# Locality of interatomic interactions

Jack Thomas (Orsay)

Joint work with Huajie Chen (Beijing Normal University), Christoph Ortner (University of British Columbia), and Antoine Levitt (Orsay)

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# Outline

# Set-up

- Many-body Schrödinger equation: $\mathcal{H}_{\text{tot}}\Psi = E\Psi$
- Born–Oppenheimer: solve for the electrons $\mathcal{H}_{\text{BO}} = \mathcal{H}_{\text{BO}}(\boldsymbol{r})$ [where $\boldsymbol{r} = (\boldsymbol{r}_1, \dots, \boldsymbol{r}_{N_{\text{at}}}) \in (\mathbb{R}^d)^{N_{\text{at}}}$]
- Kohn–Sham equations:

KS DFT

$$\mathcal{H}\psi_i(x) := \Big( -\tfrac{1}{2}\Delta + V(x) \Big)\psi_i(x) = \varepsilon_i \psi_i(x)$$

$$\rho(x,y) := \sum_i f(\varepsilon_i)\psi_i^\star(x)\psi_i(y), \qquad \rho(x) := \rho(x,x)$$

where $f(\varepsilon_i)$ are the single particle occupation numbers
$V = V[\rho] \rightsquigarrow$ self-consistent field,

- Discretization: $\mathcal{H}\psi_i = \varepsilon_i S \psi_i$ where $\mathcal{H} \in \mathbb{R}^{N_{\text{b}}N_{\text{at}} \times N_{\text{b}}N_{\text{at}}}$

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Linear Scaling Algorithms
e.g. [Goedecker 1999]

$\Uparrow$

**Density matrix**

$\rho(x, y)$ is short-ranged in $|x - y|$
[Kohn 1996]

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Machine Learned Interatomic Potentials
e.g. [Musil et al. 2021]

Geometry Relaxation
e.g. [Chen Lu Ortner 2018, Ortner JT 2020]

$\Uparrow$ $\Uparrow$ $\Uparrow$

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[Kohn 1996]

**Site Energy Decomposition**

$$E(\boldsymbol{r}) = \sum_{\ell} E_{\ell}(\boldsymbol{r}), \qquad \left| \frac{\partial E_{\ell}}{\partial \boldsymbol{r}_k} \right| \lesssim e^{-\gamma r_{\ell k}}$$

e.g. [Chen Ortner 2016, Nazar Ortner 2017, Ortner JT Chen 2020, JT 2020]

$\Downarrow$

Decay of the forces:

$$\frac{\partial^2 E(\boldsymbol{r})}{\partial \boldsymbol{r}_{\ell} \partial \boldsymbol{r}_k} \quad \text{etc.}$$

$\Leftarrow$

Multiscale Methods
e.g. [Csányi et al. 2005]

# Notation

- Recall: $\mathcal{H}\psi_i = \varepsilon_i \psi_i$, $\mathcal{H} \in \mathbb{R}^{N_\mathrm{b} N_\mathrm{at} \times N_\mathrm{b} N_\mathrm{at}}$ given by

[Take $S = \mathrm{id}$ by considering Löwdin transform: $S^{-T/2} H S^{1/2}$]

Orbitals

Spectrum

$$\mathcal{H}_{\ell k, ab} := \int \phi_{\ell a}(x) \Big[ -\frac{1}{2}\Delta + V(x) \Big] \phi_{kb}(x) \mathrm{d}x$$

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- **Assume**: $|\mathcal{H}_{\ell k}| \lesssim e^{-\gamma_0 r_{\ell k}}$ $\qquad [r_{\ell k} := |\boldsymbol{r}_\ell - \boldsymbol{r}_k|]$
- Density matrix: $F(\mathcal{H})$
- Band energy: $E := \mathrm{Tr}\big(\mathcal{H}F(\mathcal{H})\big)$

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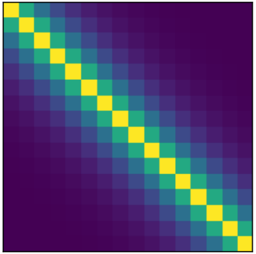
Matrix entries



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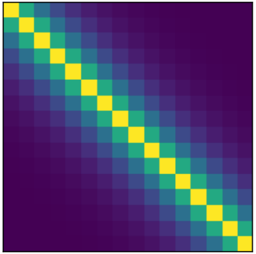
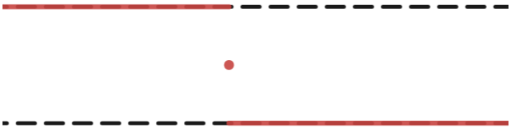
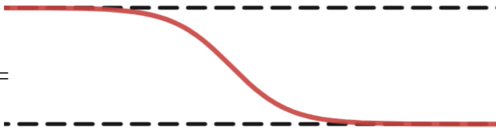


$F =$



$\mu = \varepsilon_\mathrm{F}$

$F^\beta =$



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# Density matrix (banded matrices)

[Benzi Boito Razouk 2013]

- Suppose $\mathcal{H}$ is $m-$banded:

$$\mathcal{H}_{\ell k} = 0 \quad \text{for all } r_{\ell k} > m$$

- Then, $[\mathcal{H}^N]_{\ell k} = 0$ for all $r_{\ell k} > mN$
- That is, $P_N(\mathcal{H})_{\ell k} = 0$ for all $N < \frac{1}{m} r_{\ell k}$

