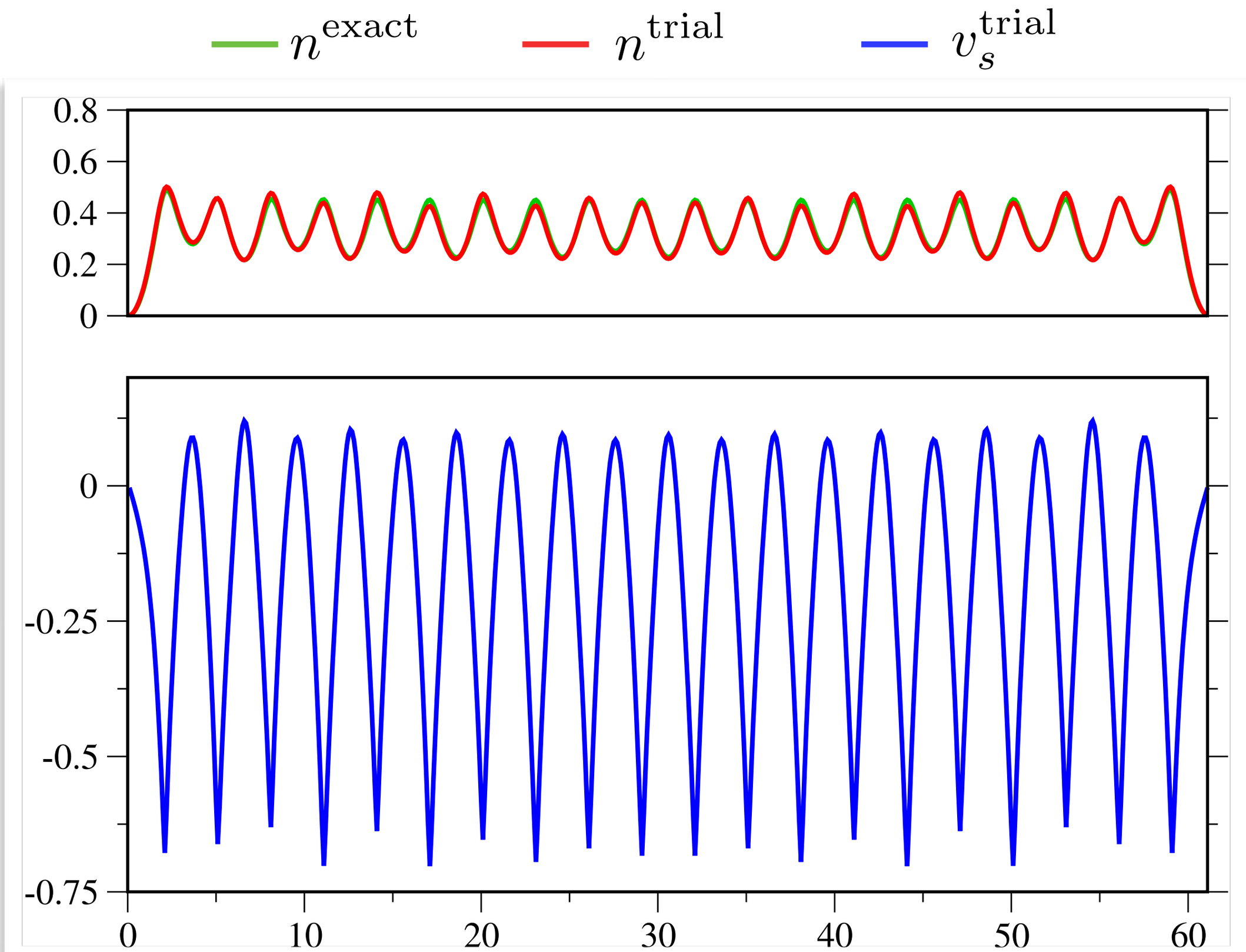

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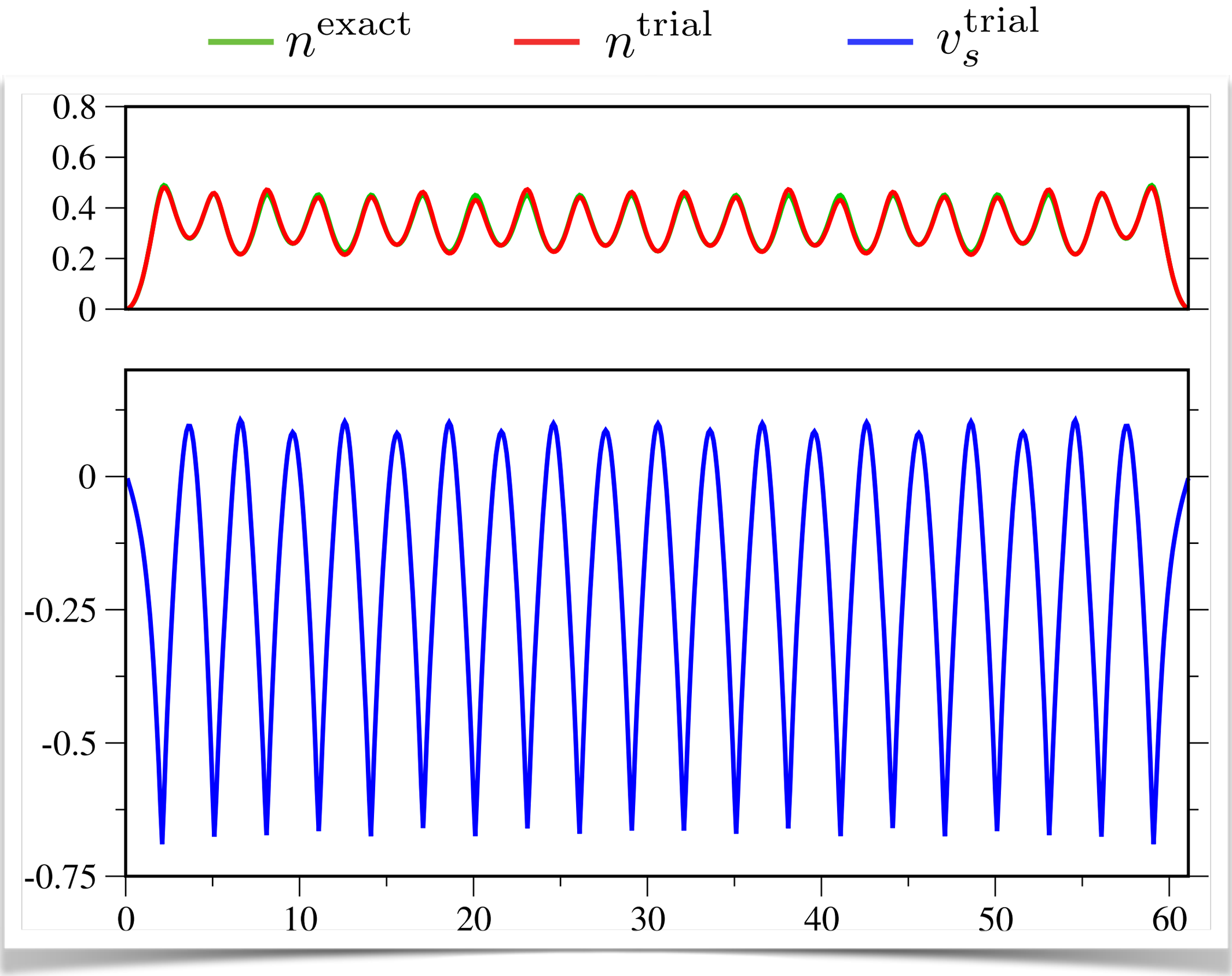

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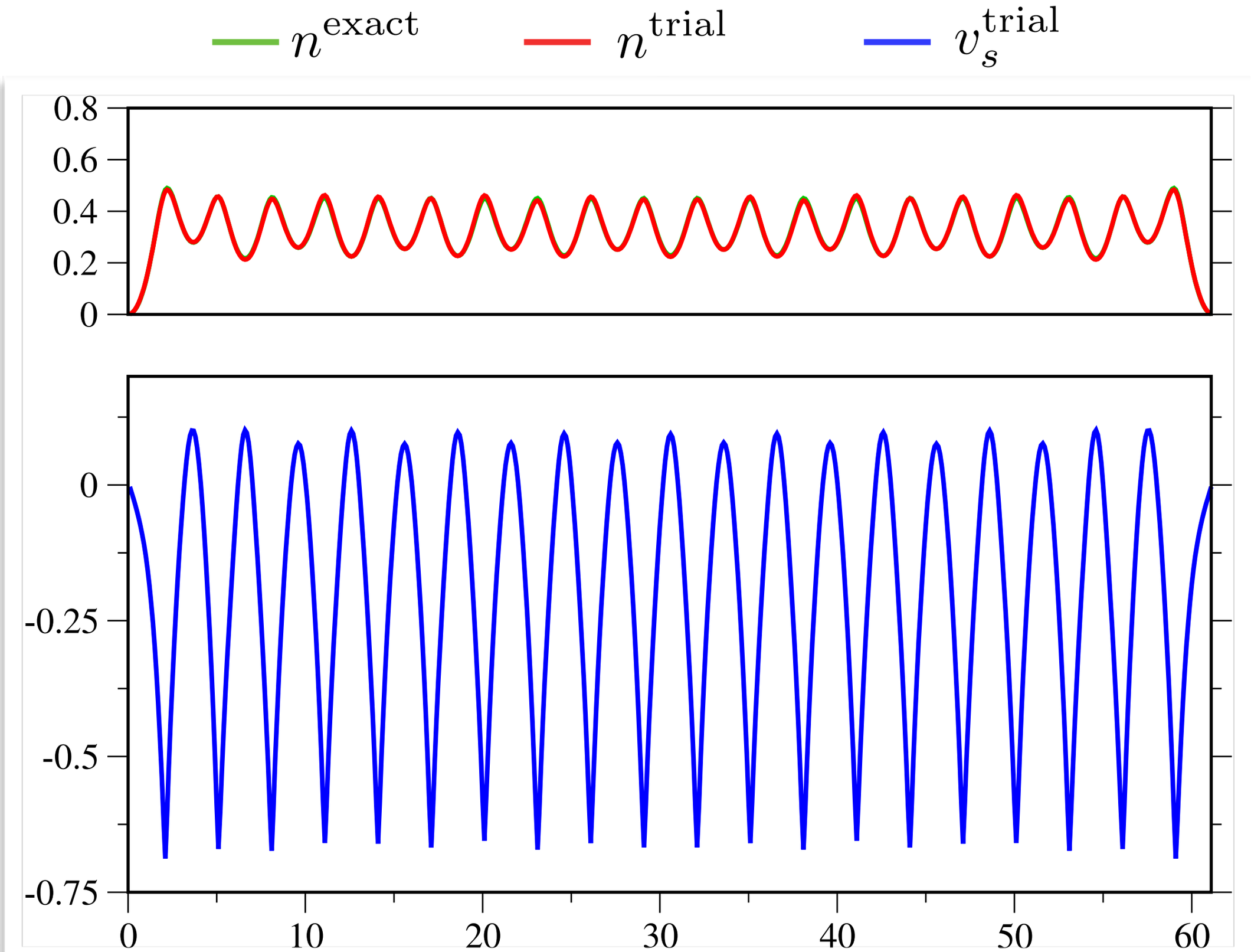

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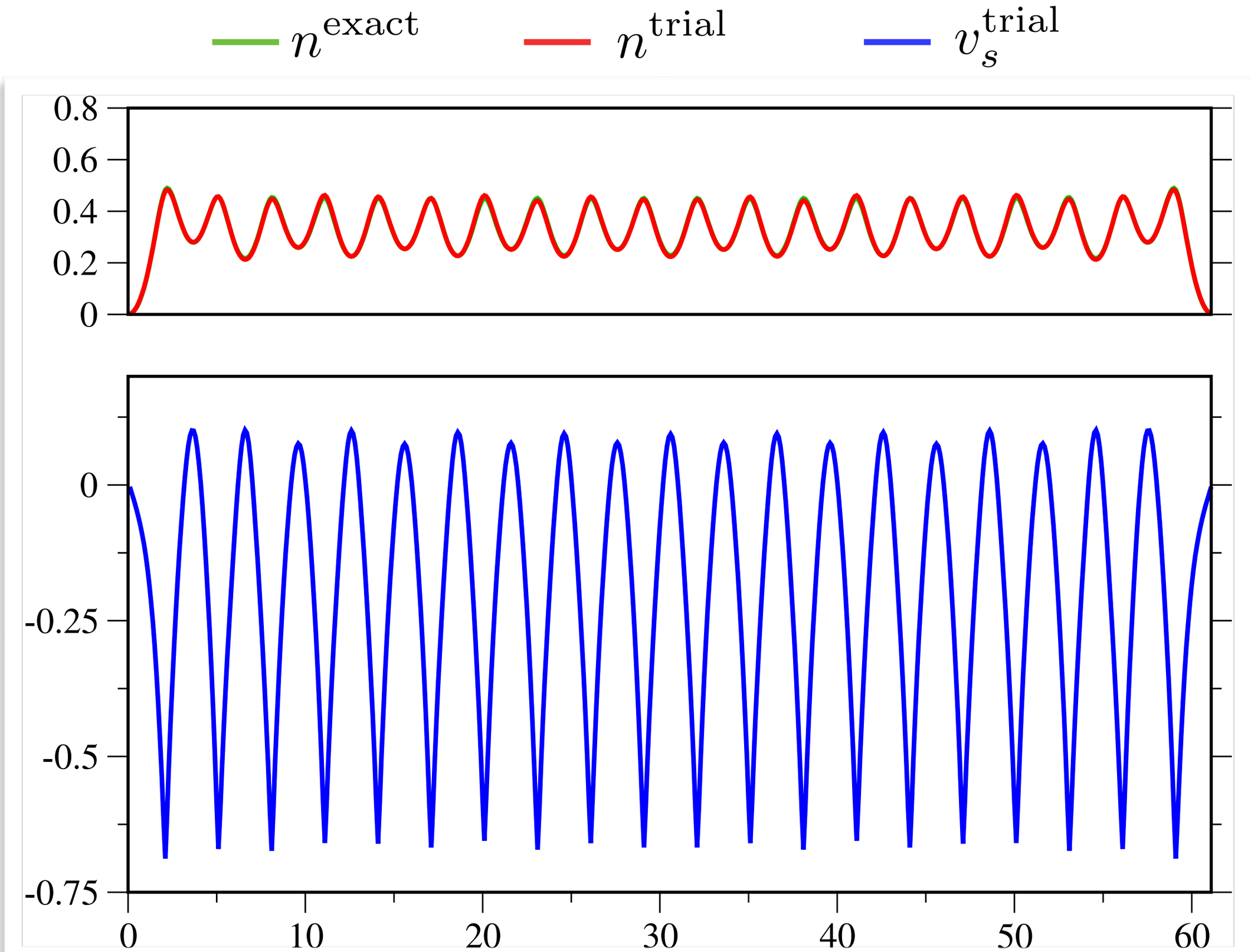


In DFT literature, divide KS potential into original $v(x)$ plus correction

$$v_s(x) \stackrel{\text{def}}{=} v(x) + v_{\text{HXC}}(x)$$

Mean-field-like picture:

$$\hat{H}_s = \hat{T} + \int_x v_{\text{HXC}}(x)\hat{n}(x) + \int_x v(x)\hat{n}(x)$$

Accounts for missing interactions

Is DFT a mean-field theory?

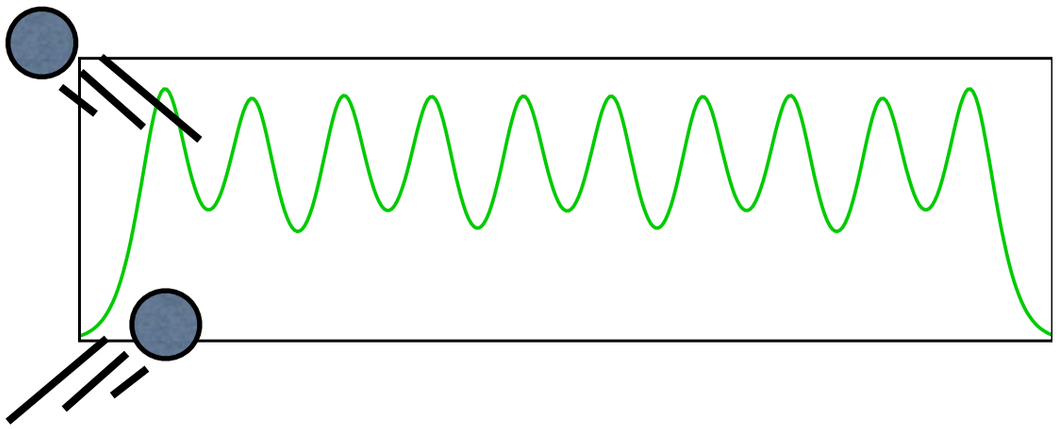
No: exact theory gives exact energy and ground-state density