$P_N \in \mathcal{P}_N$
polynomials of
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- Therefore,

$$\begin{aligned} \left|F(\mathcal{H})_{\ell k}\right| &= \min_{P \in \mathcal{P}_N} \left| \left[F(\mathcal{H}) - P(\mathcal{H})\right]_{\ell k} \right| \\ &\leq \min_{P \in \mathcal{P}_N} \left\|F - P\right\|_{L^\infty(\sigma(\mathcal{H}))} \end{aligned}$$

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- Locality $\longleftrightarrow$ Polynomial approximation on the spectrum
  $\longleftrightarrow$ spectral gap or $\beta < \infty$
  (insulators or finite temperature)

# Density matrix (banded matrices)

## Upper Bounds:

- Finite temperature ($\beta < \infty$):

$$\left|F(\mathcal{H})_{\ell k}\right| \leq \frac{2\|F\|_{L^\infty(\mathcal{E}_\chi)}}{\chi - 1}\chi^{-N}$$

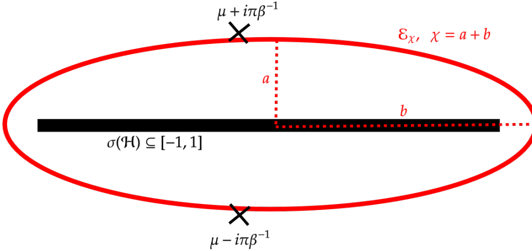
where $F$ is analytic on $\mathcal{E}_\chi$.

[Proof: Chebyshev coefficients decay exponentially depending on region of analyticity]

**Decay rate $\longleftrightarrow$ polynomial approx.**

For $N < \frac{r_{\ell k}}{m}$,

$$\left|F(\mathcal{H})_{\ell k}\right| \leq \min_{P \in \mathcal{P}_N} \left\|F - P\right\|_{L^\infty(\sigma(\mathcal{H}))}$$



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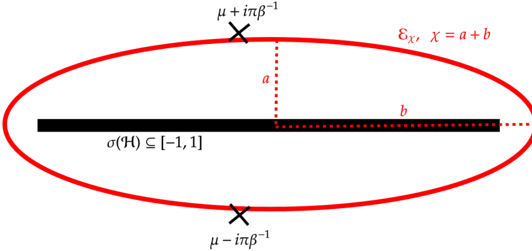

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- Insulators ($g > 0$): [Hasson 2007]

$$\left|F(\mathcal{H})_{\ell k}\right| \leq \frac{C}{\sqrt{N}}\sqrt{\frac{2-g}{2+g}}^{N}$$

where $g$ is the spectral gap.

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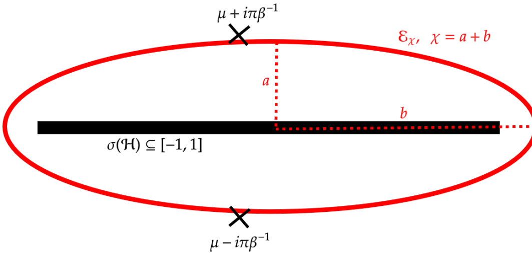



[Symmetric gap]

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### Decay rate $\longleftrightarrow$ polynomial approx.

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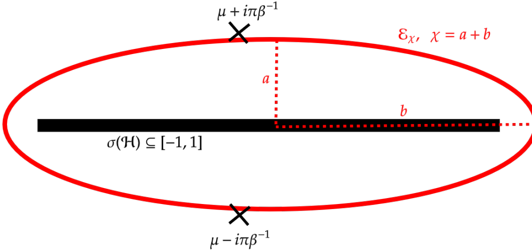



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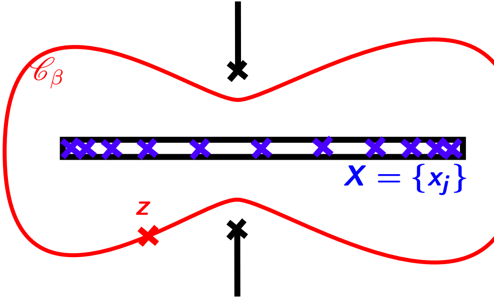
Asymptotically optimal rates:

General $\sigma(\mathcal{H})$ with $\beta < \infty$ or $g > 0$



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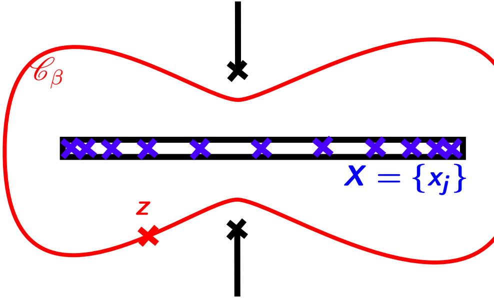

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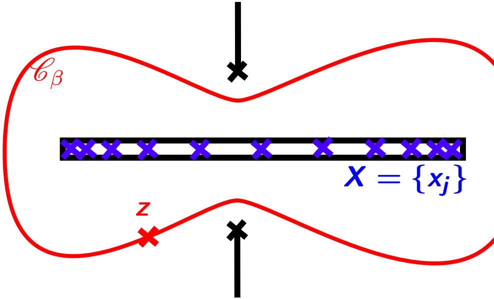

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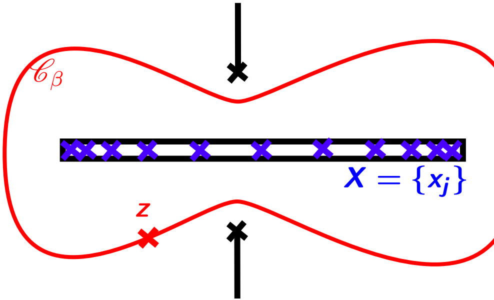

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**Hermite Integral formula**

Let $\mathscr{C}$ contour encircling $X \cup \{x\}$,

$$I_X F(x) - F(x) = \oint_{\mathscr{C}} \frac{\ell(x)}{\ell(z)} \frac{F(z)}{x - z} \frac{\mathrm{d}z}{2\pi i}$$

where $\ell(x) := \prod_{j=0}^N (x - x_j)$ is the *node polynomial*

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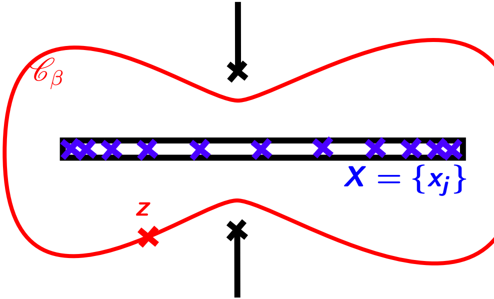

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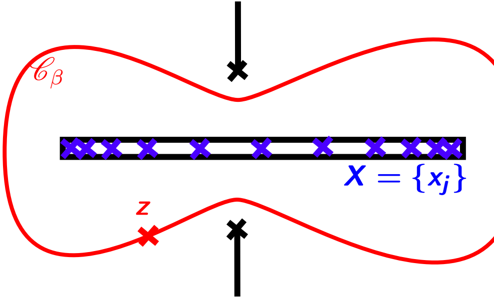


Proof:

$$\ell_j(x) = \prod_{k \neq j} \frac{x - x_k}{x_j - x_k} = \frac{\ell(x)/(x - x_j)}{\prod_{k \neq j}(x_j - x_k)} = \oint_{\mathscr{C}_j} \frac{\ell(x)/(x - z)}{\prod_{k \neq j}(z - x_k)} \frac{1}{z - x_j} \frac{\mathrm{d}z}{2\pi i} = \oint_{\mathscr{C}_j} \frac{\ell(x)}{\ell(z)} \frac{1}{x - z} \frac{\mathrm{d}z}{2\pi i}$$

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For $X = \{x_j\}_{j=0}^N$ with $N < \frac{r_{\ell k}}{m}$

$$\left|F(\mathcal{H})_{\ell k}\right| \leq \min_{P \in \mathcal{P}_n} \left\|F - P\right\|_{L^\infty(\sigma(\mathcal{H}))}$$

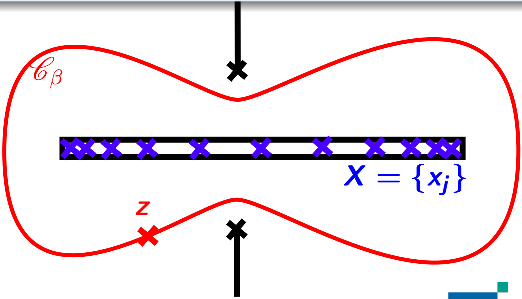
$$\leq \frac{\|F\|_{\mathscr{C}}}{\operatorname{dist}\big(\sigma(\mathcal{H}), \mathscr{C}\big)} \sup_{x \in \sigma(\mathcal{H}), z \in \mathscr{C}} \left|\frac{\ell(x)}{\ell(z)}\right|$$

where $\ell(x) := \prod_{j=0}^N (x - x_j)$

- **Goal:** Understand the asymptotic behaviour of

$$\left|\frac{\ell(x)}{\ell(z)}\right| \qquad \text{as } N \to \infty$$

- How to choose $X$?



# Link to (Logarithmic) Potential Theory

- Define $\nu_N := \frac{1}{N}\sum_{j=0}^N \delta_{x_j}$ and note

$$\log\left[\left|\ell(x)\right|^{\frac{1}{N}}\right] = \frac{1}{N}\sum_j \log\left|x - x_j\right|$$
$$= \int \log|x-t|\,\mathrm{d}\nu_N(t)$$

**Decay rate $\longleftrightarrow$ polynomial approx.**

For $X = \{x_j\}_{j=0}^N$ with $N < \frac{r_{\ell k}}{m}$

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- If $\nu_N \rightharpoonup^\star \nu$, then

$$\lim_{N \to \infty} |\ell(x)|^{\frac{1}{N}} = e^{-U^\nu(x)} \qquad \text{where} \qquad U^\nu(x) := \int \log \frac{1}{|x - t|} \mathrm{d}\nu(t)$$

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For $X = \{x_j\}_{j=0}^N$ with $N < \frac{r_{\ell k}}{m}$

$$\left| F(\mathcal{H})_{\ell k} \right| \lesssim \sup_{x \in \sigma(\mathcal{H}), z \in \mathscr{C}} \left| \frac{\ell(x)}{\ell(z)} \right|$$

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where $\ell(x) := \prod_{j=0}^N (x - x_j)$

- Define $\nu_N := \frac{1}{N}\sum_{j=0}^N \delta_{x_j}$ and note

$$\log\left[\left|\ell(x)\right|^{\frac{1}{N}}\right] = \frac{1}{N}\sum_j \log|x - x_j|$$
$$= \int \log|x - t|\,\mathrm{d}\nu_N(t)$$