Yes: using any other properties of KS system is a type of approximation

One such approximation: band gap $\approx$ real gap

Exact charge gap

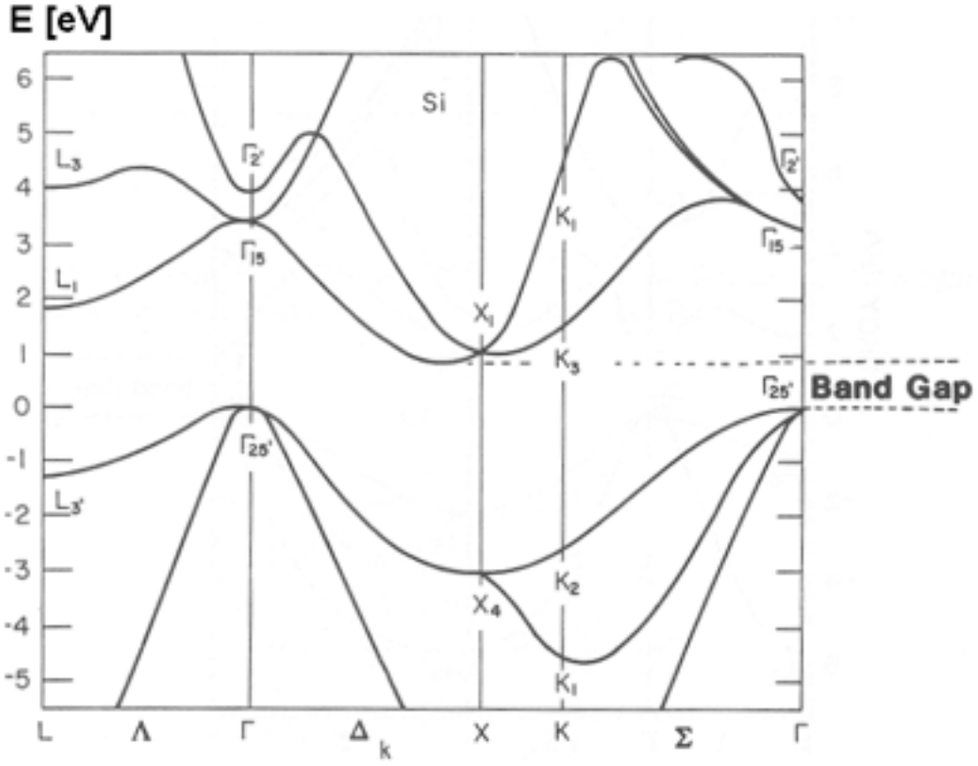
$$E_g = I - A$$



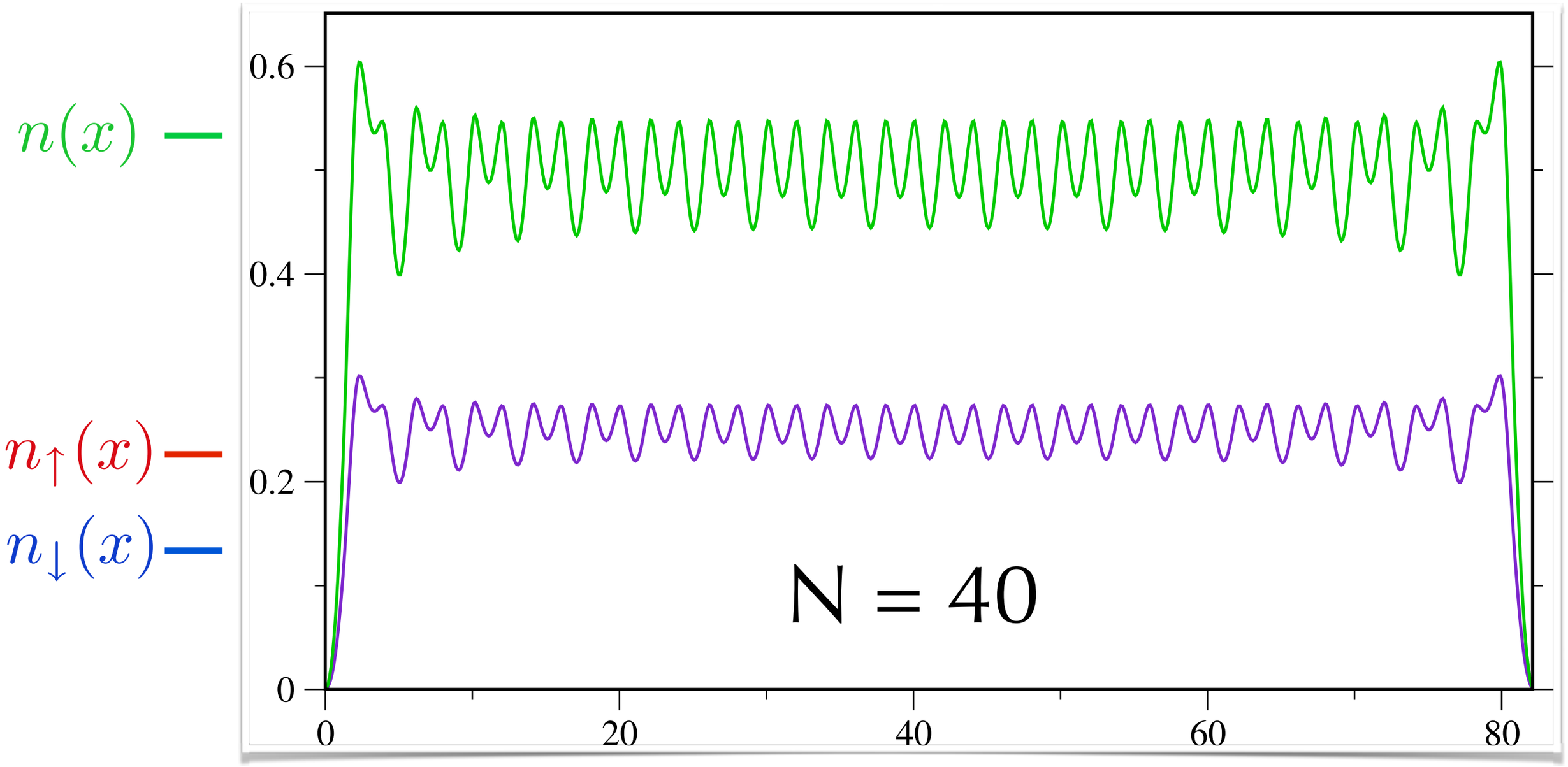
$$I = E_{N-1} - E_N$$

$$A = E_N - E_{N+1}$$

KS band gap

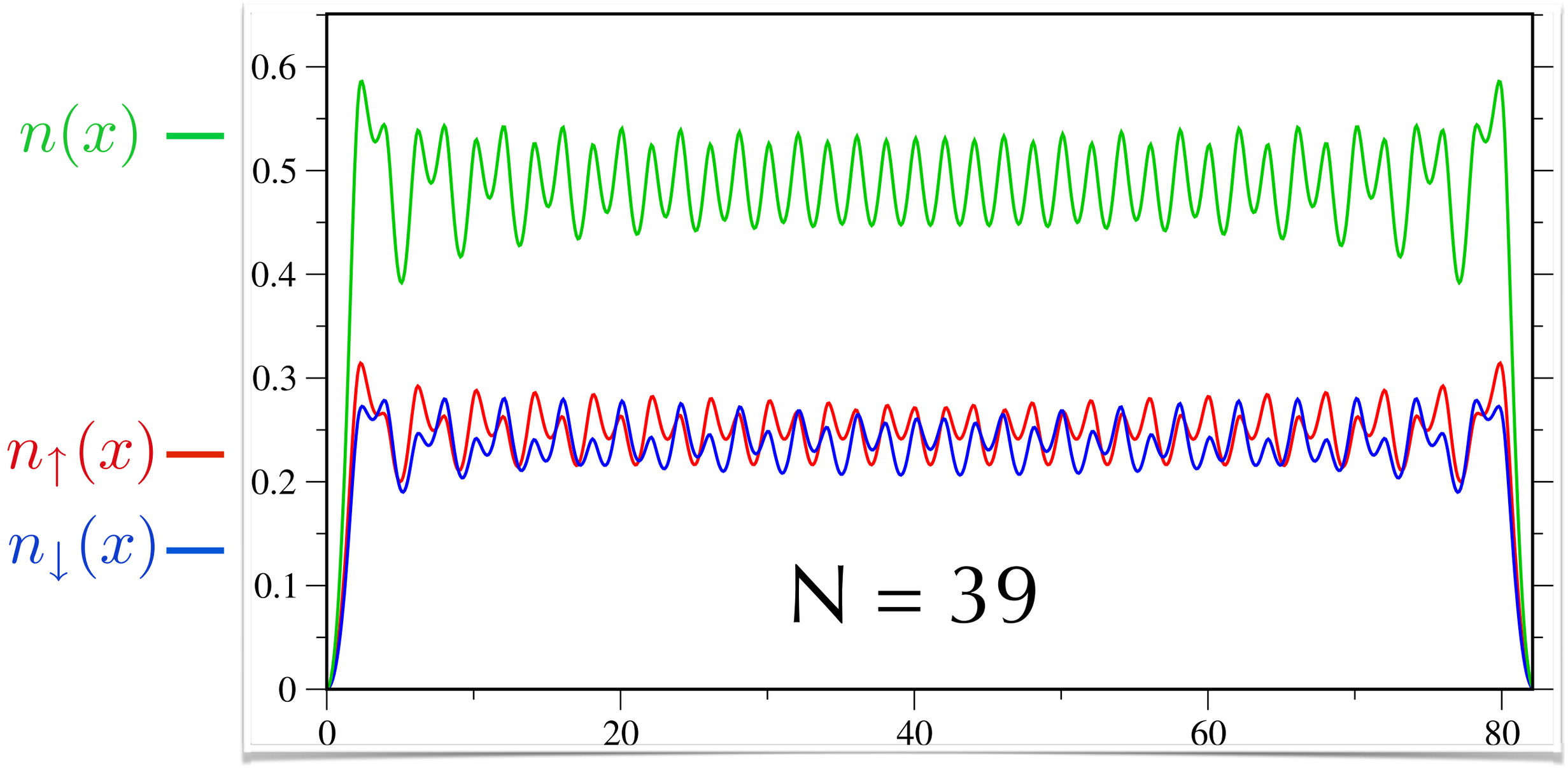


Computing interacting charge gap



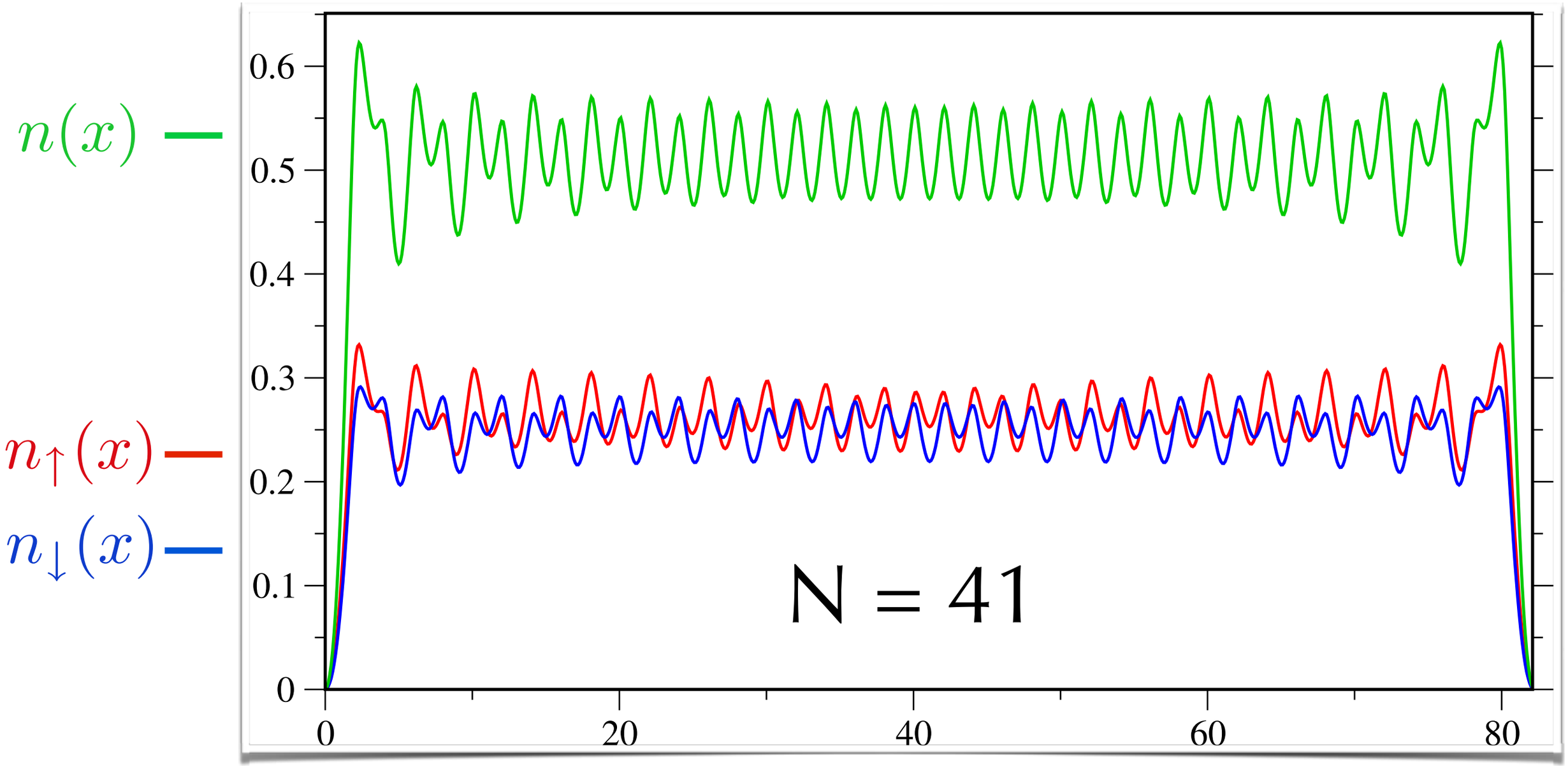
Charge Gap: $E_g = E_{N+1} - 2E_N + E_{N-1}$

Computing interacting charge gap



Charge Gap: $E_g = E_{N+1} - 2E_N + E_{N-1}$

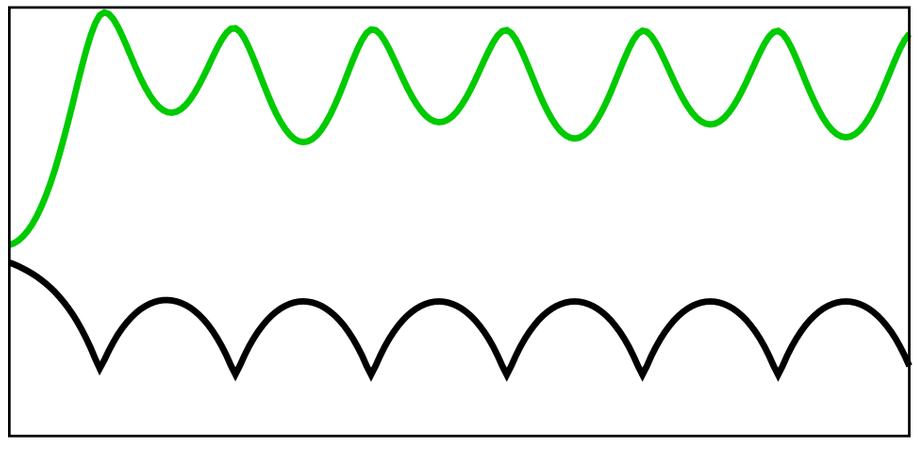
Computing interacting charge gap



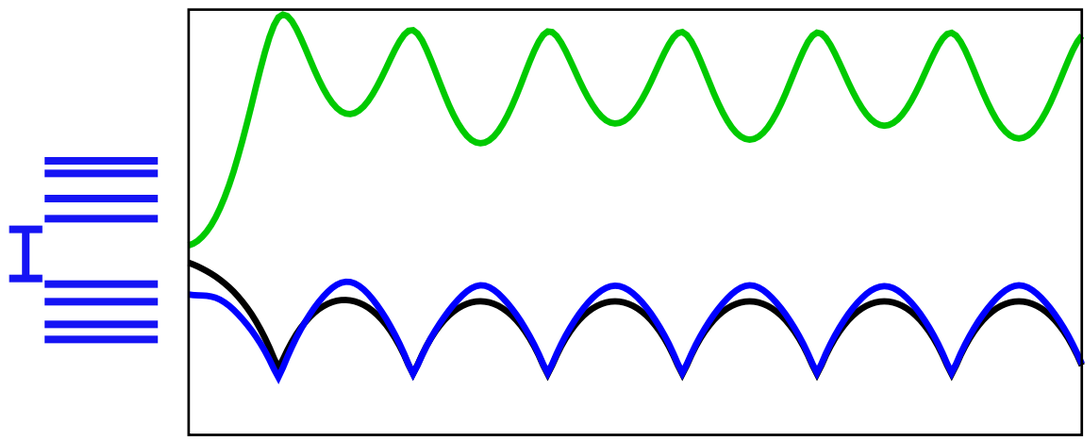
Charge Gap: $E_g = E_{N+1} - 2E_N + E_{N-1}$

Computing exact KS band gap

1. Compute exact density of N-electron system.

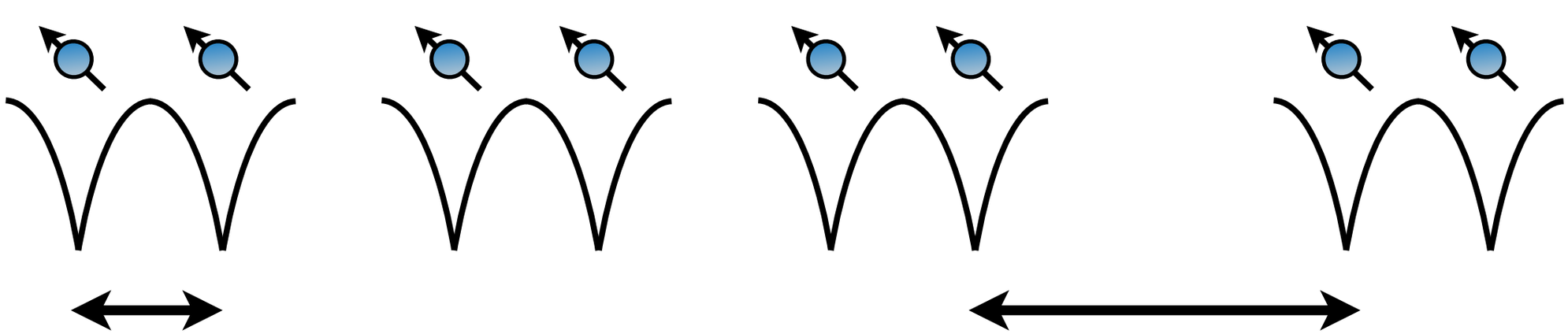


2. Obtain (exact) Kohn-Sham potential and read off Kohn-Sham gap



Weakly correlated systems: H_2 chains

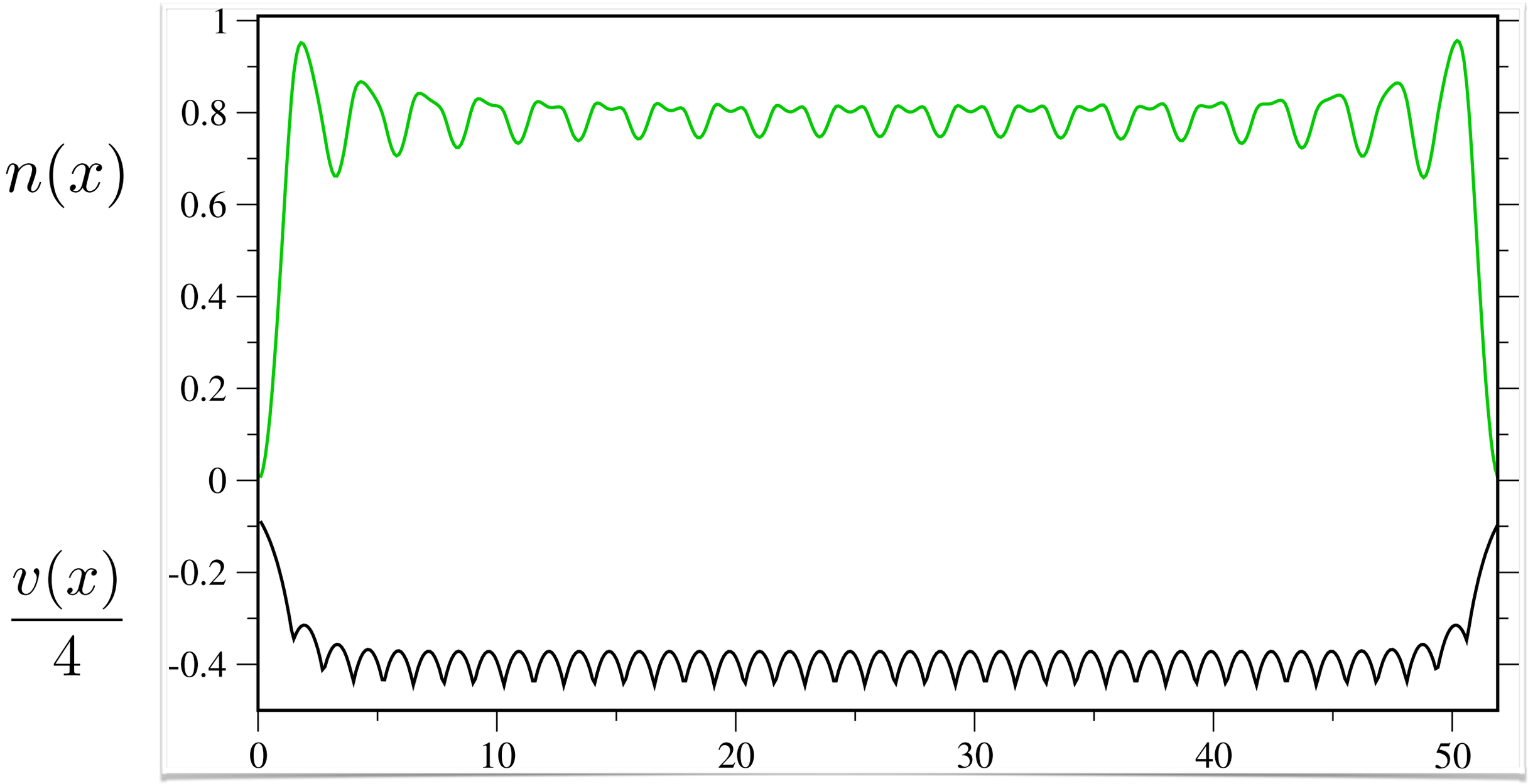
Chain of H_2 molecules,
model band insulator



<u>fixed</u> H_2 equil
length 1.26

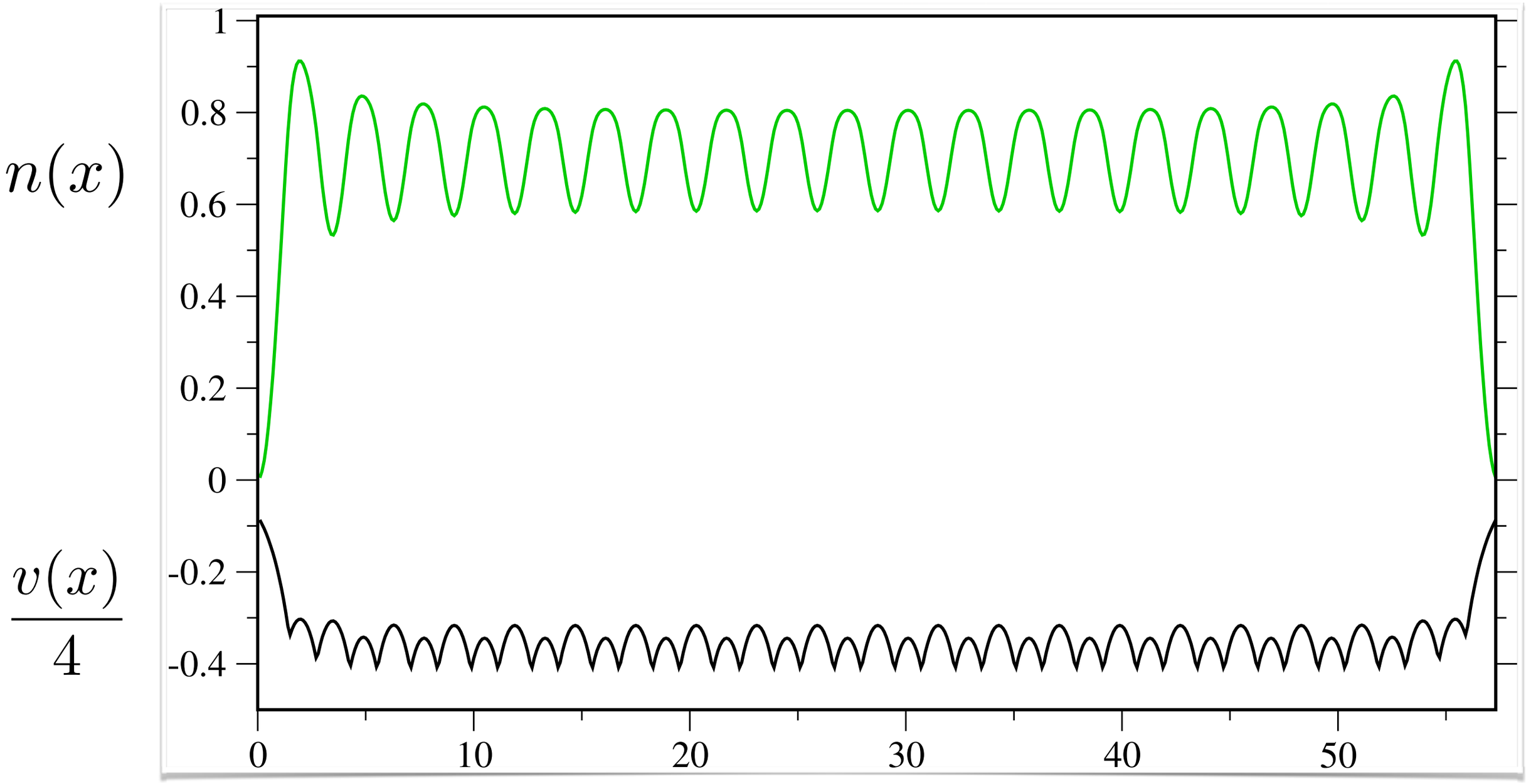
parameter:
bond length “b”

H_2 chains (40 atoms)



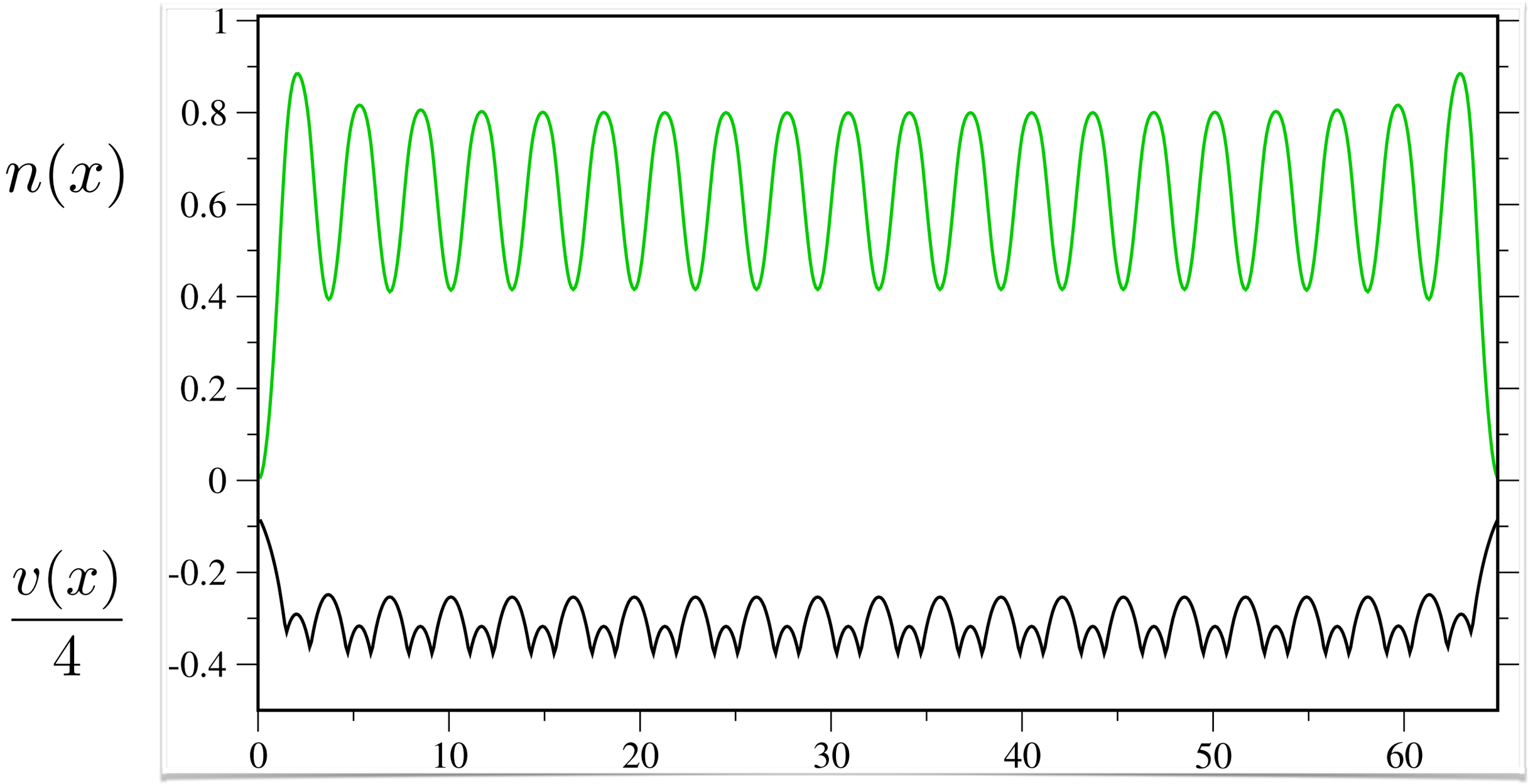
b = 1.26

H_2 chains (40 atoms)