- If $\nu_N \rightharpoonup^\star \nu$, then

$$\lim_{N\to\infty} |\ell(x)|^{\frac{1}{N}} = e^{-U^\nu(x)} \qquad \text{where} \qquad U^\nu(x) := \int \log\frac{1}{|x-t|}\mathrm{d}\nu(t)$$

- Decay rate $\longleftrightarrow$ asymptotic rate for polynomial approx.
  $\longleftrightarrow$ behaviour of $\left|\frac{\ell(x)}{\ell(z)}\right|$ for $x \in \sigma(\mathcal{H})$ and $z \in \mathscr{C}$
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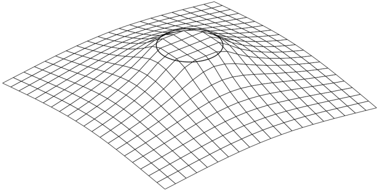

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- $\exists!$ solution to this Green's function problem

# $\Sigma = [-1, 1]$

Define $g_\Sigma(z) := \mathrm{Re}\, G_\Sigma(z)$ where

Conformal mapping problem: $G_{[-1,1]} : \mathbb{C}_+ \to \mathbb{C}$ s.t.

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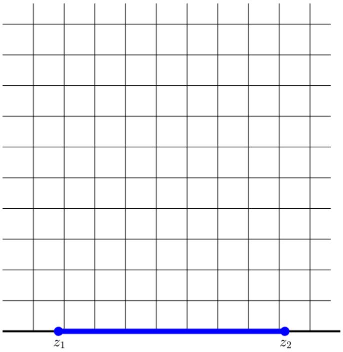


$G_{[-1,1]}$
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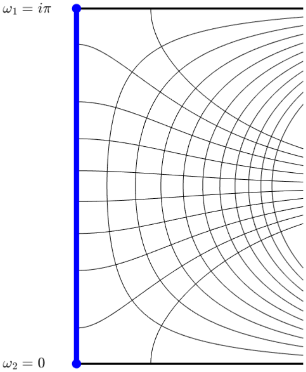

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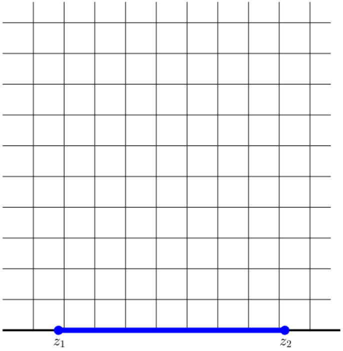
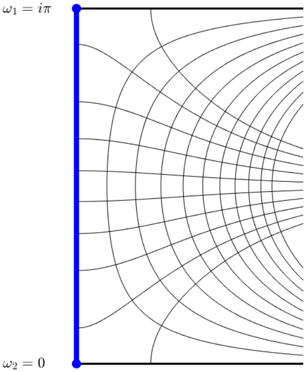



$\xrightarrow{G_{[-1,1]}}$



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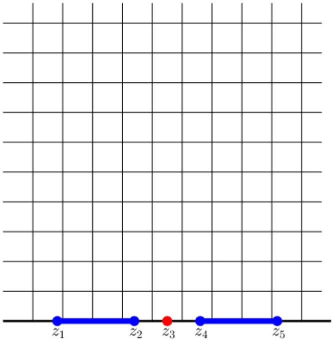


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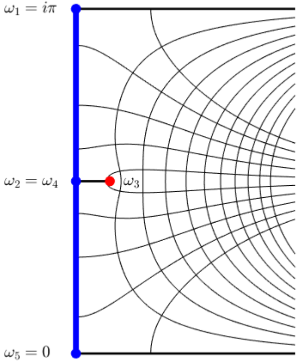

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for some $z_3 \in [a, b]$

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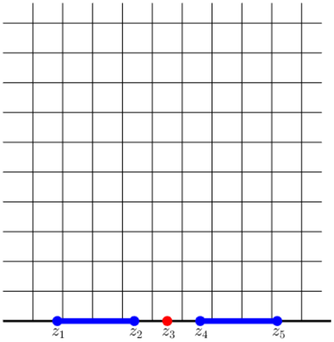


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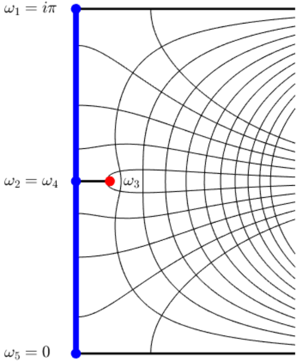

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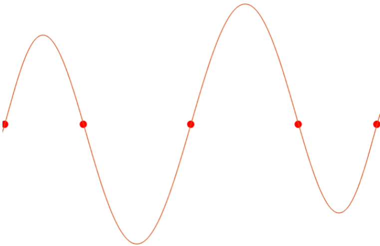

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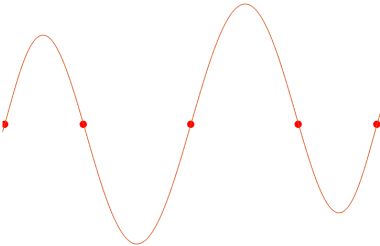

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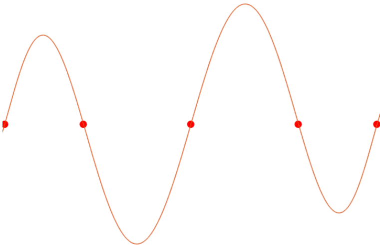

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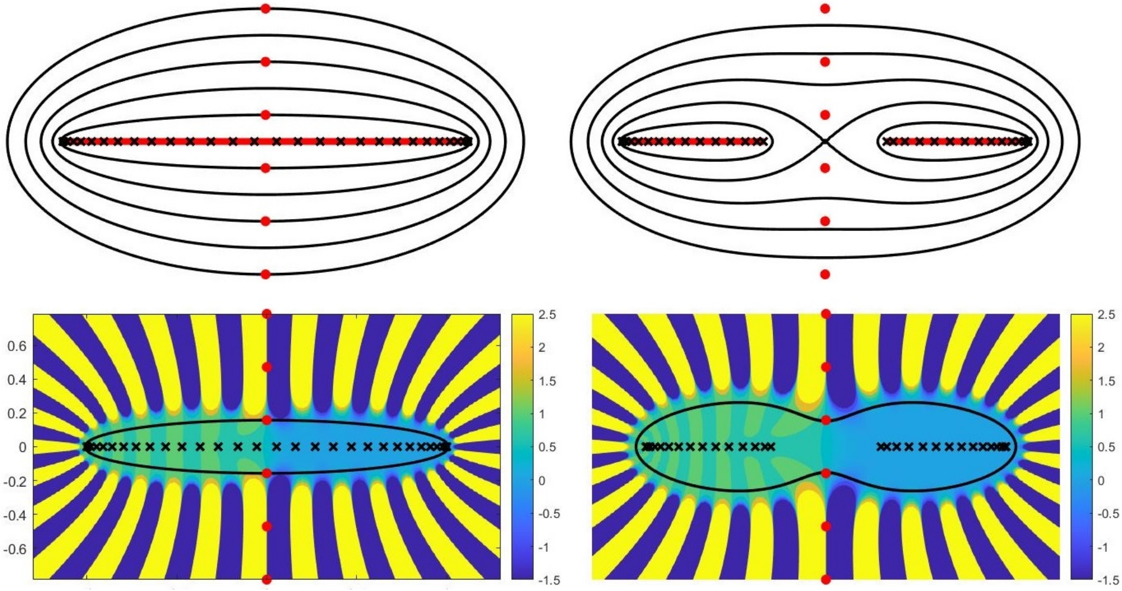
More



# Summary: Density matrices

Banded matrices:

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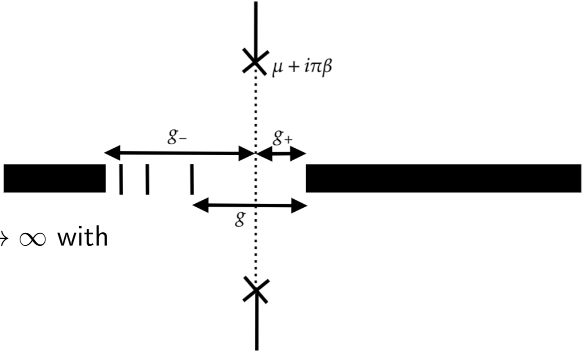

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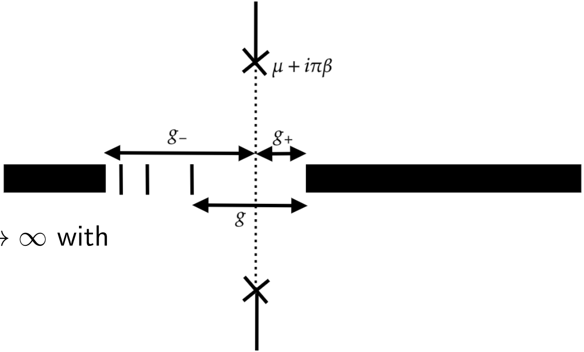


**Remarks:**

- point spectrum
- $g$ vs $\sqrt{g}$?
- banded matrices $\rightsquigarrow$ exponential decay (Combes–Thomas)

# Outline

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TABLE I. Quantities used for determination of the functions and their fitted values: lattice parameter $a_0$; elastic constants $C_{11}$, $C_{12}$, and $C_{44}$; sublimation energy $E_s$; vacancy formation energy $E_{1V}^F$; the energy difference between bcc and fcc phases for Ni; and the hydrogen heat of solution and migration energy in Ni.

| | Experiment | Fit |
|---|---|---|
| $a_0$(Å) | 3.52[a] | 3.52 |
| $C_{11}$ ($10^{12}$ dynes/cm$^2$) | 2.465[b] | 2.452 |
| $C_{12}$ ($10^{12}$ dynes/cm$^2$) | 1.473[b] | 1.452 |
| $C_{44}$ ($10^{12}$ dynes/cm$^2$) | 1.247[b] | 1.233 |
| $E_s$ (eV) | 4.45[c] | 4.45 |
| $E_{1V}^F$ (eV) | 1.4[d] | 1.43 |
| ($E_{bcc}-E_{fcc}$) (eV) | 0.06[e] | 0.14 |
| H heat of solution (eV) | 0.16[f] | 0.22 |
| H migration energy (eV) | 0.41[g] | 0.41 |

[a] Ref. 13.
[b] Ref. 14.
[c] Ref. 15.
[d] Ref. 16.
[e] Ref. 17.
[f] Ref. 18.
[g] Ref. 19.