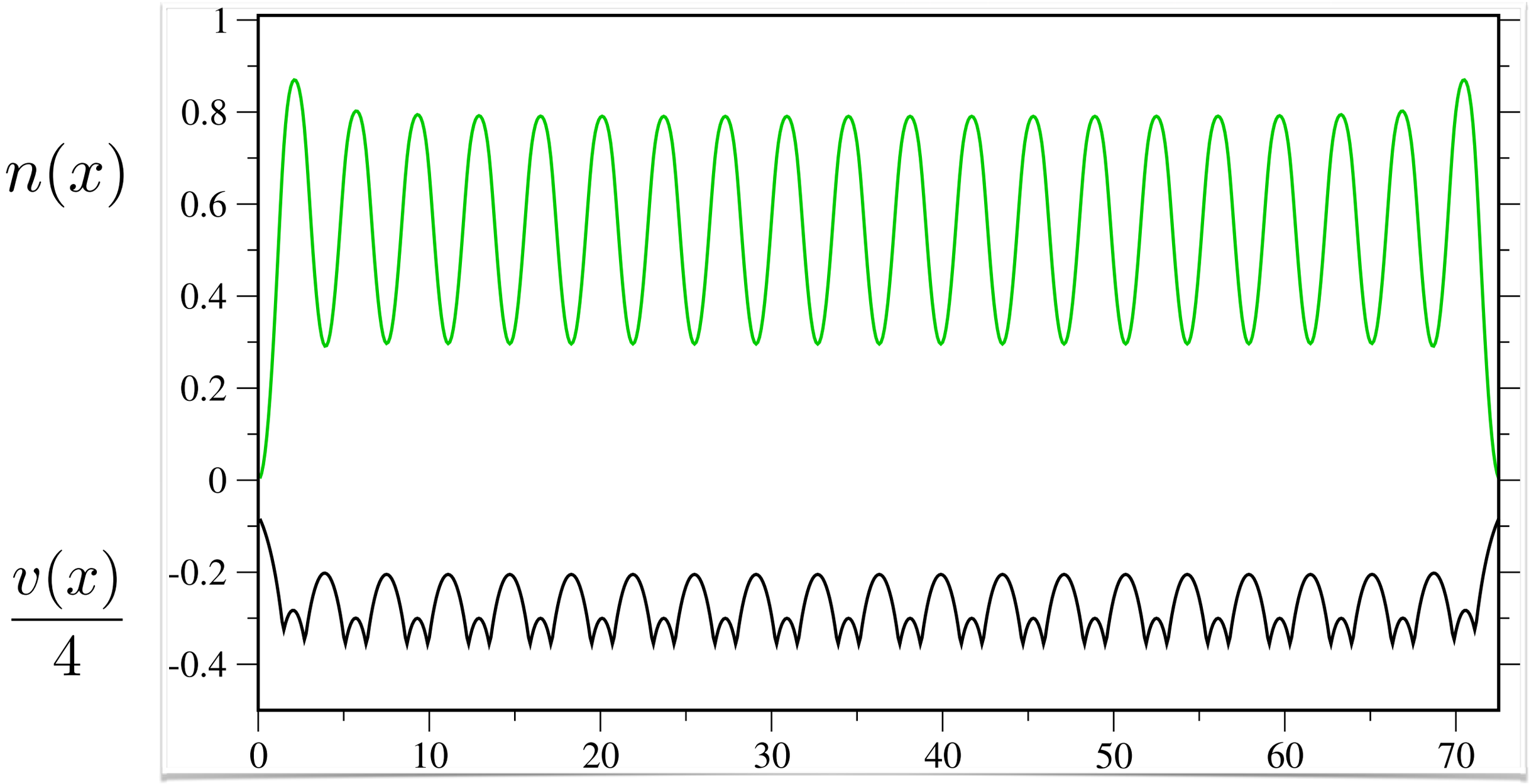
b = 1.54

H_2 chains (40 atoms)



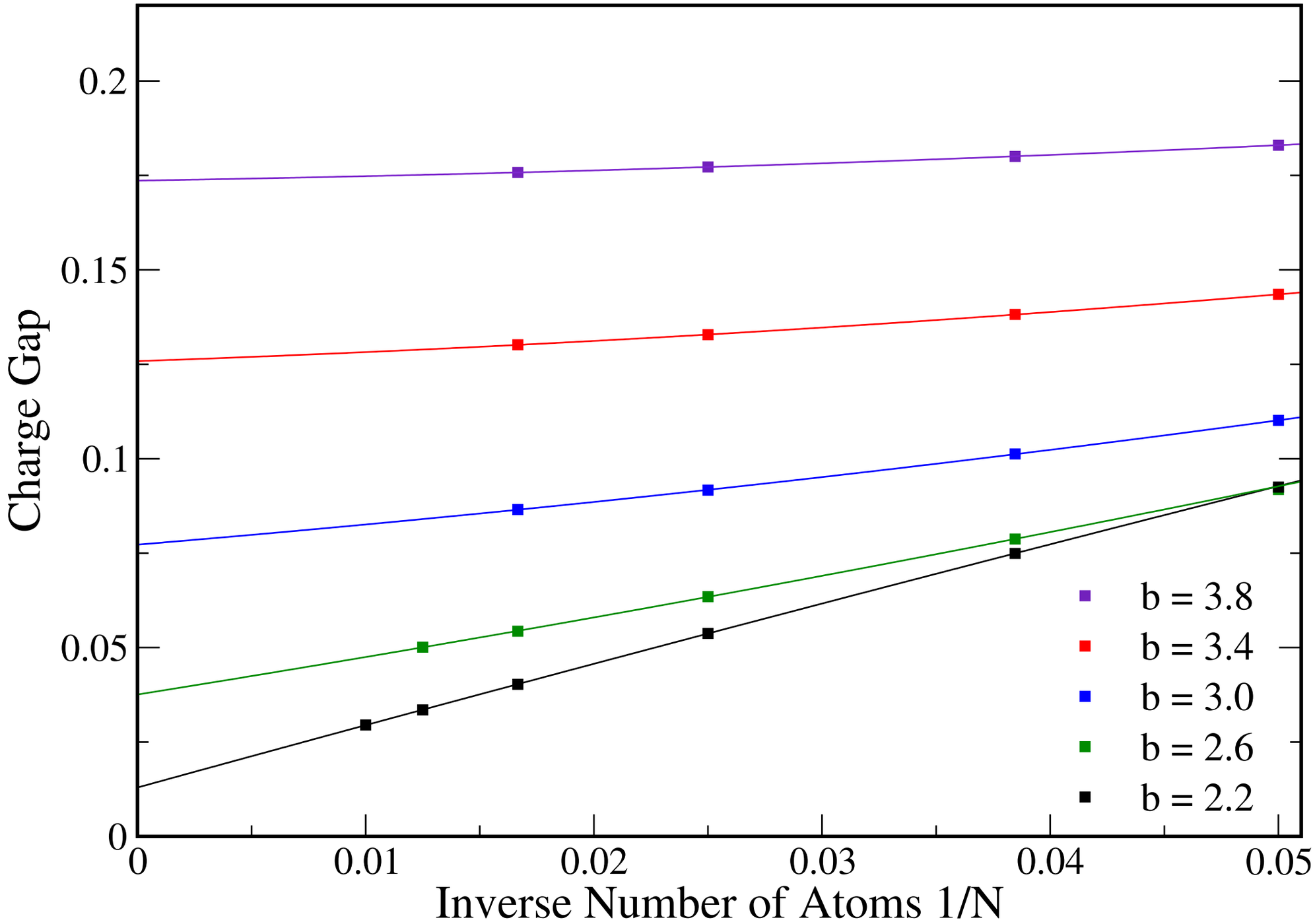
b = 1.94

H_2 chains (40 atoms)

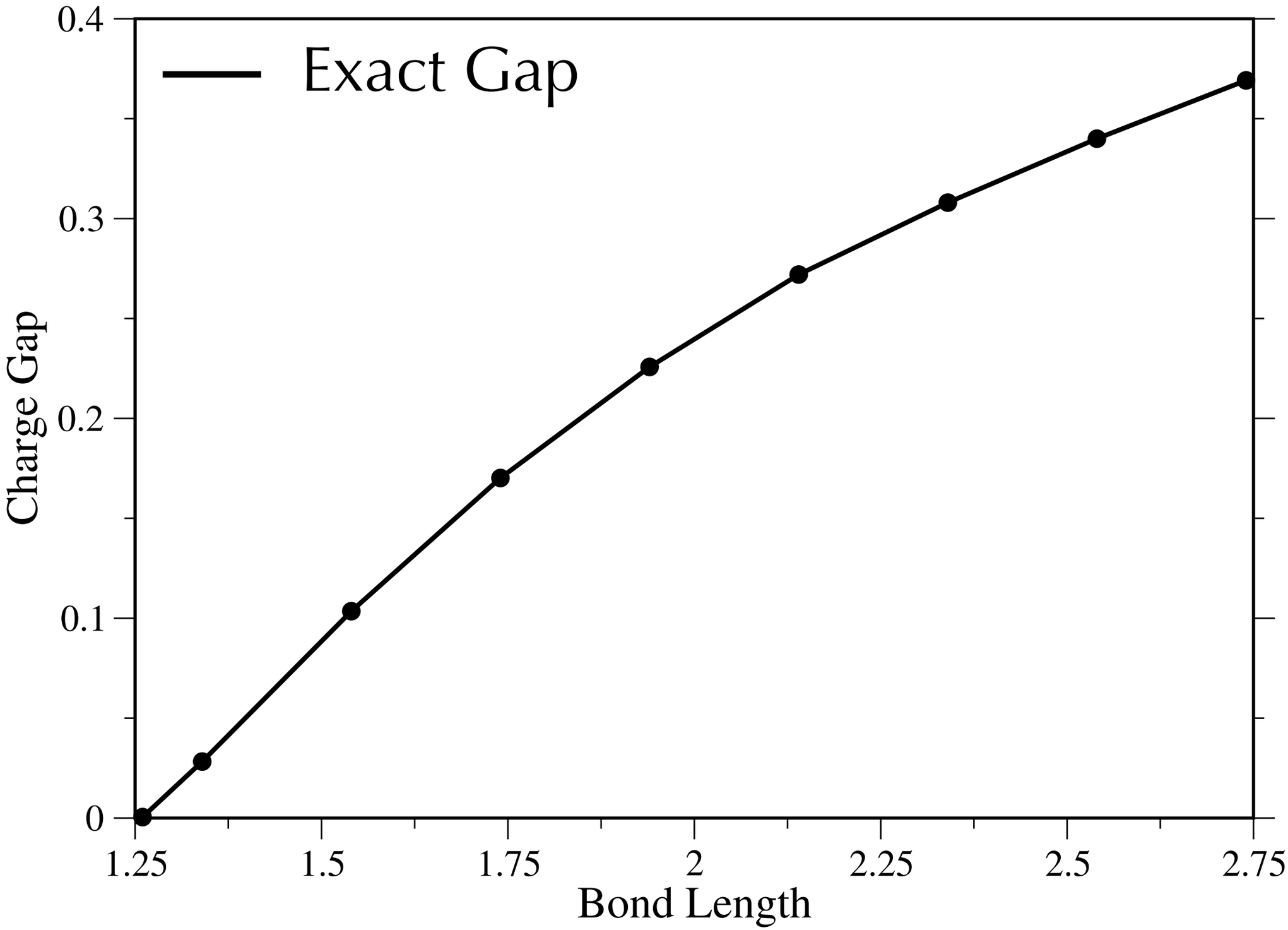


b = 2.34

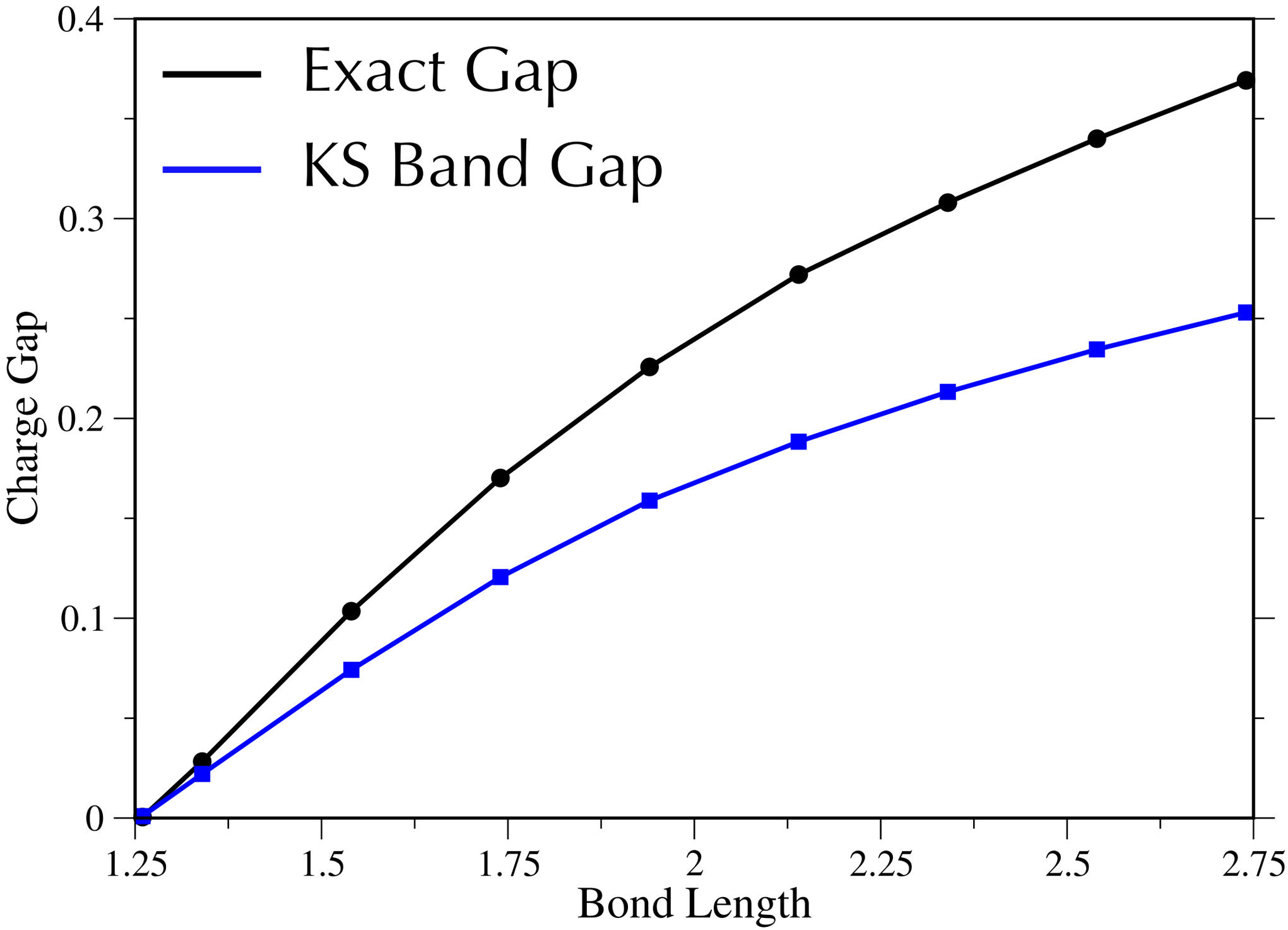
Extrapolate all results to thermodynamic limit



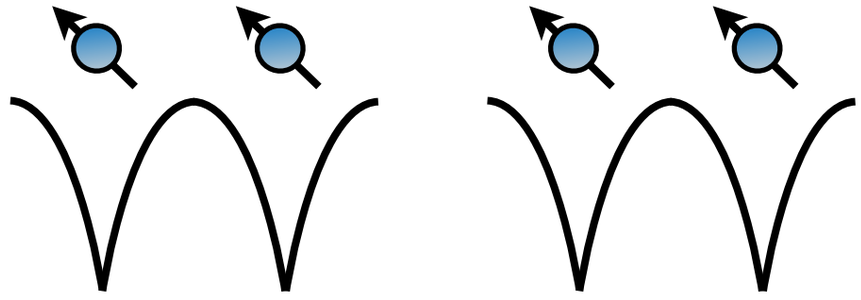
H_2 chains


Exact Gap
Charge Gap
0.4
0.3
0.2
0.1
0
1.25
1.5
1.75
2
2.25
2.5
2.75
Bond Length

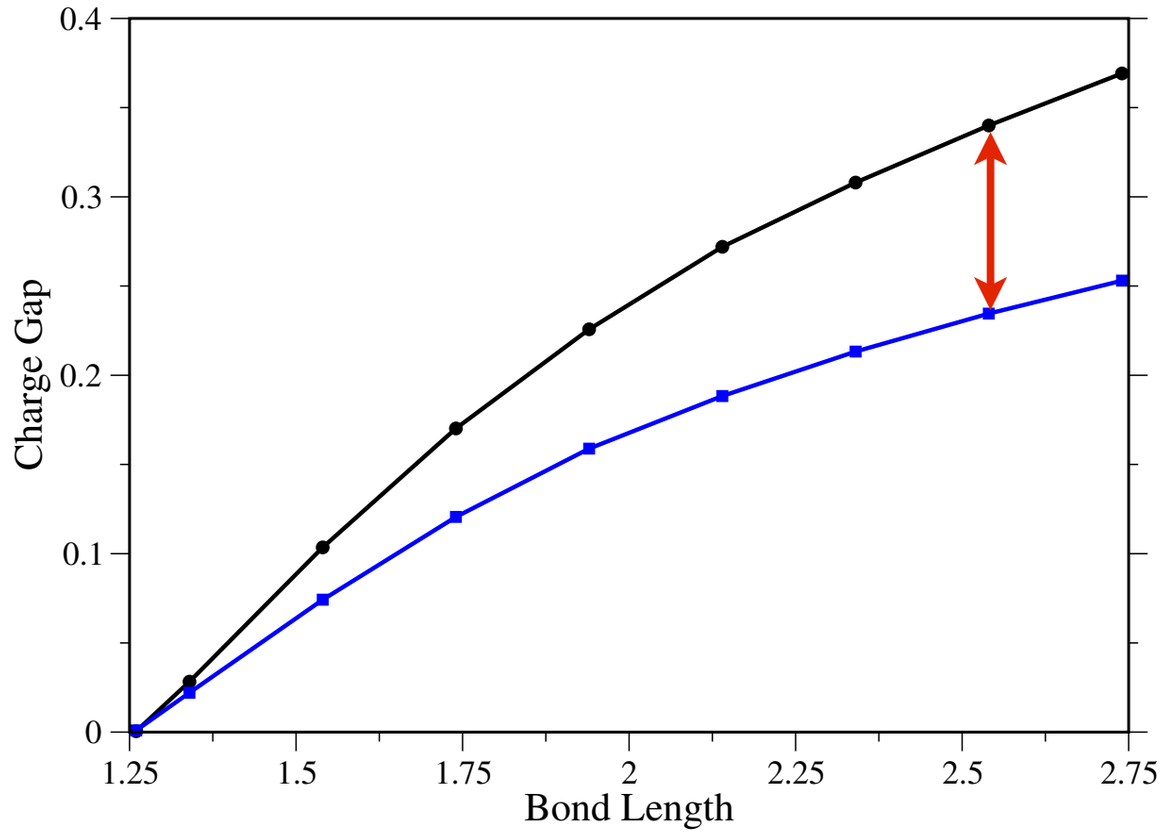
H_2 chains


Exact Gap
KS Band Gap
Charge Gap
0.4
0.3
0.2
0.1
0
1.25
1.5
1.75
2
2.25
2.5
2.75
Bond Length

Expect KS system gapped since even # electrons in unit cell

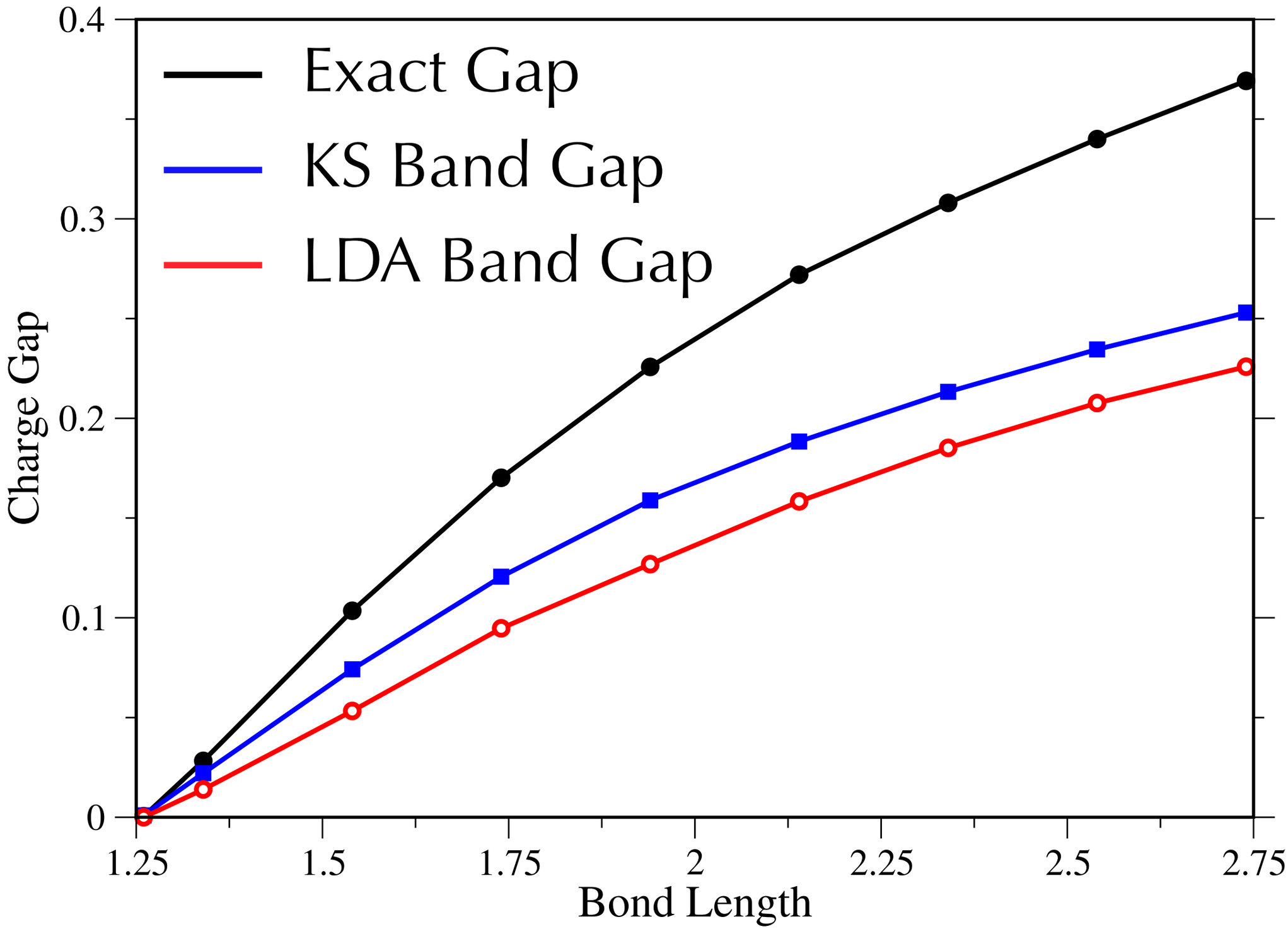


Extra missing piece called <u>derivative discontinuity</u>,* absent from many approximate functionals