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Overall, the most satisfactory parameter set thus far discovered is the following:

$$A = 7.049\,556\,277\,, \quad B = 0.602\,224\,558\,4\,,$$
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$$\lambda = 21.0\,, \quad \gamma = 1.20\,.$$

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**Not systematically improvable...**

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$$\lambda = 21.0\,, \quad \gamma = 1.20\,.$$

# Classical Interatomic Potentials: $E(\boldsymbol{r}) = \sum_\ell E_\ell\big(\{\boldsymbol{r}_{\ell k}\}_{r_{\ell k} < r_{\rm cut}}\big)$

Embedded Atom Method (EAM):

$$E_\ell(\boldsymbol{r}) = F\Big(\sum_{k \neq \ell} \rho(r_{\ell k})\Big) + \frac{1}{2} \sum_{k \neq \ell} \phi(r_{\ell k})$$

Daw, Baskes. Phys. Rev. Lett. 50 (1983)
Daw, Baskes. Phys. Rev. B 29 (1984)

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Stillinger, Weber. Phys. Rev. B 31 (1985)

**Not systematically improvable...**

Machine Learning:

$$E_\ell(\boldsymbol{r}) = E_\ell(\boldsymbol{r}; \boldsymbol{\theta})$$

universal approximator

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kernel method

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symmetric polynomials

Behler, Parrinello. Phys. Rev. Lett. 98 (2007)
Bartok, Kondor, Csanyi. Phys. Rev. Lett. 104 (2010)
Braams, Bowman. Int. Rev. Phys. Chem. 28 (2009)
Shapeev. Multiscale Model. Simul., 14 (2016)

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Atomic cluster expansion (ACE)

Behler, Parrinello. Phys. Rev. Lett. 98 (2007)
Bartok, Kondor, Csanyi. Phys. Rev. Lett. 104 (2010)
Braams, Bowman. Int. Rev. Phys. Chem. 28 (2009)
Shapeev. Multiscale Model. Simul., 14 (2016)
Drautz. Phys. Rev. B 100 (2019)
Bachmayr *et al.* J. Comp. Phys. 454 (2022)

# Locality: Spatial Decomposition

**Interatomic potentials**

$$E(\boldsymbol{r}) = \sum_{\ell} \varepsilon\left(\boldsymbol{\theta}; \{\boldsymbol{r}_{\ell k}\}_{k \neq \ell}\right)$$

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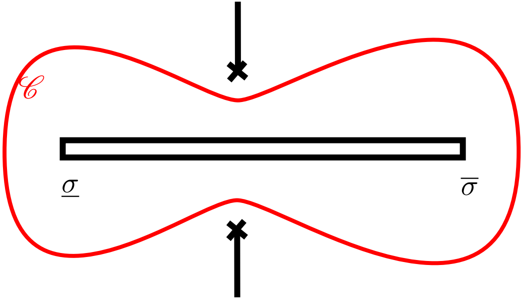

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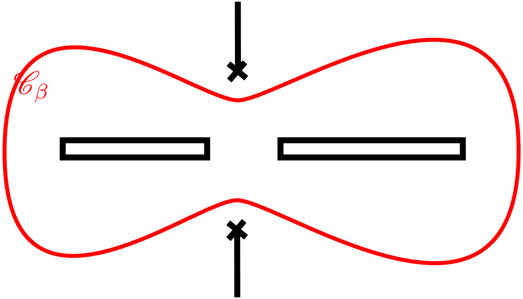

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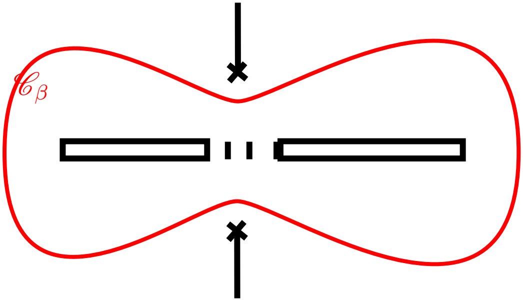

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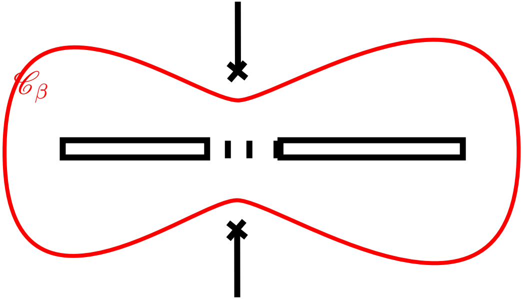

# Locality: Spatial Decomposition

**Tight-binding**

$$E(\boldsymbol{r}) = \sum_{\ell} \left[\mathcal{H} F(\mathcal{H})\right]_{\ell\ell} = \sum_{\ell} E_{\ell}(\boldsymbol{r})$$

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Numerics

$\eta > 0$ depends on:

- locality of $\mathcal{H}$,
- analyticity of $z \mapsto zF(z)$,
- spectrum $\sigma(\mathcal{H})$.

**Interatomic potentials**

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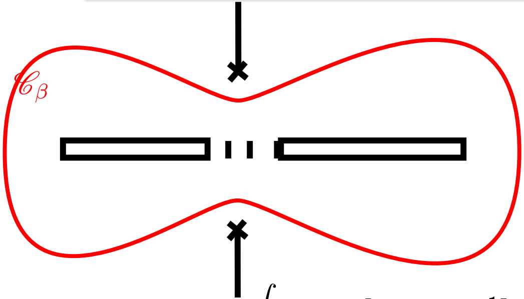


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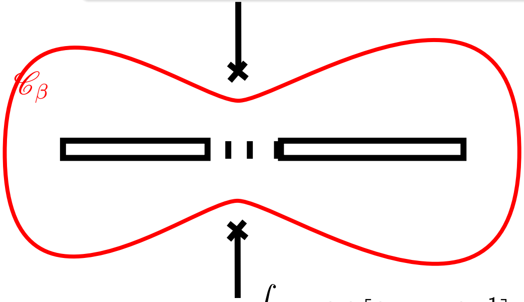


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[Chen, Ortner. Multiscale Model. Simul., 2016]
[Chen, Lu, Ortner. Arch. Rat. Mech. An., 2018]
[Ortner, JT, Chen. ESAIM: M2AN, 2020] - estimates for point defects

# "Proof": Locality Estimates

**Theorem:**

$$\left| \frac{\partial E_\ell(\boldsymbol{r})}{\partial \boldsymbol{r}_k} \right| \leq C e^{-\eta\, r_{\ell k}}$$

$\eta > 0$ depends on:

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## "Proof": Locality Estimates

$$\frac{\partial E_\ell(\boldsymbol{r})}{\partial \boldsymbol{r}_k} = \oint_{\mathscr{C}} zF(z)\Big[(z-\mathcal{H})^{-1}\frac{\partial \mathcal{H}(\boldsymbol{r})}{\partial \boldsymbol{r}_k}(z-\mathcal{H})^{-1}\Big]_{\ell\ell}\frac{\mathrm{d}z}{2\pi i}$$

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**Resolvent Estimates: Sketch for $m$-banded Hamiltonians**

Same argument as before: for $mN < r_{\ell k}$,

$$\begin{aligned}\left|(z-\mathcal{H})^{-1}_{\ell k}\right| &= \min_{P_N\in\mathcal{P}_N}\left|\left[(z-\mathcal{H})^{-1} - P_N(\mathcal{H})\right]_{\ell k}\right| \\ &\leq \min_{P_N\in\mathcal{P}_N}\left\|(z-\cdot\,)^{-1} - P_N\right\|_{L^\infty(\sigma(\mathcal{H}))} \\ &\lesssim e^{-\frac{\gamma}{m}r_{\ell k}}\end{aligned}$$

where $\gamma \sim \mathrm{dist}(z, \sigma(\mathcal{H}))$.

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# Outline

# Body-ordered approximations

**Interatomic potentials**

$$E(\boldsymbol{r}) = \sum_{\ell} E_\ell(\boldsymbol{r}; \boldsymbol{\theta})$$

$E_\ell$ - short-ranged & "simple"

More details

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$$E_\ell(\boldsymbol{r}) \approx V_0 + \sum_{k\neq\ell} V_1(\boldsymbol{r}_{\ell k}) + \sum_{k_1,k_2\neq\ell} V_2(\boldsymbol{r}_{\ell k_1},\boldsymbol{r}_{\ell k_2}) + \cdots + \sum_{k_1,\ldots,k_N\neq\ell} V_N(\boldsymbol{r}_{\ell k_1},\ldots,\boldsymbol{r}_{\ell k_N})$$

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*"In view of the fact that the Si crystal consists of atoms held in place by strong and directional bonds, it seems reasonable at first sight that the corresponding $\Phi$ could be approximated by a combination of pair and triplet potentials, $V_1$ and $V_2$."*
— Stillinger, Weber. Phys. Rev. B 31 (1985)

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> *“In this so-called many-body expansion of Φ, it is usually believed that the series has a quick convergence, therefore, the higher moments may be neglected.”*
>
> — Haliciogli, Pamuk, Erkoc. Phys Status Solidi B 149 (1988)

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*"...the many-body potentials in general exhibit a rather slow convergence."*

*"It is sometimes argued that a potential expansion converges only slowly with respect to the order of the potentials and is thus impractical for use in molecular dynamics simulations."*

— Drautz, Fähnle, Sanchez. J. Phys. Condens. Matter 16 (2004)

More details

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*"The convergence of the expansion is slow and, for example, for bulk metals potentials $V_K$ up to $K \geq 15$ are required."*
— Drautz. Phys. Rev. B 99 (2019)

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Based on the vacuum cluster expansion
"Incorporating environment information leads to exponential convergence" $\implies$ replace $V_n$ with $V_{nN}$

More details

# Body-ordered approximations $\varepsilon(x) := xF(x)$

**Main idea**: Polynomials are body-ordered:

$$[\mathcal{H}^n]_{\ell\ell} = \sum_{\ell_1,\dots,\ell_{n-1}} \mathcal{H}_{\ell\ell_1}\mathcal{H}_{\ell_1\ell_2}\dots\mathcal{H}_{\ell_{n-1}\ell}$$

*[“spatial correlations”, “moments”* $(\mathcal{H}^n)_{\ell\ell} = \int x^n \mathrm{d}D_\ell(x)$*]*

**Recall**

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**Recall**

$E_\ell = \varepsilon(\mathcal{H})_{\ell\ell} = \int \varepsilon \,\mathrm{d}D_\ell$