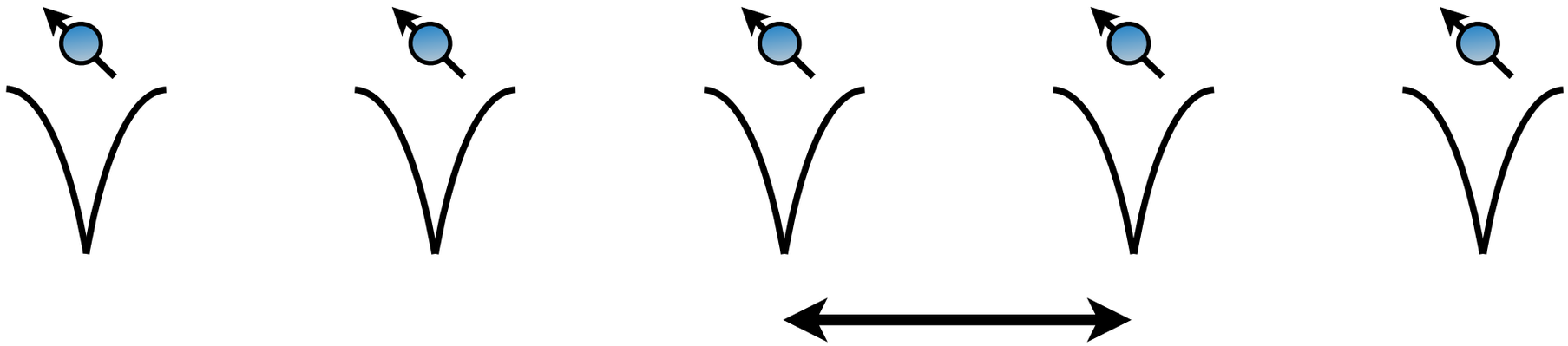
*Perdew, Parr, Levy, Balduz, PRL **49**, 1691 (1982)

Also check standard approx's:



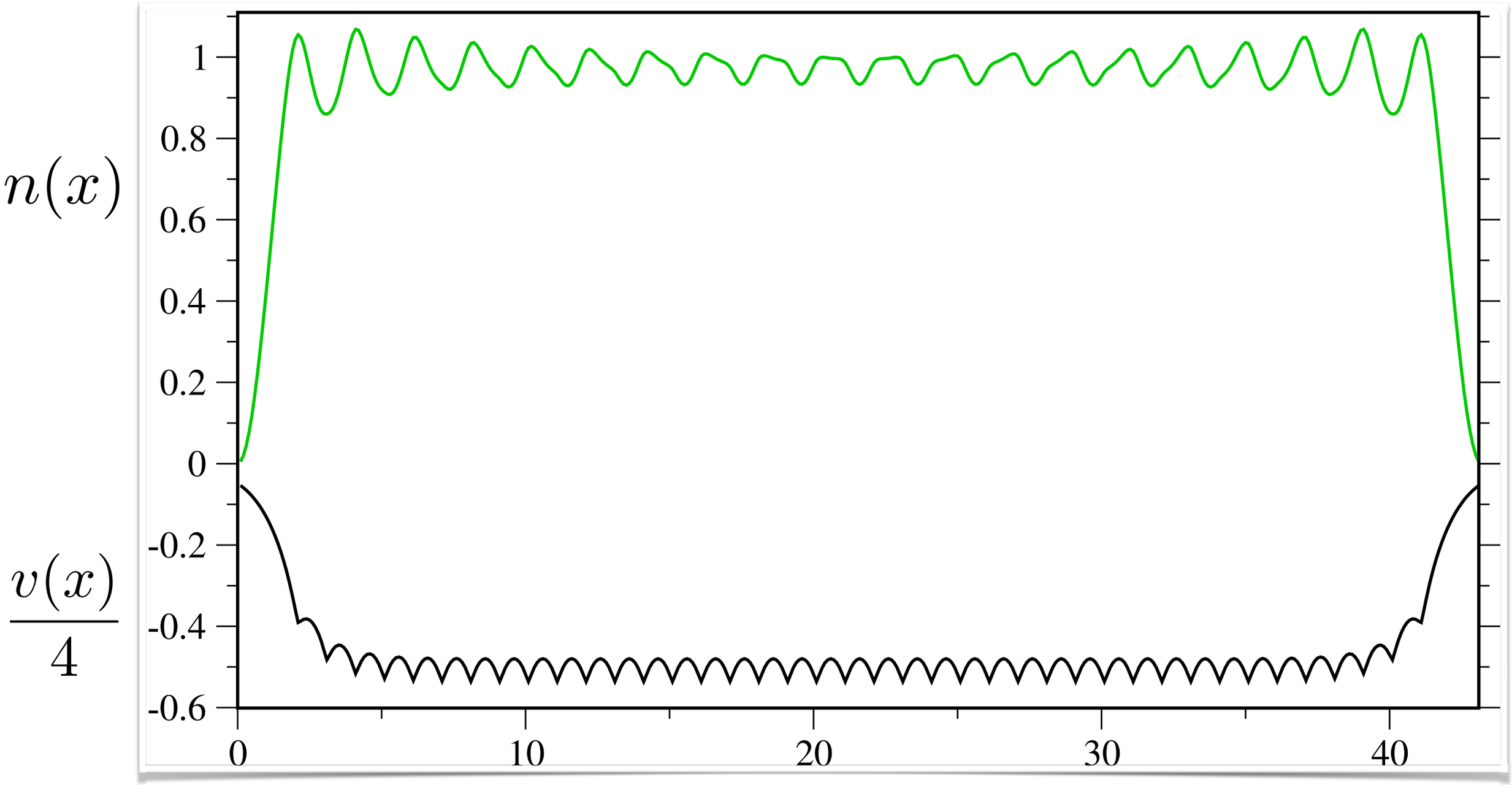
Strong correlated systems: H chains

Chain of H atoms, model
Mott insulator



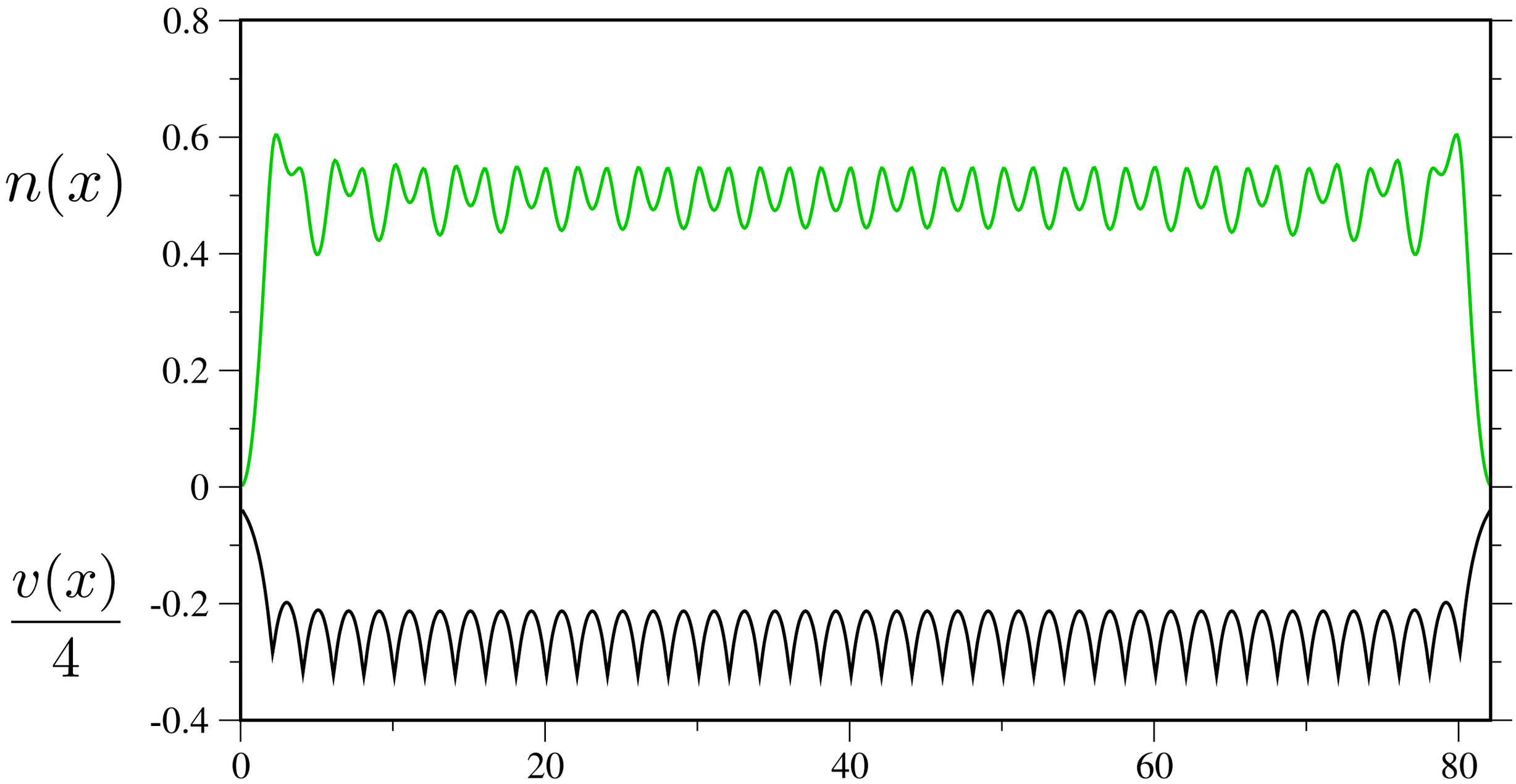
parameter: bond length “b”

H chains (40 atoms)



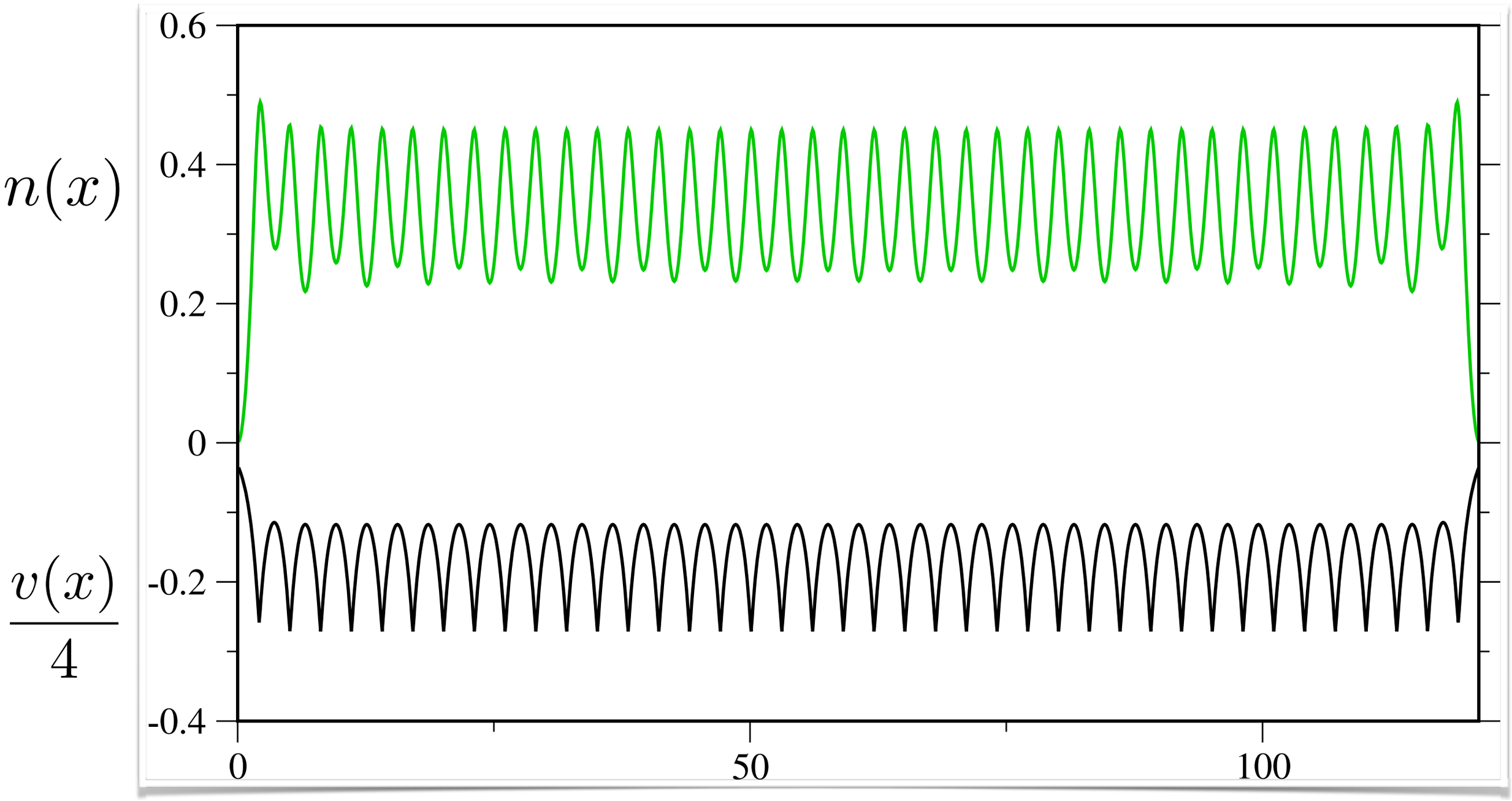
b = 1.0

H chains (40 atoms)



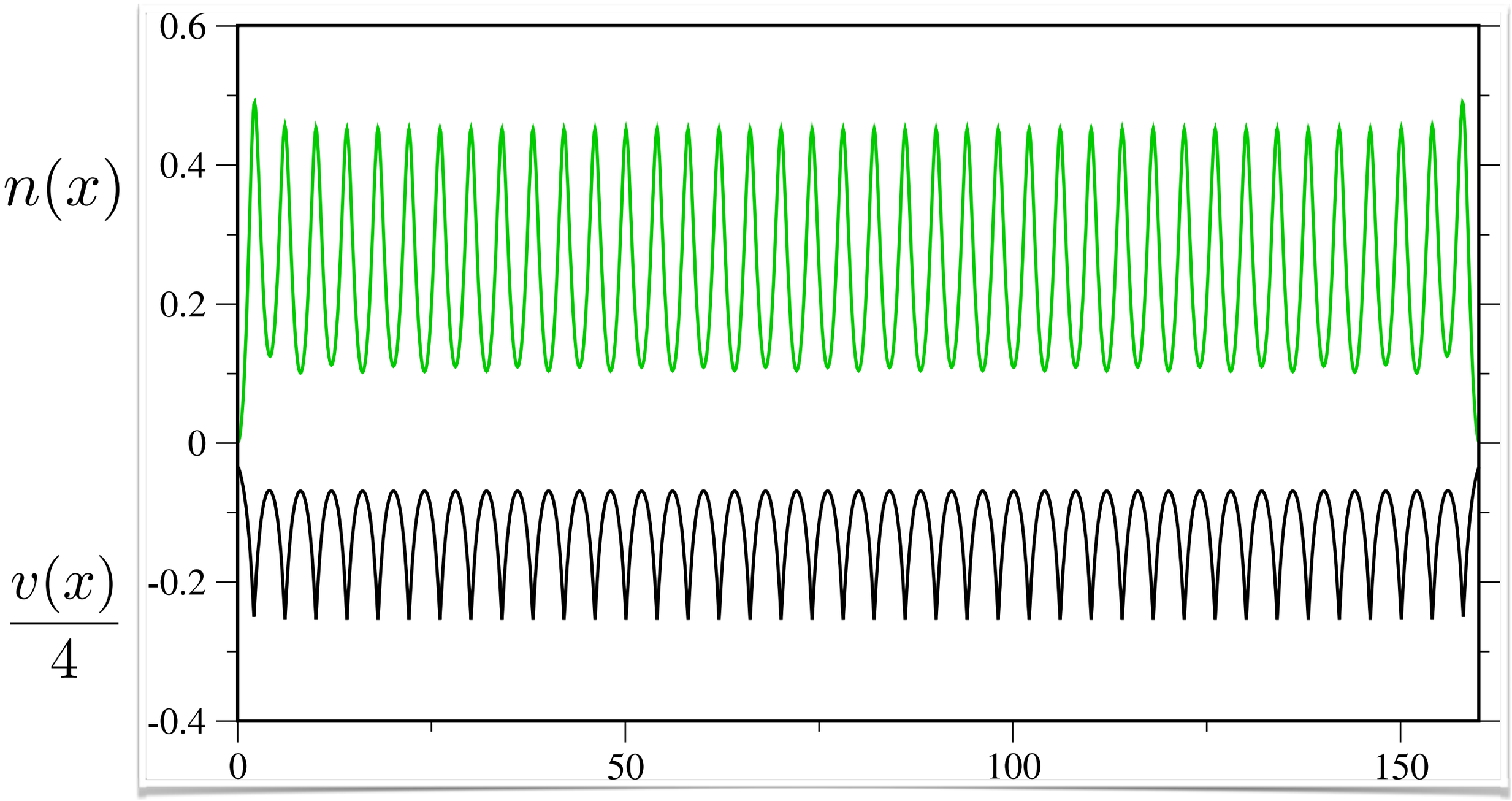
b = 2.0

H chains (40 atoms)



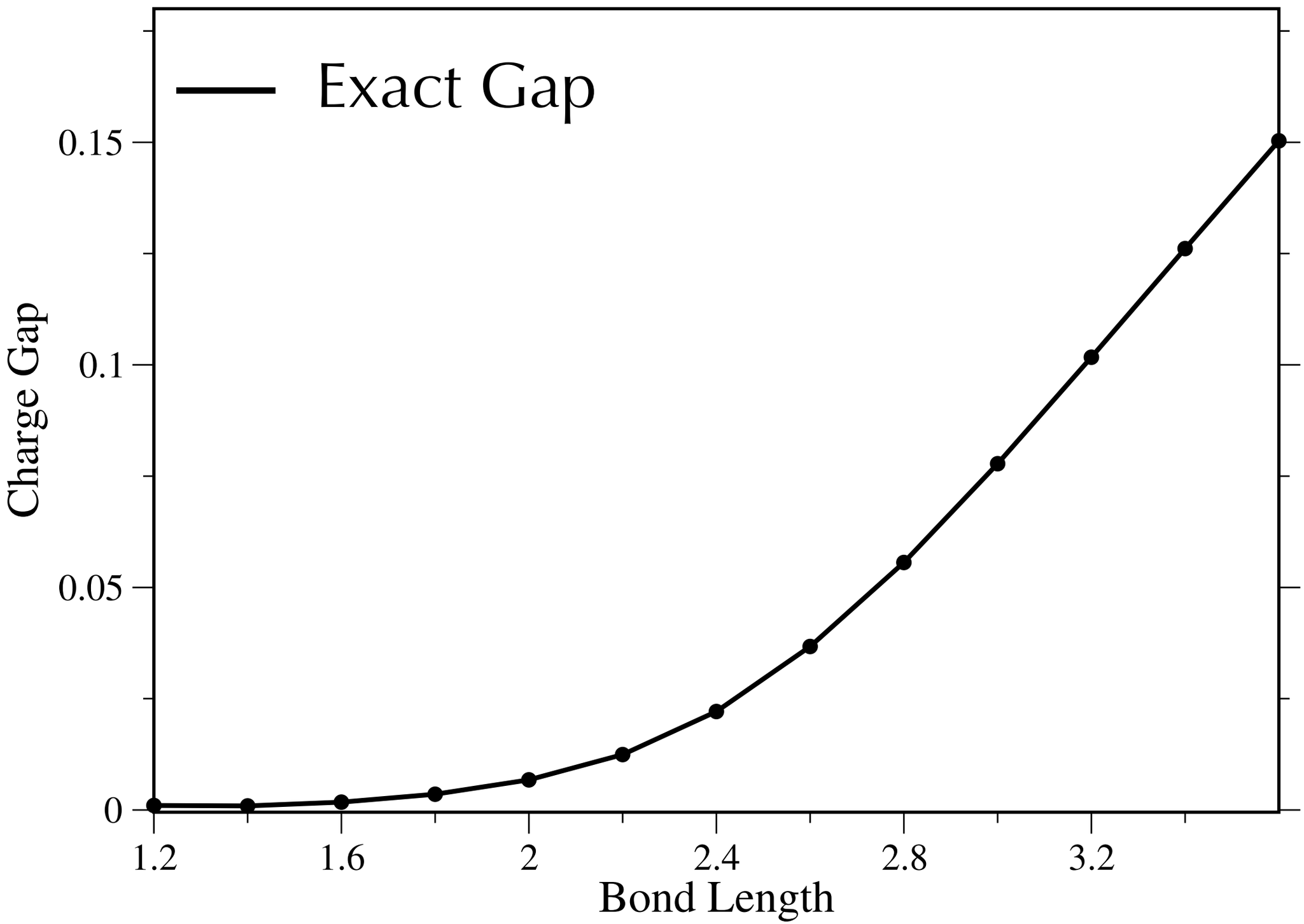
b = 3.0

H chains (40 atoms)

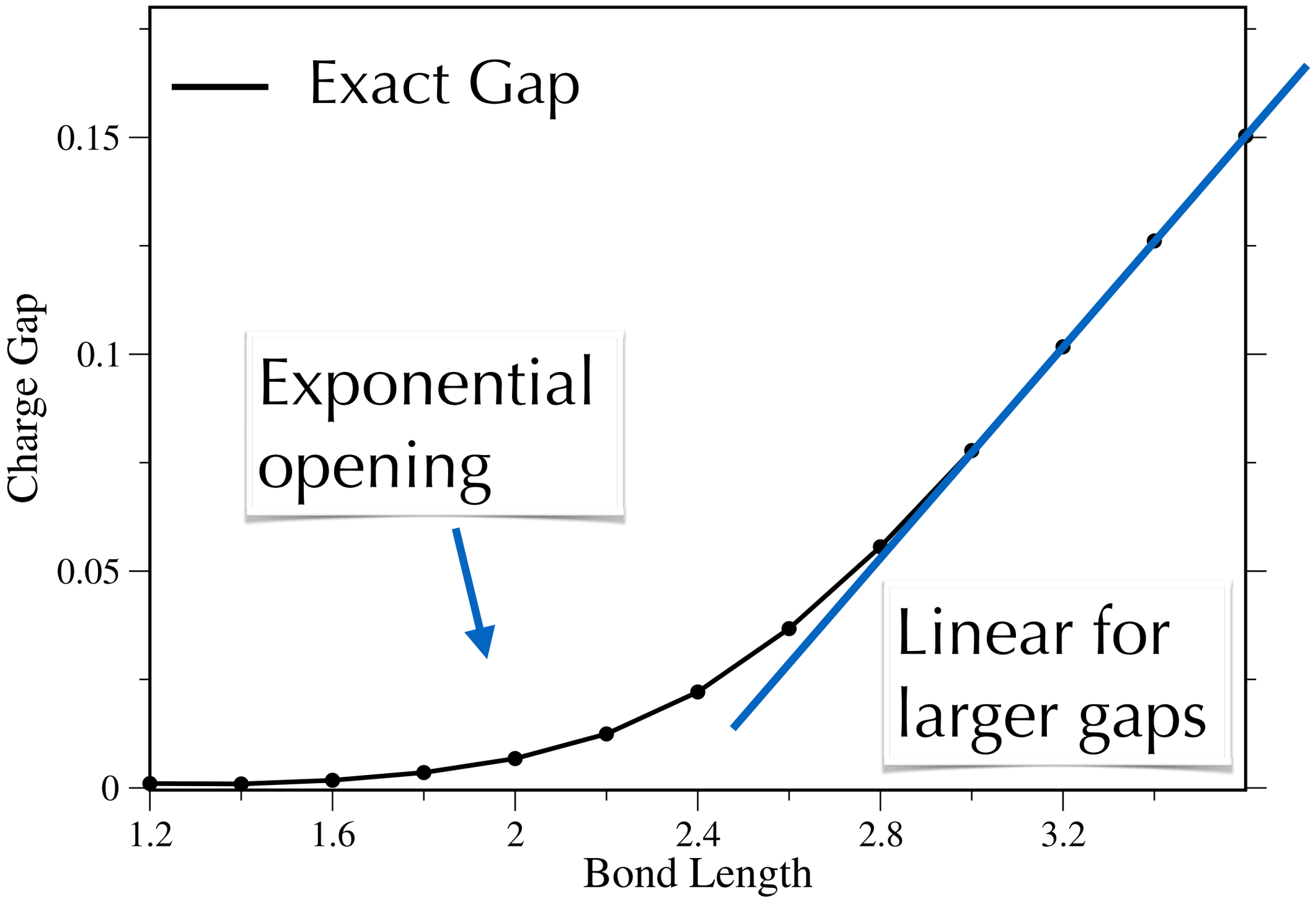


b = 4.0

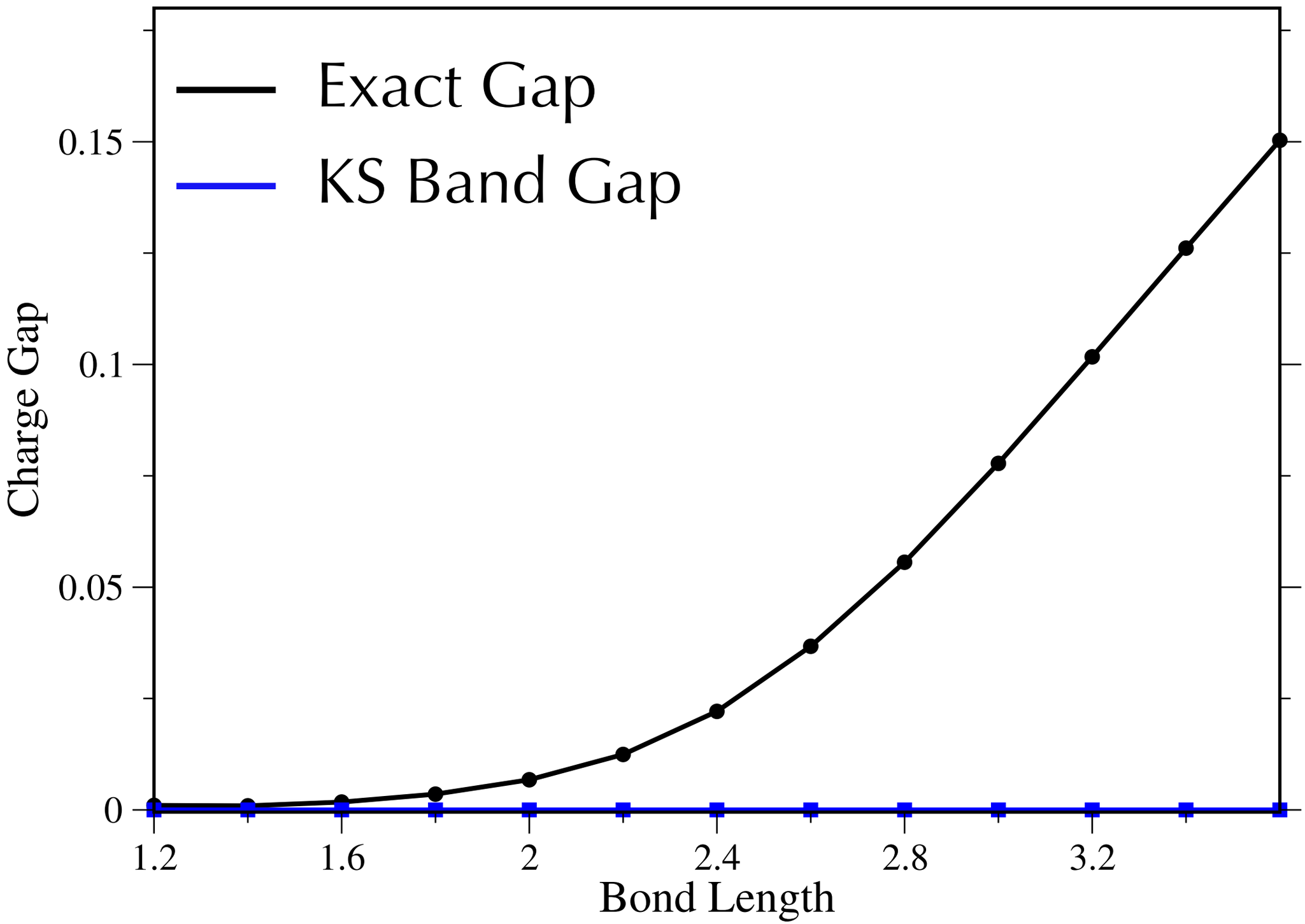
H chains



Similarity to 1d Hubbard model:

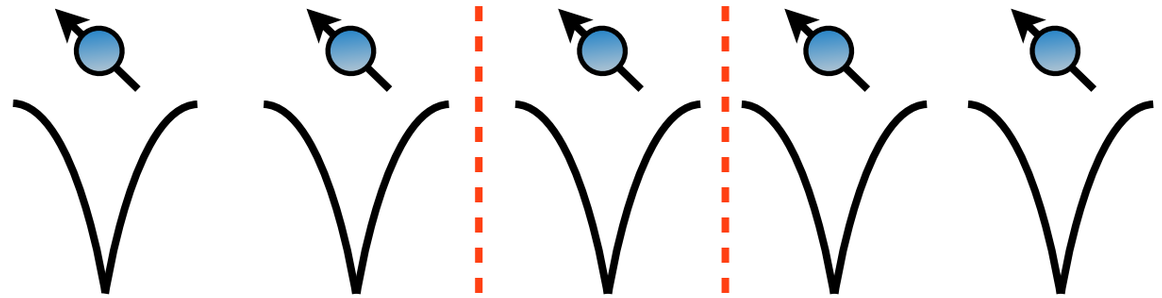


H chains


Exact Gap
KS Band Gap
Charge Gap
0.15
0.1
0.05
0
1.2
1.6
2
2.4
2.8
3.2
Bond Length

H chains Mott insulators,
one electron per unit cell

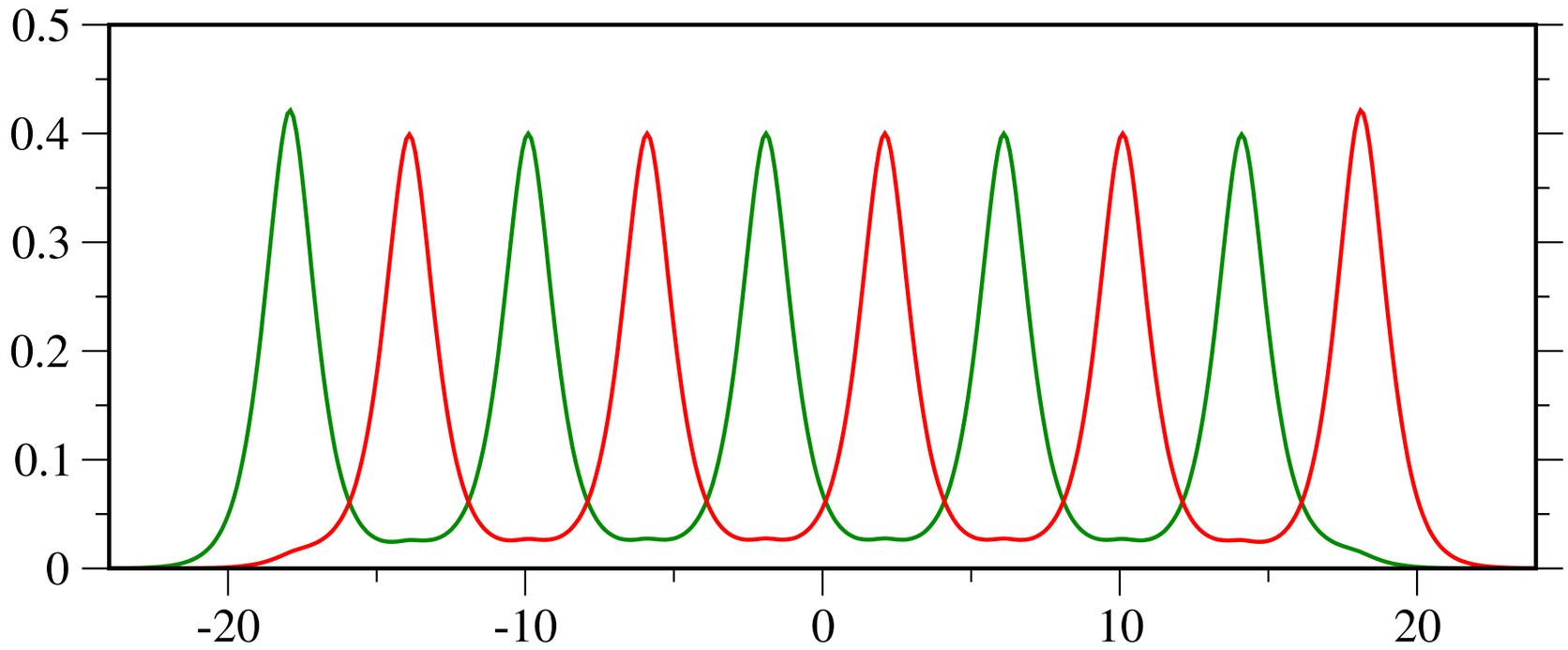
$\Longrightarrow$ lowest band of Kohn-Sham system
half full



Not failure of DFT per se—taking KS band gap
an uncontrolled approximation

But comparing to LDA yields another twist…

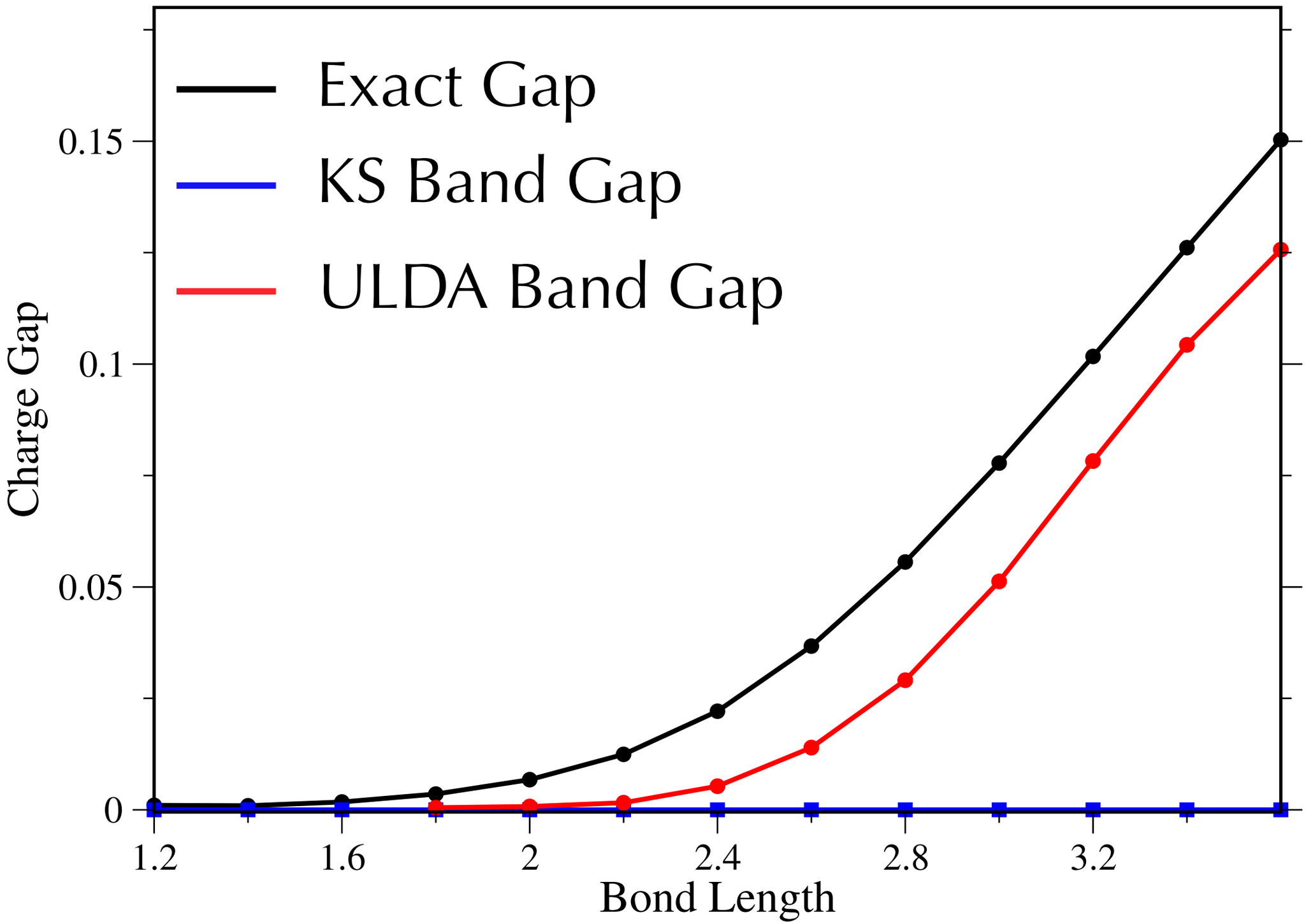
(Unrestricted) LDA approx spontaneously breaks spin symmetry:



b=4, 10 atom system

well-known “spin contamination” effect

Unrestricted LDA gap “better” than exact KS gap



Future work on gaps:

- Benchmark gaps with standard approx's (Hybrids, LDA+U)
- Benchmark newer approx's (range-separated hybrids)
- Obtain argument for generality of ULDA gap, useful approach for more realistic systems?

Application #2:

Convergence of KS Equations

Recall last section:

Interacting sys. $\hat{H} = \hat{T} + \hat{V}_{\text{ee}} + \int_x v(x)\,\hat{n}(x)$

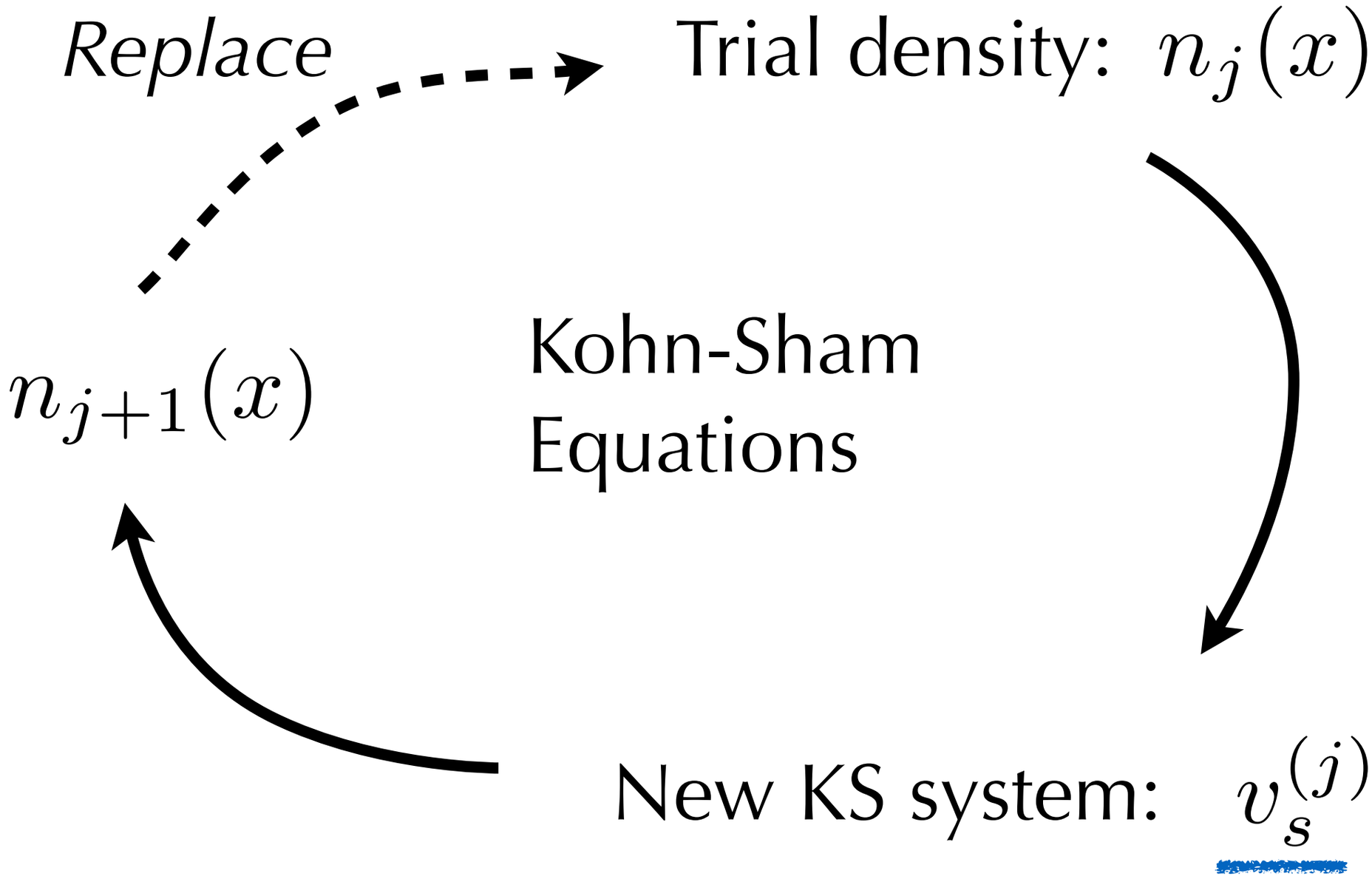
Exact density $n(x)$

"inversion"

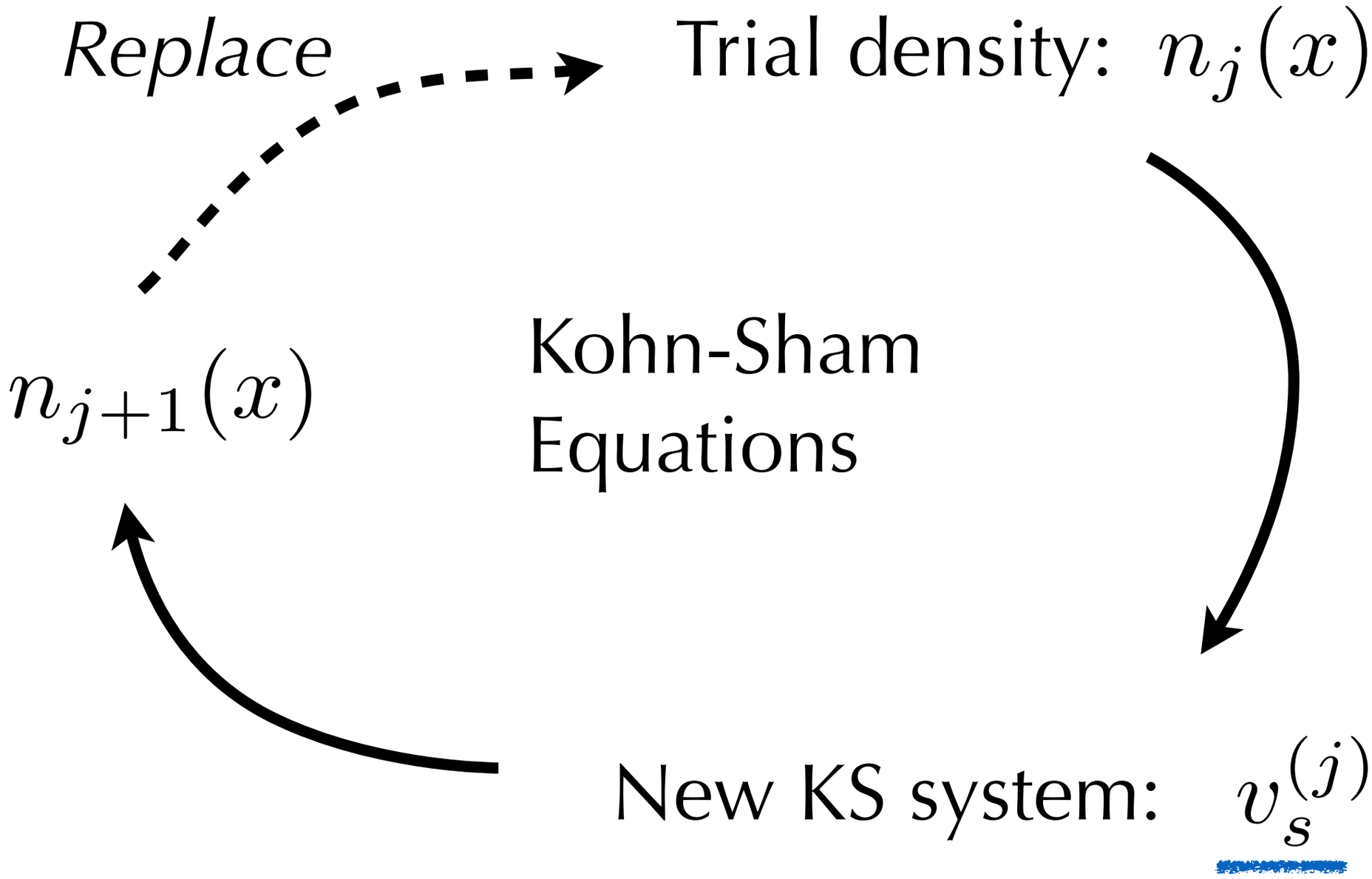
Exact KS system $\hat{H}_s = \hat{T} + \int_x v_s(x)\hat{n}(x)$

Gaps, etc.

But in real DFT applications:



But in real DFT applications:



Trial density: $n_j(x)$

New KS system: $v_s^{(j)}$

Recall: $v_s(x) = v(x) + v_{\mathrm{HXC}}(x)$

Definition of $v_{\mathrm{HXC}}(x)$

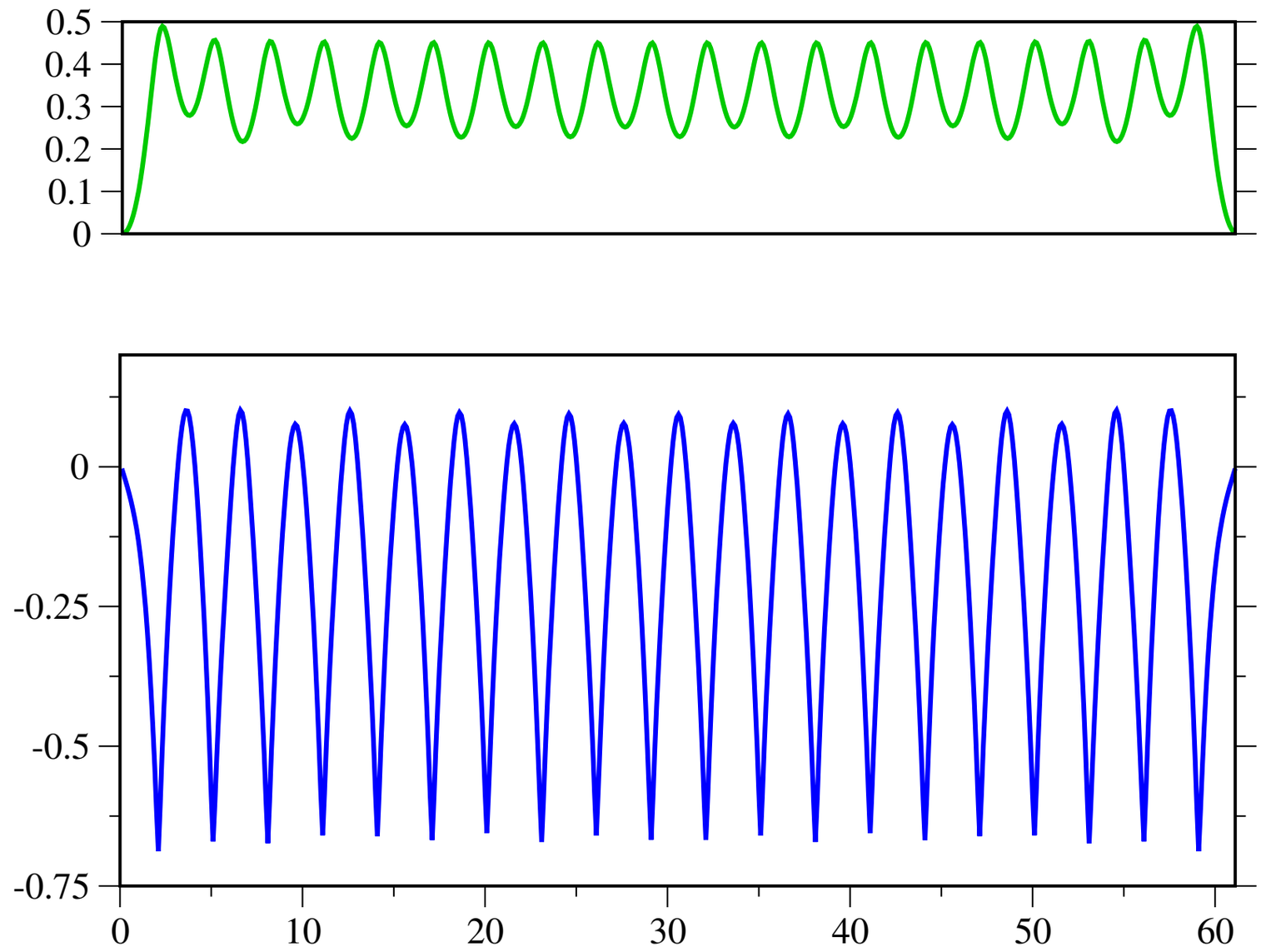
Obtain KS potential supporting $n_j(x)$

(saw this before)

$n_j(x)$

no interactions

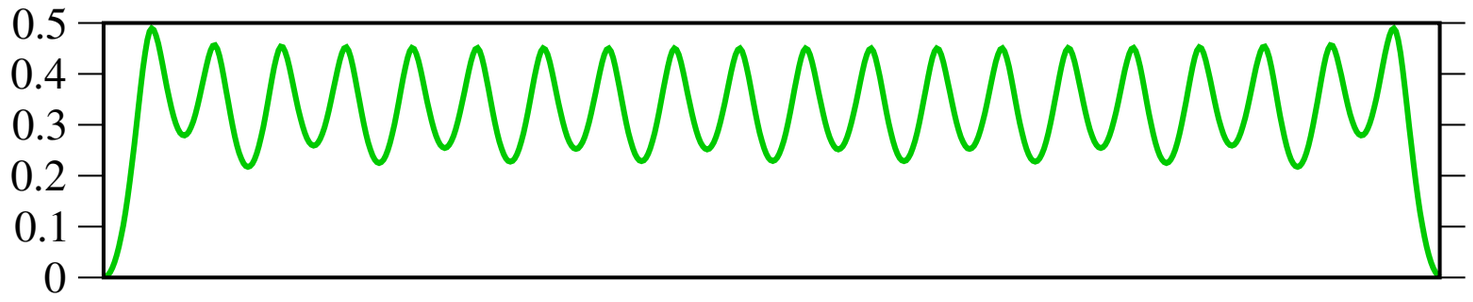
$v_s[n_j](x)$



NEW

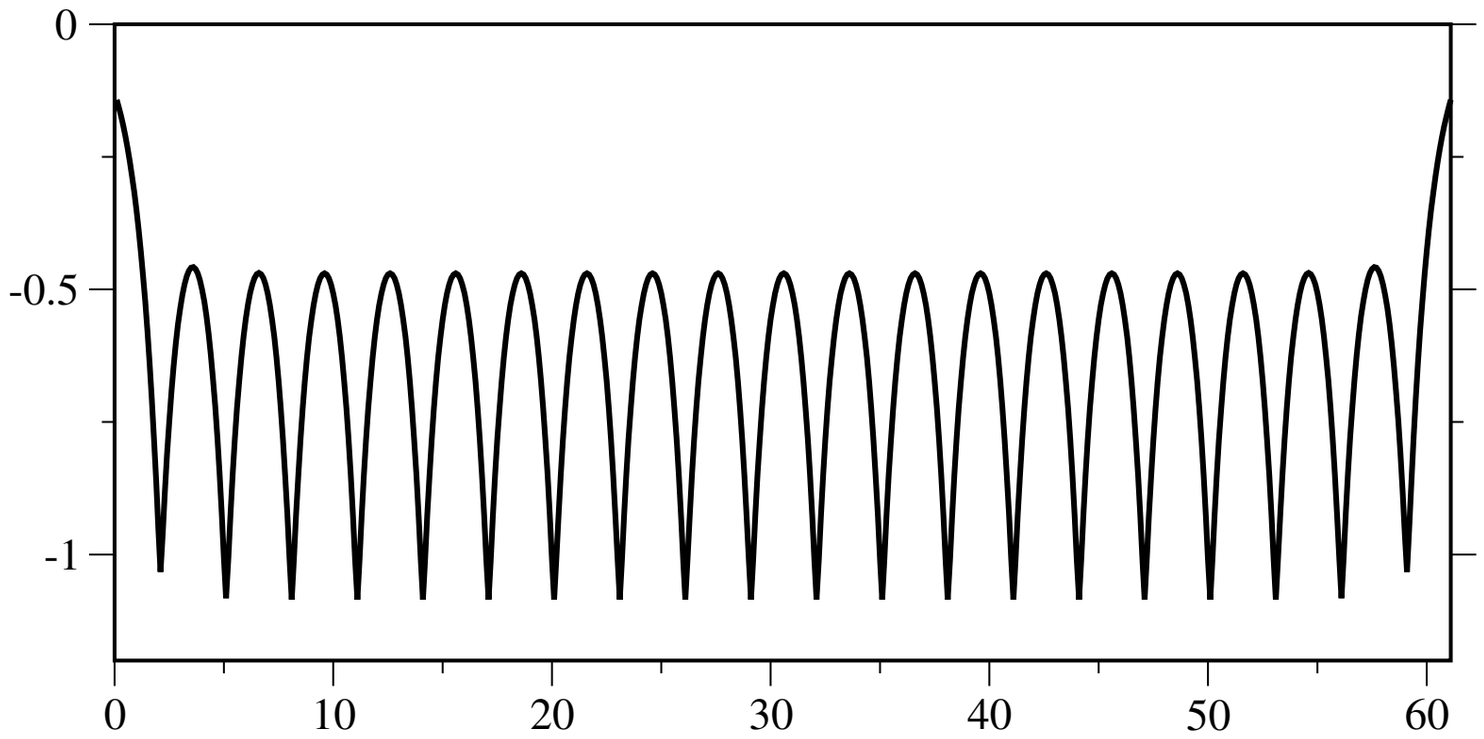
Obtain interacting-system potential supporting $n_j(x)$

$n_j(x)$



with interactions

$v[n_j](x)$



$$v_{\text{HXC}}[n_j](x) = v_s[n_j](x) - v[n_j](x)$$

new "mean-field" correction to potential

New Kohn-Sham system:

$$\hat{H}_s = \hat{T} + \int_x v_{\text{HXC}}[n_j](x)\hat{n}(x) + \int_x v(x)\hat{n}(x)$$

Solve to get new trial density…

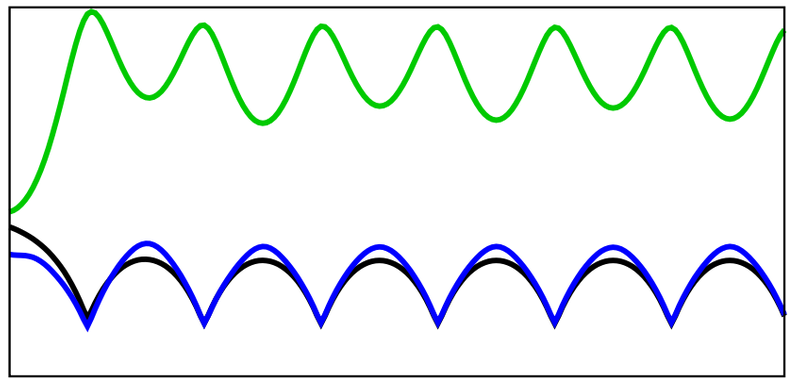
Exact functional

Only new ingredient is “interacting inversion”, requires solving many interacting systems.

Being able to compute both:

$v_s[n](x)$

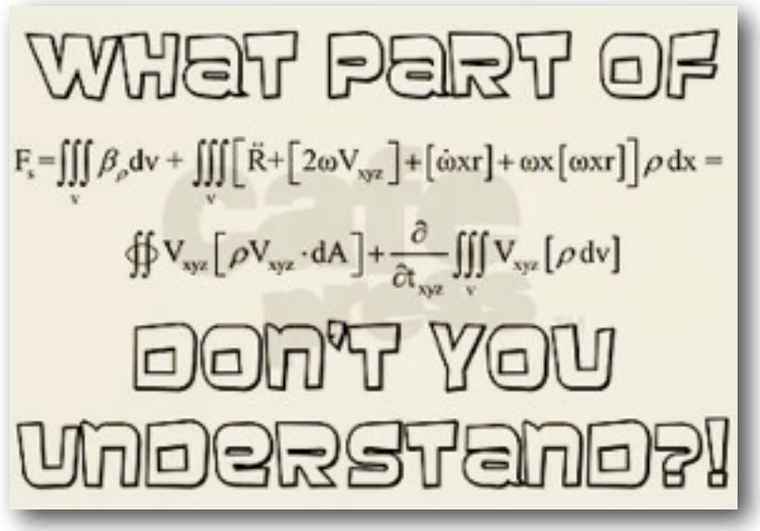
$v[n](x)$



Means having the “exact functional”

Exact functional

Often discussed as a closed-form analytic expression:



Our perspective: exact functional is an algorithm

Exact functional

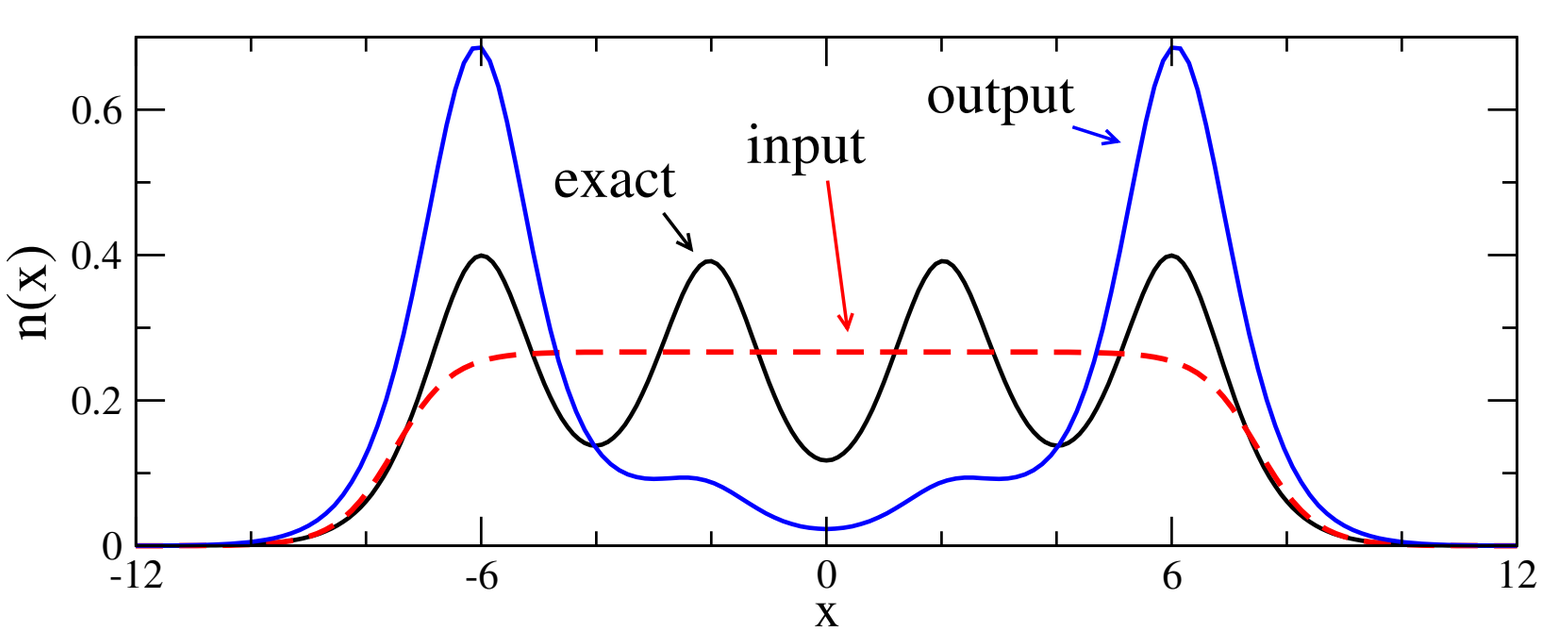
What's the application?

Learn how DFT behaves with exact functional.
Any failures are fundamental.
Otherwise they are failures of approximations.

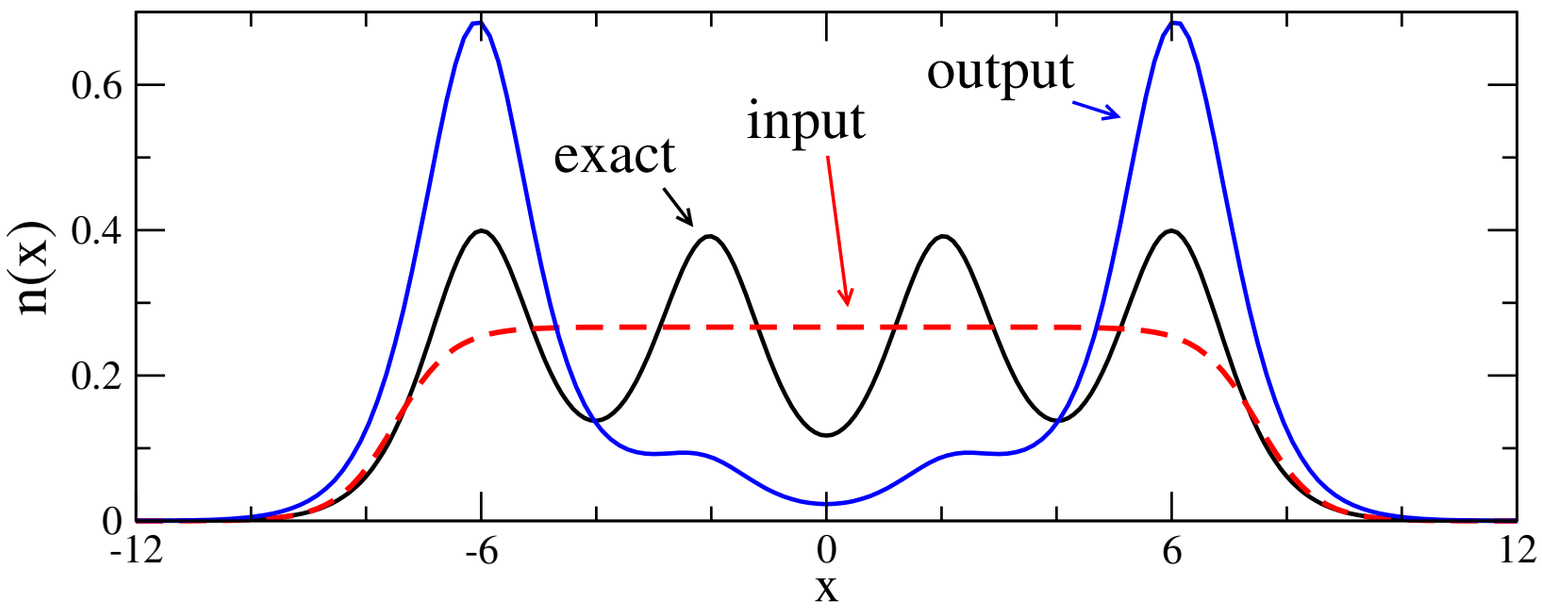
Convergence

Do the KS equations always converge using the exact functional?

Test calculations using DMRG on small chains:



Convergence



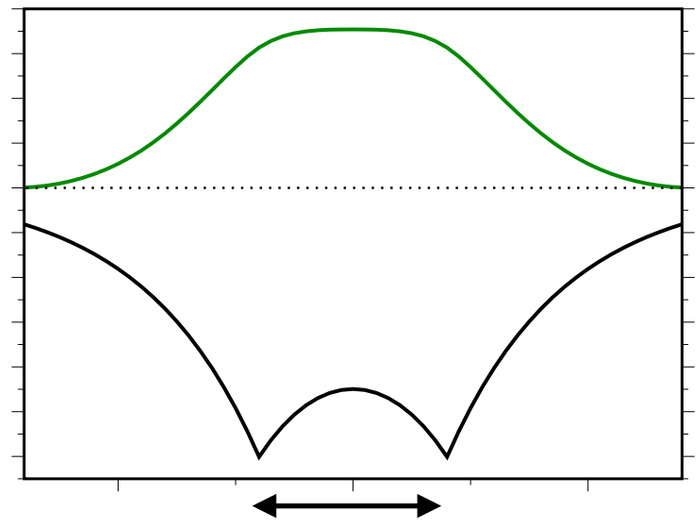
One step of the KS equations

Already looks to overshoot…
Is damping enough to fix?

$$n_\lambda(x) = \lambda\, n_{j+1}(x) + (1-\lambda)\, n_j(x)$$

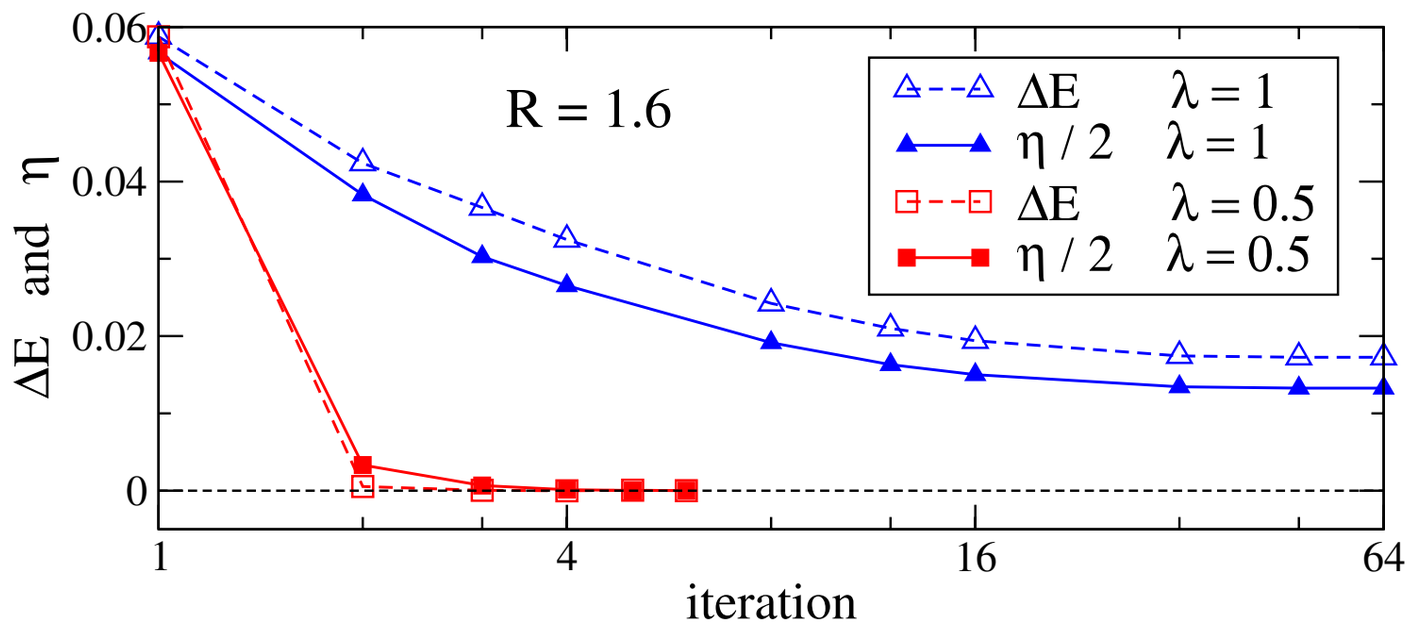
Convergence

Test 1: weakly correlated H_2 molecule



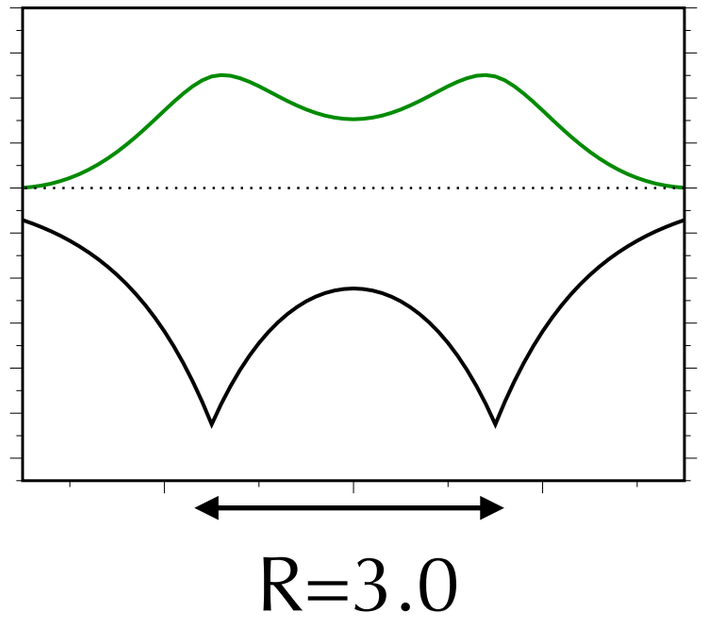
R=1.6

Damping helps, but not required:

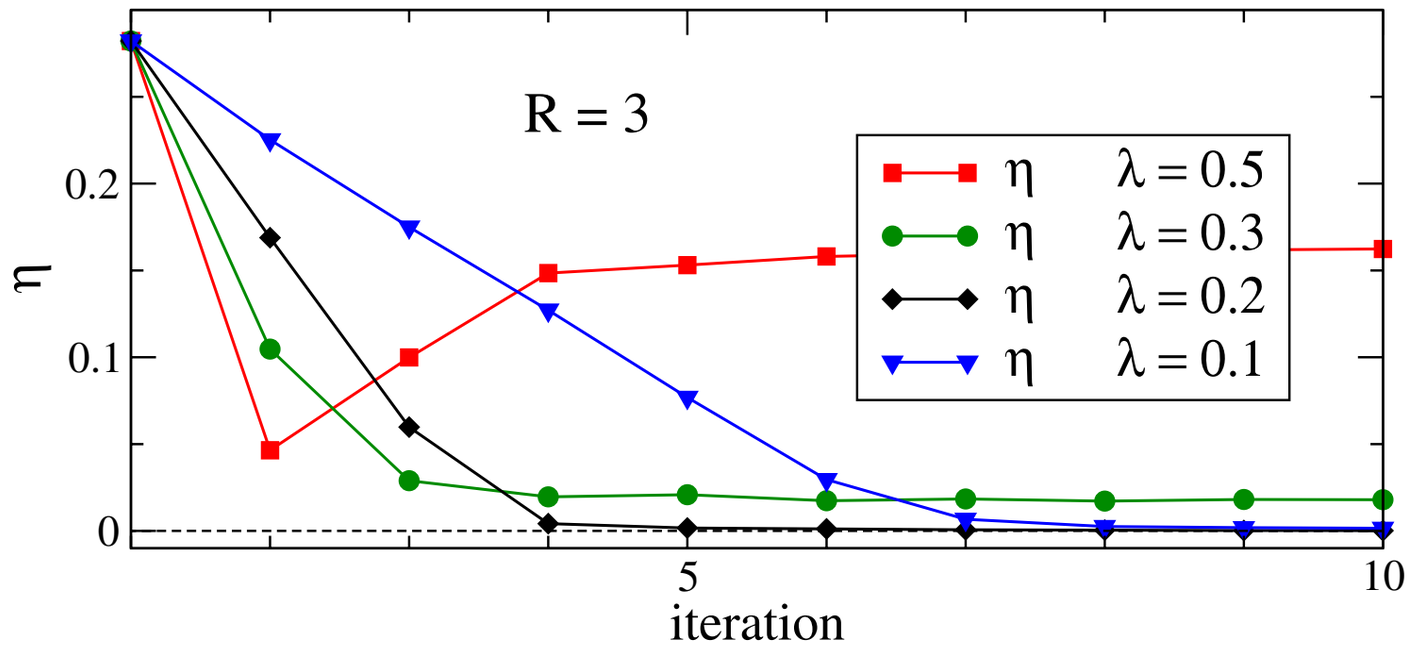


Convergence

Test 2: strongly correlated
H_2 molecule



Convergence requires $\lambda < 0.5$

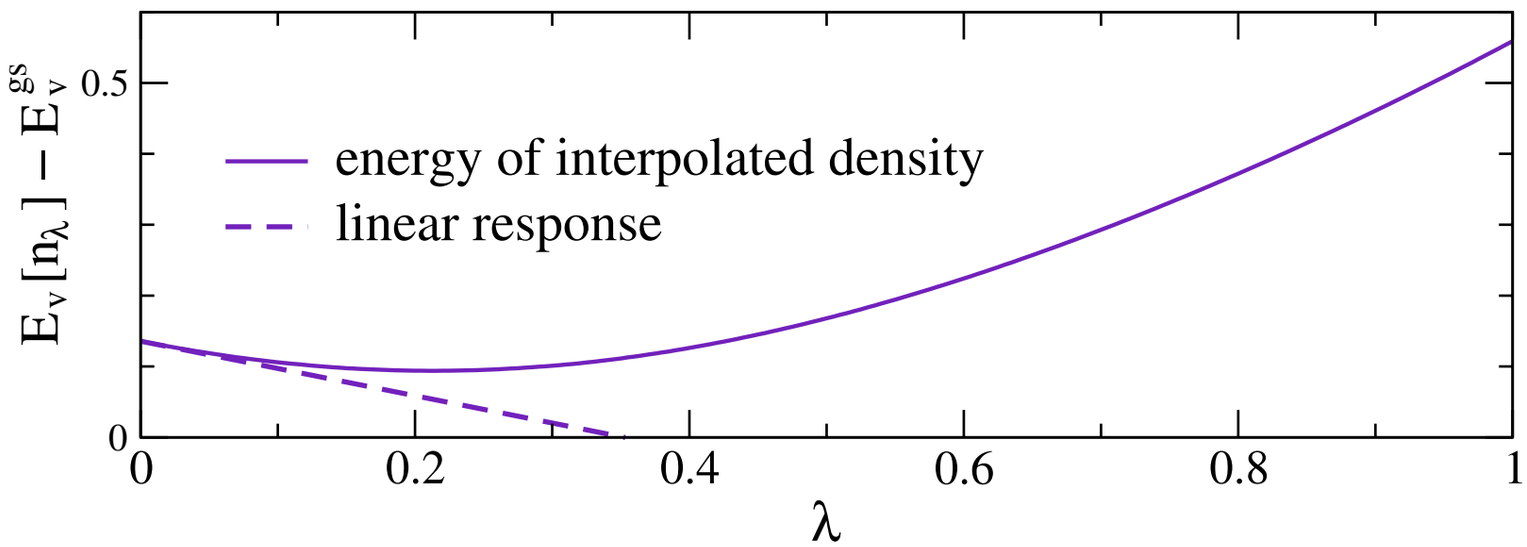


Convergence

Is damping always enough?

Yes! Can prove via linear response that energy always goes down for small enough damping.

Wagner, Stoudenmire, Burke, White, PRL **111**, 093003 (2013)



Combined with convexity of exact functional, guarantees convergence.

Future Directions

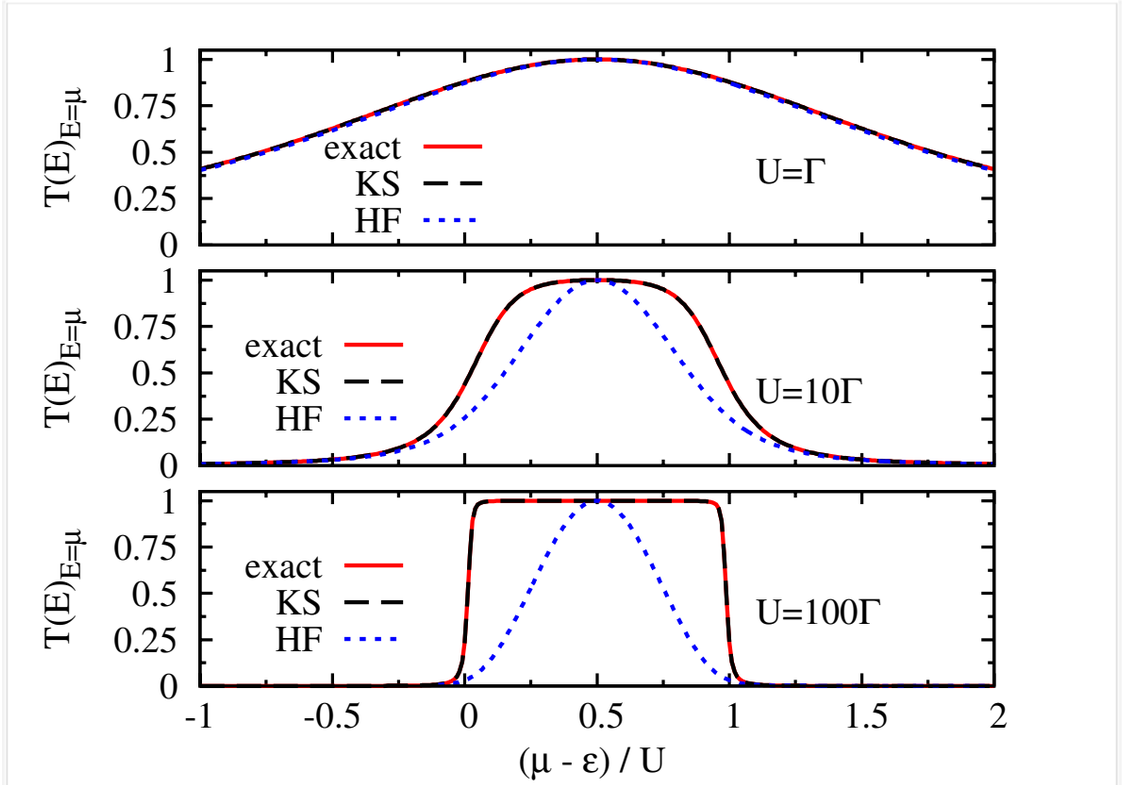
Gaps are an example where *exact* Kohn-Sham system fails to reproduce exact properties.

What about transport?

Common approx: $G(k,\omega) \rightarrow G^{\mathrm{KS}}(k,\omega)$

Yields exact transport properties of single-impurity Anderson model!

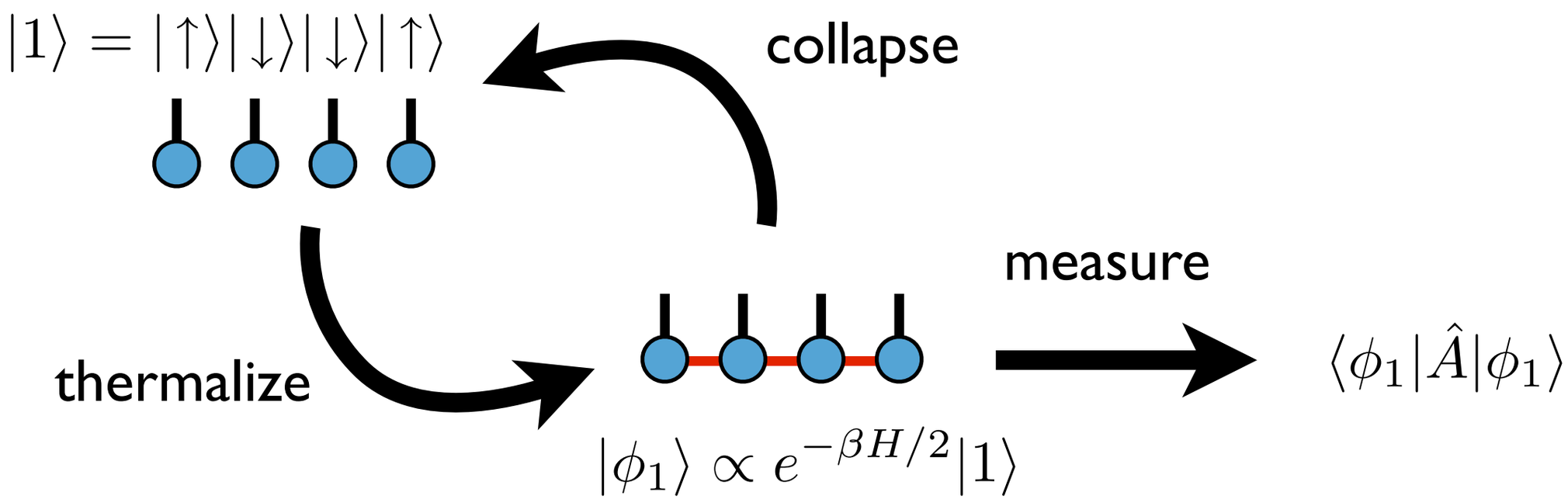
Continuum models?



Bergfield, Liu, Burke, Phys. Rev. Lett **108**, 066801 (2012)

Combine METTS* algorithm with continuum. Test thermal DFT approximations, cold atoms systems at finite T.

- DMRG/QMC hybrid
- Quantum Monte Carlo with no sign problem
- (Does have the “DMRG problem”)



*White, PRL **102**, 190601 (2009)

Stoudenmire, White, NJP **12**, 055026 (2010

Combine METTS* algorithm with continuum. Test thermal DFT approximations, cold atoms systems at finite T.

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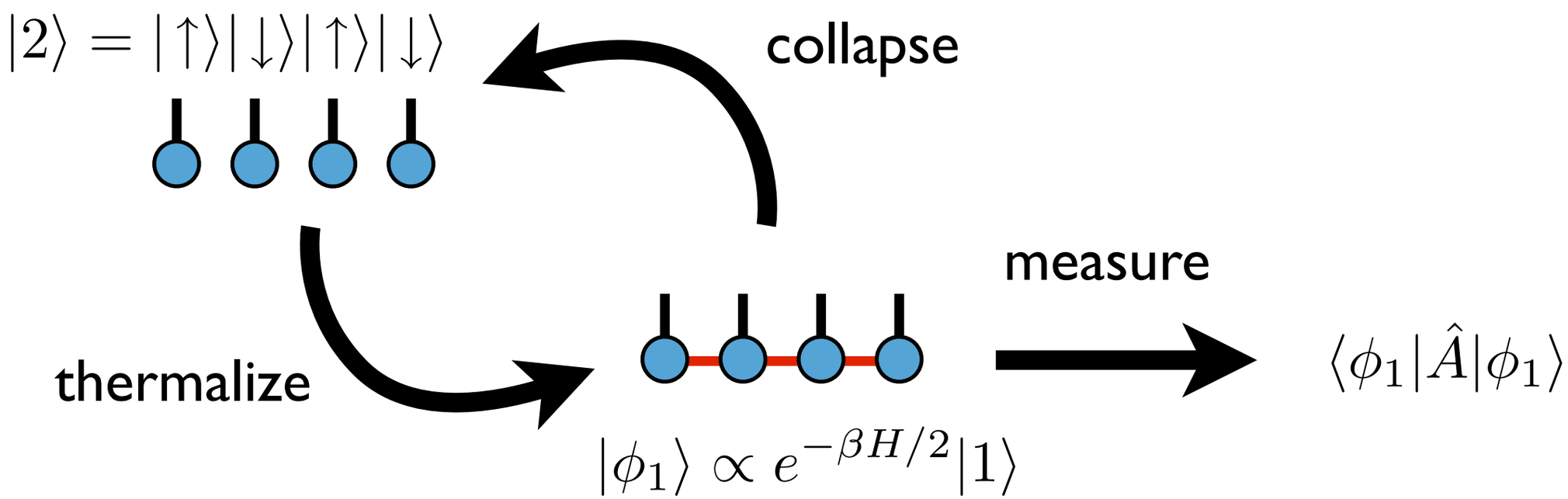
- Quantum Monte Carlo with no sign problem
- (Does have the “DMRG problem”)



*White, PRL **102**, 190601 (2009)

Stoudenmire, White, NJP **12**, 055026 (2010

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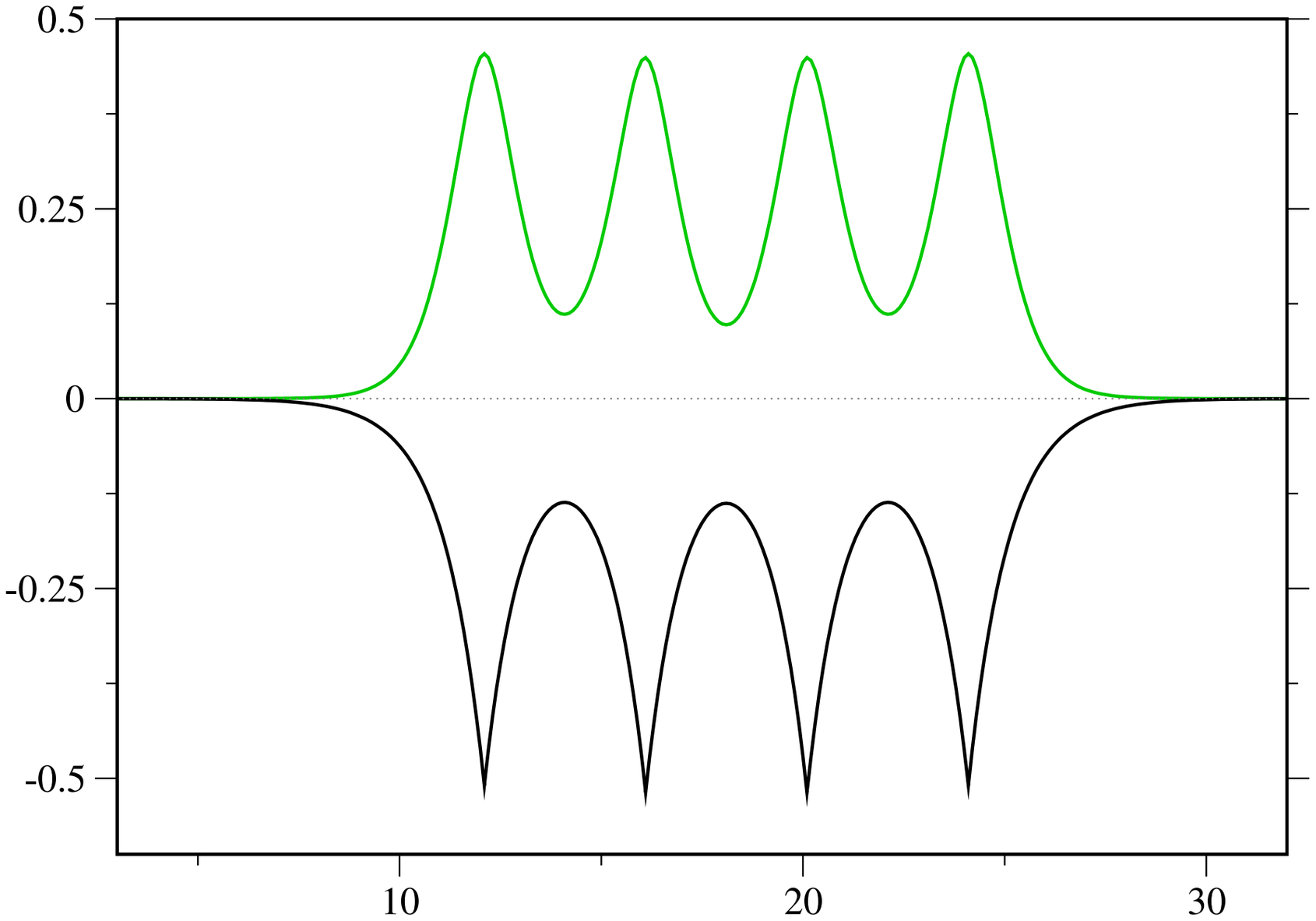
Compare to continuum. (Good student project.)



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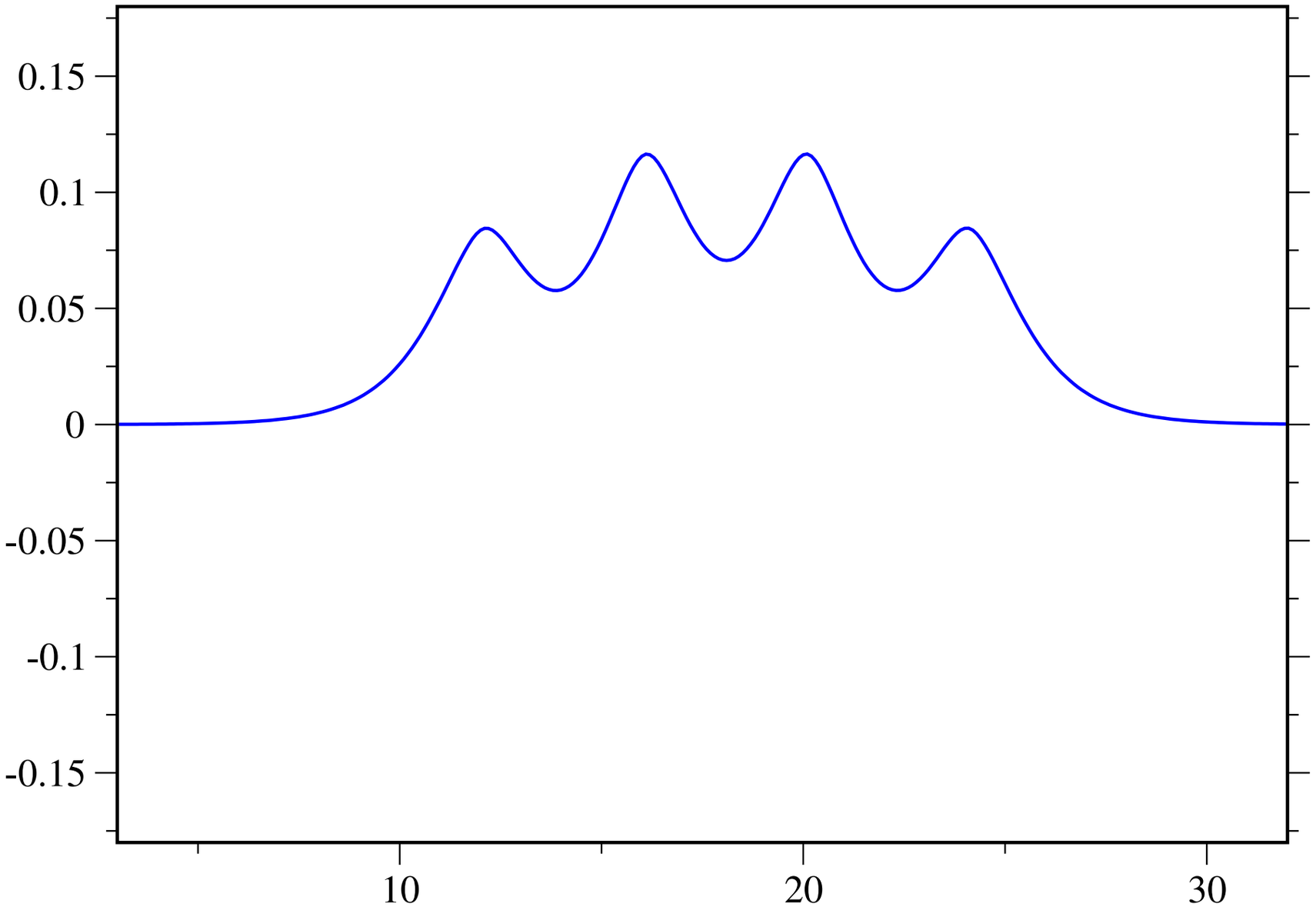

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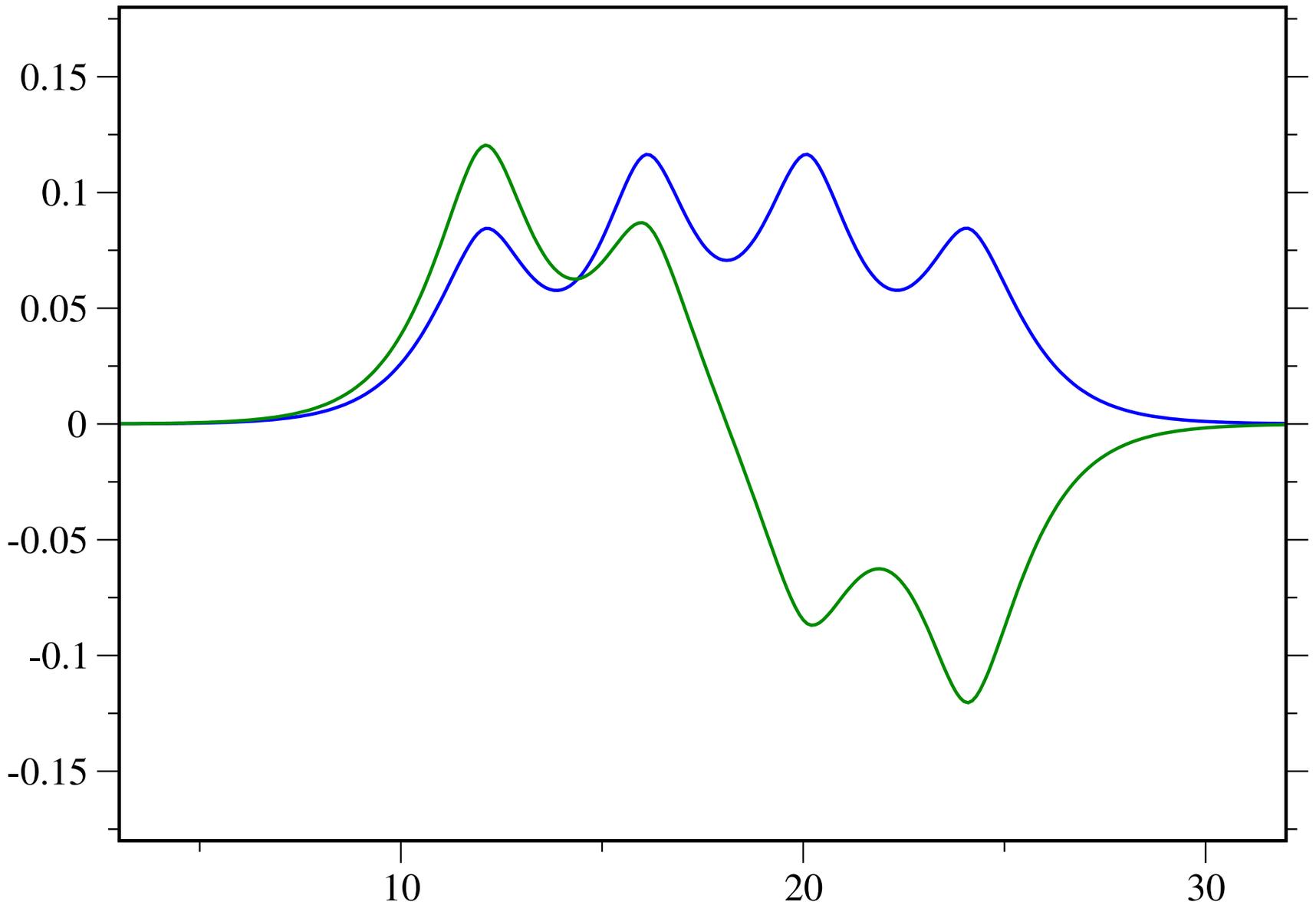

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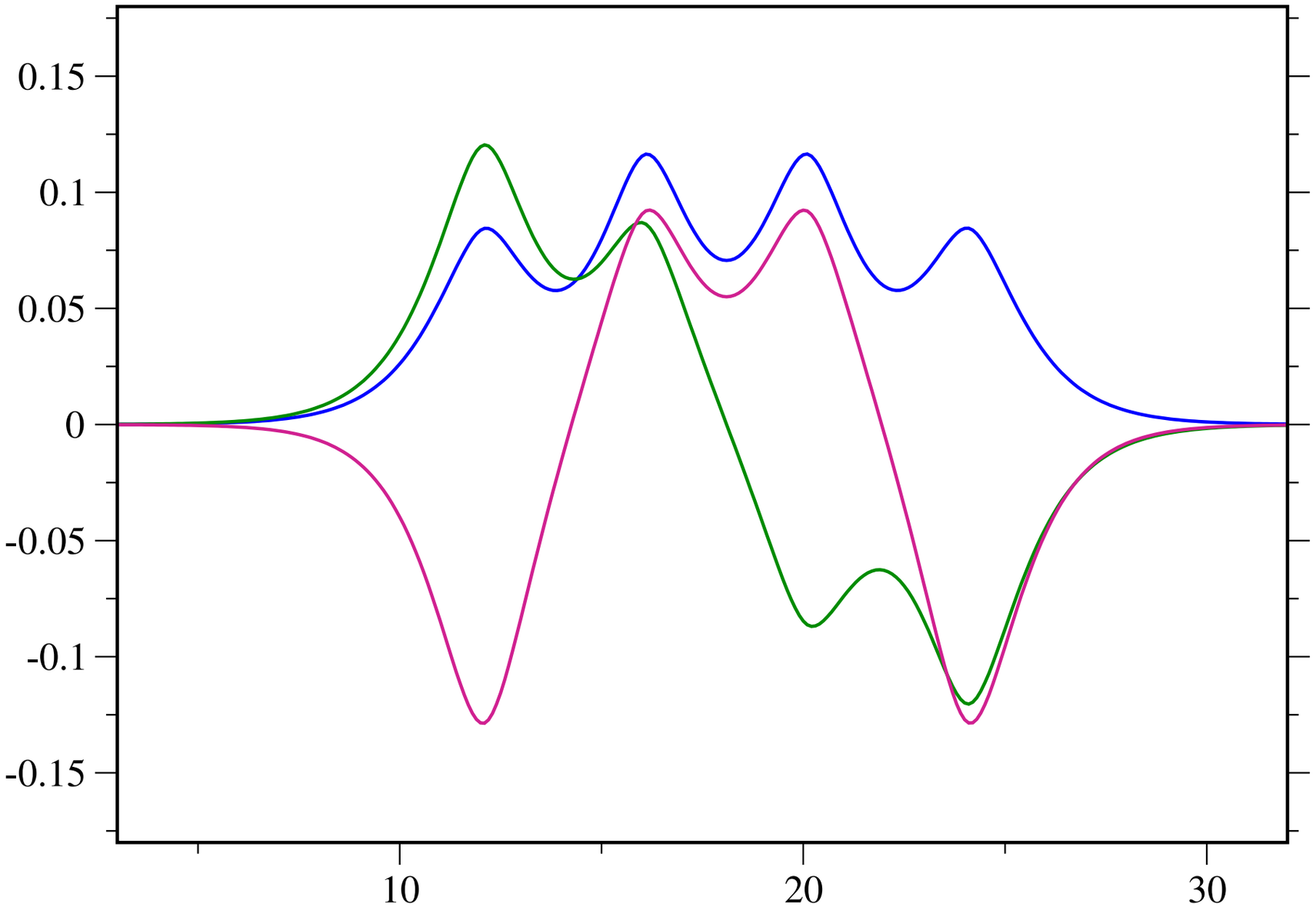

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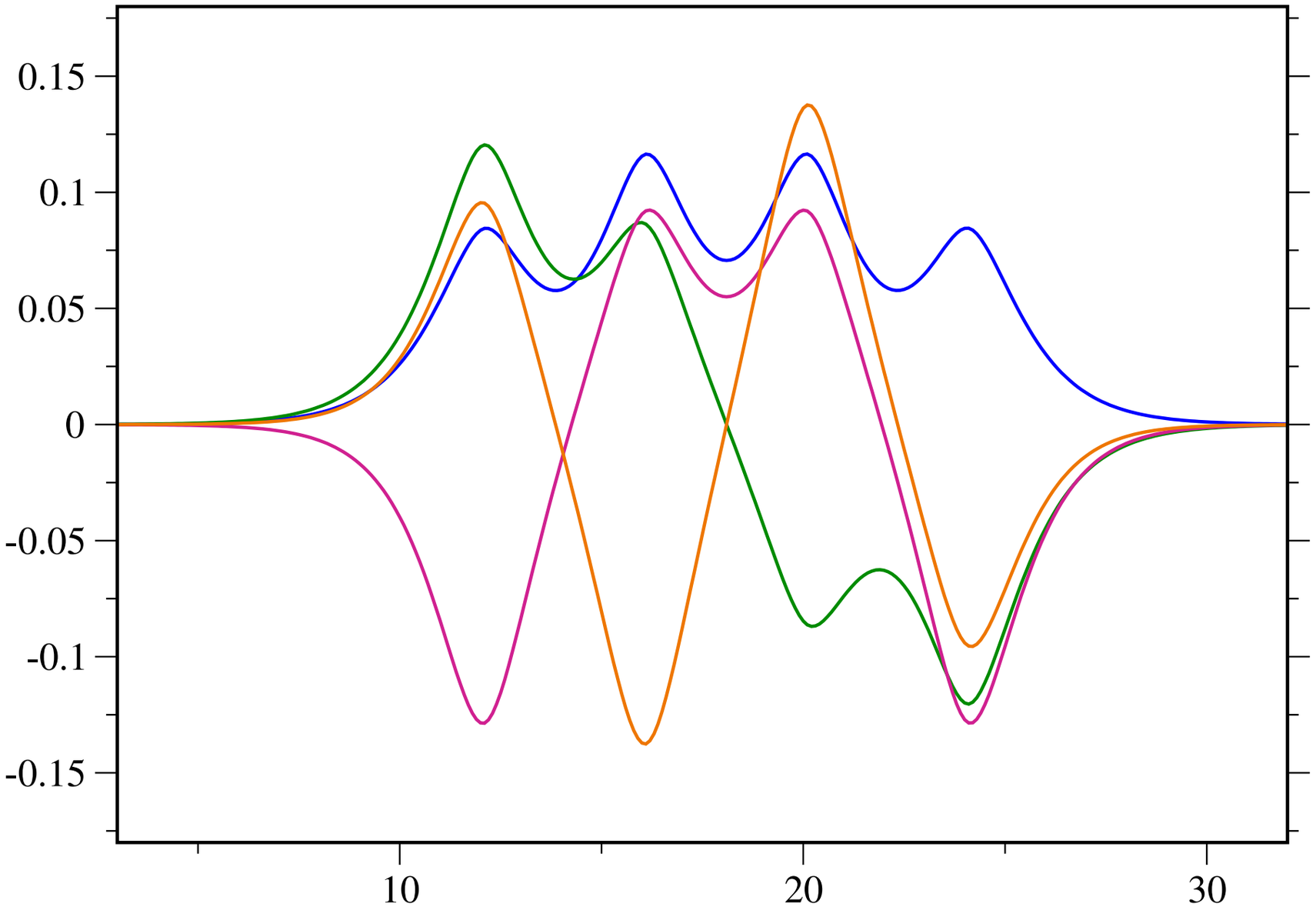

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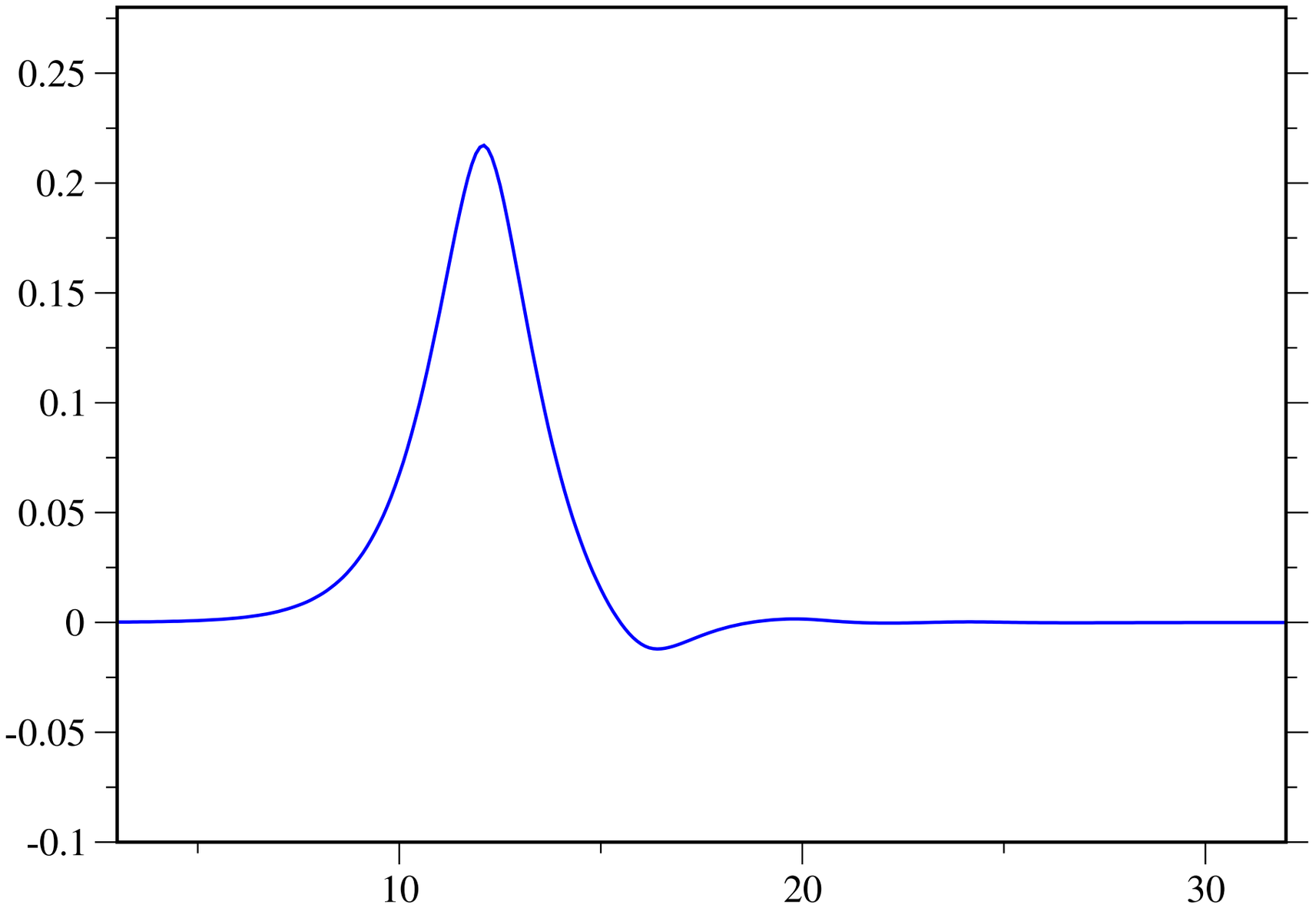

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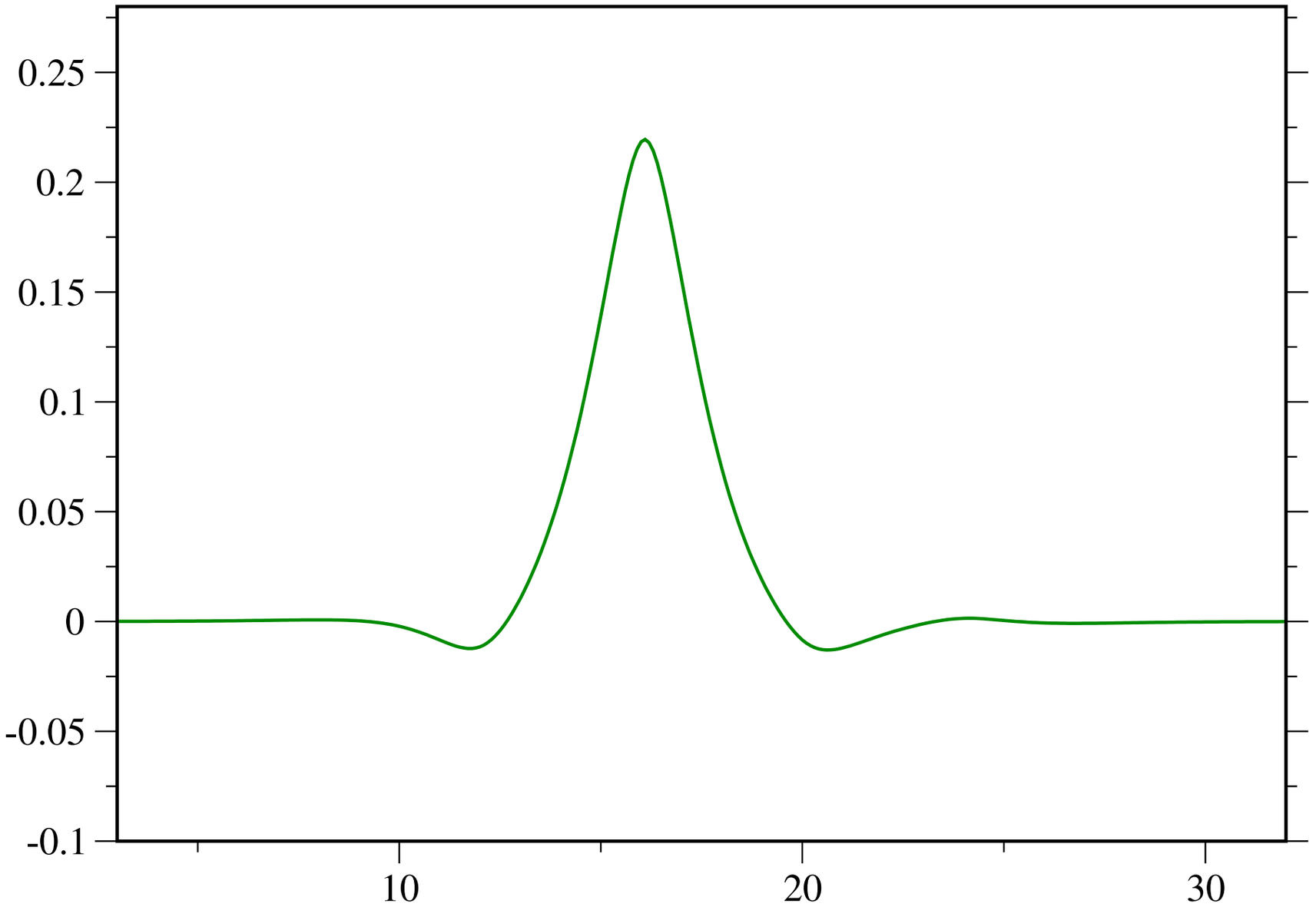

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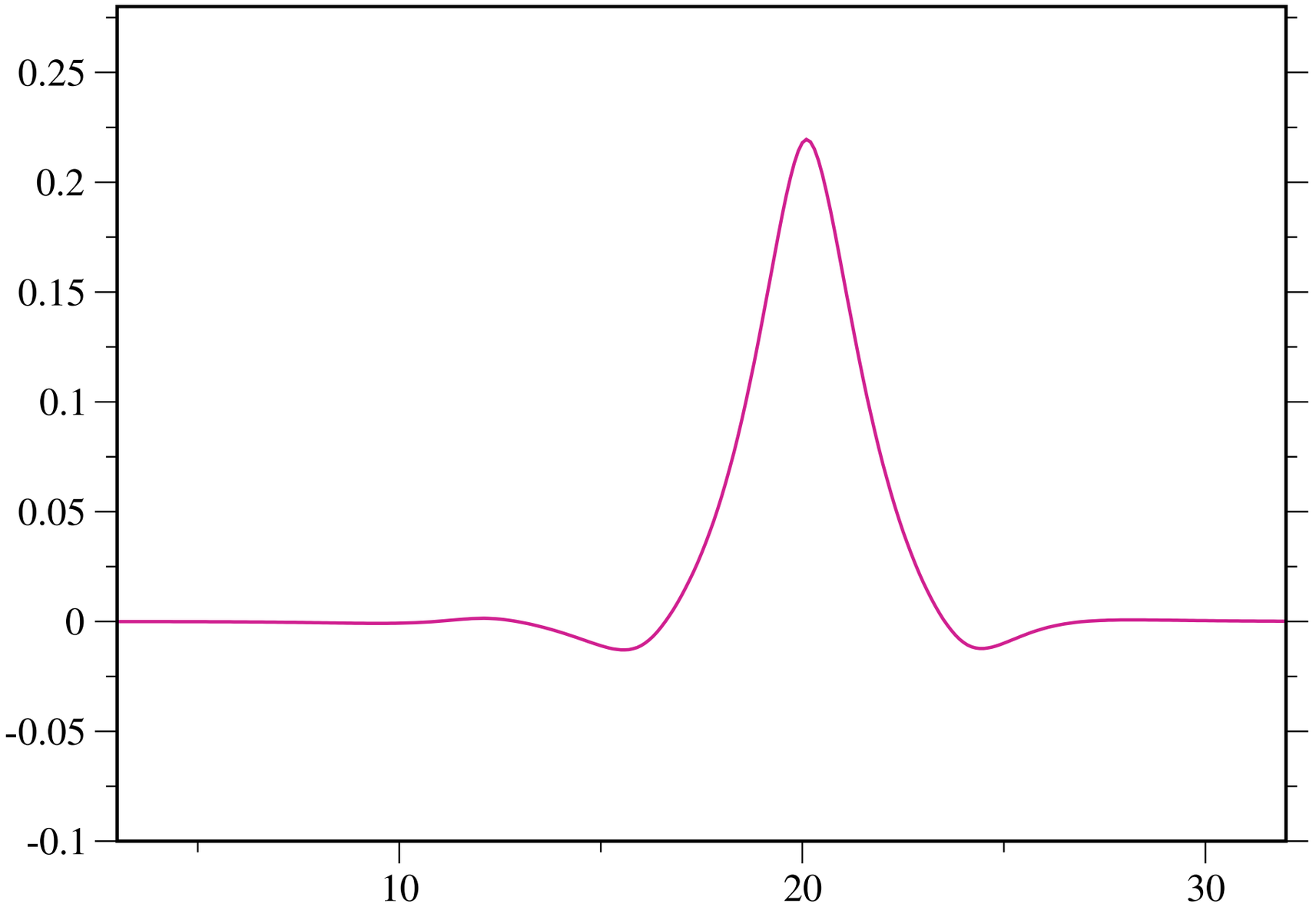

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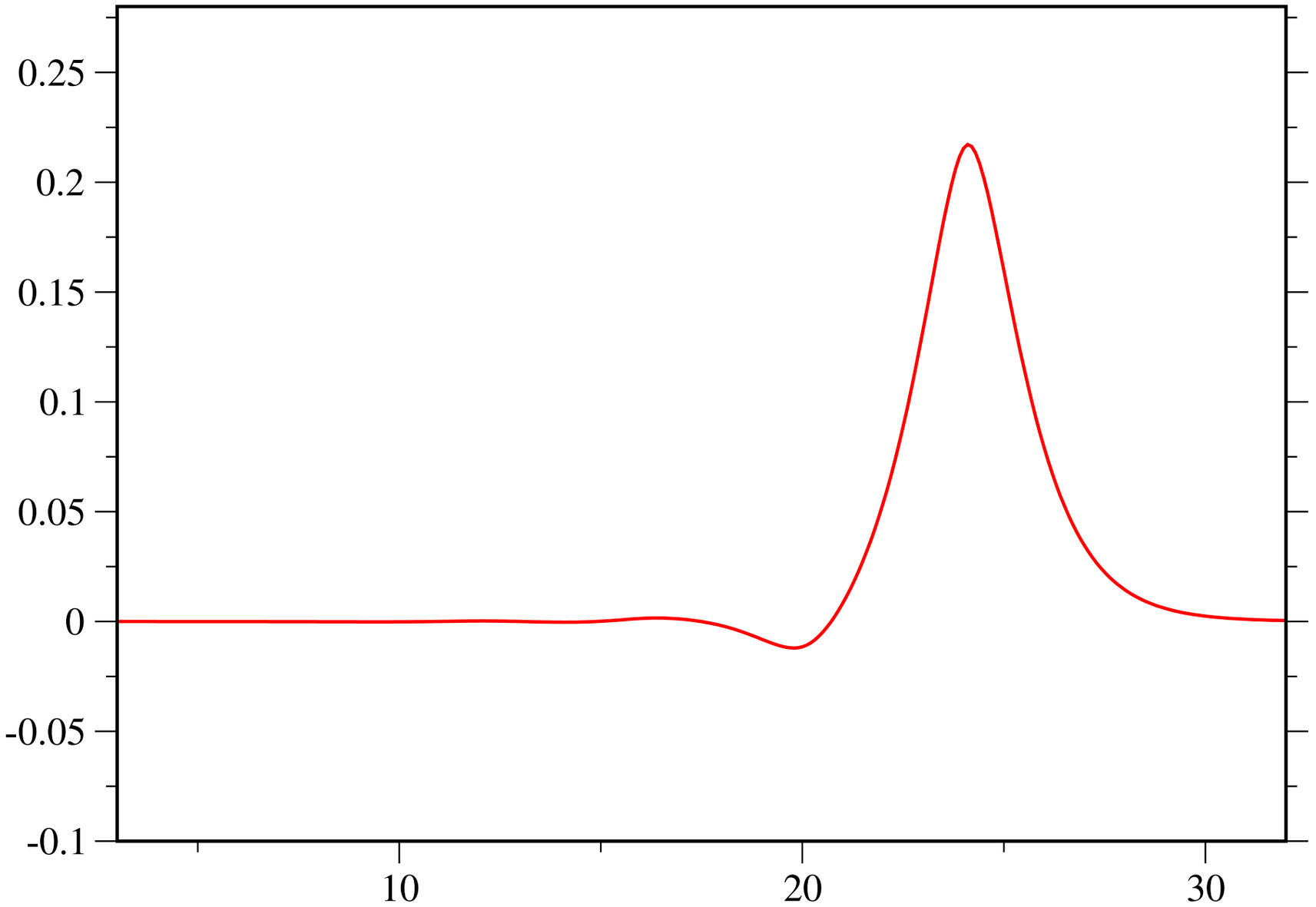

Summary

- Can extend DMRG to solve continuum 1d systems.
- Computing exact quantities appearing in density functional gives insight into gaps, KS equations
- Much more to explore including:
  - Quasi-1d cold atom/molecule systems
  - Transport approx's in DFT
  - Continuum to lattice mapping