**Suppose** $\varepsilon \approx \varepsilon_N$ where $\varepsilon_N \in \mathcal{P}_N$,
**Then,** $E_\ell^N := \varepsilon_N(\mathcal{H})_{\ell\ell}$
is a body-ordered
approximation to $E_\ell$

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*["spatial correlations", "moments" $(\mathcal{H}^n)_{\ell\ell} = \int x^n \mathrm{d}D_\ell(x)$]*

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$E_\ell = \varepsilon(\mathcal{H})_{\ell\ell} = \int \varepsilon \,\mathrm{d}D_\ell$

**Suppose** $\varepsilon \approx \varepsilon_N$ where $\varepsilon_N \in \mathcal{P}_N$,
**Then,** $E_\ell^N := \varepsilon_N(\mathcal{H})_{\ell\ell}$
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**Claim:**

Proof

$$\left|E_\ell - E_\ell^N\right| \leq \sup_{z\in\sigma(\mathcal{H})} |\varepsilon(z) - \varepsilon_N(z)|$$

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**Example: Kernel Polynomial Method**

Suppose $\varepsilon(x) = \sum_{n=0}^\infty c_n P_n(x)$ with $\int P_n P_m M \mathrm{d}x = \delta_{nm}$,

$$E_\ell(x) \approx \int K_N \star \varepsilon \,\mathrm{d}D_\ell = \iint K_N(x,y)\varepsilon(y)\,\mathrm{d}y\,\mathrm{d}D_\ell(x)$$

$$\text{where} \quad K_N(x,y) := M(y)\sum_{n=0}^N P_n(x)P_m(y)$$

**Then,** $E_\ell^N = \sum_{n=0}^N c_n P_n(\mathcal{H})_{\ell\ell}$
[Silver *et al.* J. Comp. Phys. 124 (1996)]

**Theorem (JT, Chen, Ortner (2022))**

*There exists a linear* $\Theta_N\colon \mathbb{R}^N \to \mathbb{R}$ *such that*

$$\left|E_\ell(\boldsymbol{r}) - \Theta_N\big(\mathcal{H}_{\ell\ell}, \dots, [\mathcal{H}^N]_{\ell\ell}\big)\right| \leq Ce^{-\gamma_N N}$$

*where* $\lim_{N\to\infty} \gamma_N = \gamma > 0$*, and* $\gamma \sim \beta^{-1} + \sqrt{g_-}\sqrt{g_+}$.

*However,*

- *Different* $\Theta_N$ *for different phases of the material*
- *Isolated eigenvalues in the gap affect the convergence rate*

[Here, $\Theta_N\big(\mathcal{H}_{\ell\ell}, \dots, [\mathcal{H}^N]_{\ell\ell}\big)$ is body-ordered]

**Before:** choose nodes $X = \{x_j\}_{j=0}^N$ and $\varepsilon_N := I_X \varepsilon$:

$$E_\ell^N := \varepsilon_N(\mathcal{H})_{\ell\ell} = \int \varepsilon_N(x) \, \mathrm{d}D_\ell(x) = \int I_X\varepsilon(x) \, \mathrm{d}D_\ell(x) = \textstyle\sum_{j=0}^N \ell_j(\mathcal{H})_{\ell\ell} \, \varepsilon(x_j)$$

$$= \int \varepsilon \, \mathrm{d}D_\ell^N \qquad \text{where} \qquad D_\ell^N := \textstyle\sum_{j=0}^N \omega_j \, \delta(\,\cdot\, - x_j).$$

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**"Method of moments":** Choose $D_\ell^N := \Theta_N\big(\mathcal{H}_{\ell\ell}, \dots, [\mathcal{H}^N]_{\ell\ell}\big)$:

$$[\mathcal{H}^n]_{\ell\ell} = \int x^n \mathrm{d}D_\ell^N \qquad \text{for all } n = 0, 1, \dots, N$$
$$E_\ell^N := \int \varepsilon(x)\,\mathrm{d}D_\ell^N(x)$$

# Nonlinear schemes: Error estimates $E_\ell = \varepsilon(\mathcal{H})_{\ell\ell} = \int \varepsilon \, \mathrm{d}D_\ell$

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$$\begin{aligned}\left|E_\ell(\boldsymbol{r}) - E_\ell^N(\boldsymbol{r})\right| &= \min_{\varepsilon_N \in \mathcal{P}_N} \left| \int (\varepsilon - \varepsilon_N) \mathrm{d}\big(D_\ell - D_\ell^N\big) \right| \\ &\leq \|D_\ell - D_\ell^N\|_{\mathrm{TV}} \min_{\varepsilon_N \in \mathcal{P}_N} \left\|\varepsilon - \varepsilon_N\right\|_{L^\infty(\sigma(\mathcal{H}) \cup \mathrm{supp}(D_\ell^N))}\end{aligned}$$

[$\mathcal{P}_N$ = polynomials degree $N$]

## $E_\ell = \Theta_N(\mathcal{H}_{\ell\ell}, \dots, [\mathcal{H}^N]_{\ell\ell})$

**Linear schemes:**

- Chebyshev projection
  $\longrightarrow$ Kernel polynomial method[1]
- Newton–Cotes quadrature (equispaced nodes)
- Clenshaw–Curtis quadrature (Chebyshev nodes)
- General quadrature (with $\nu_N \rightharpoonup^\star \omega_\Sigma$)

**Nonlinear schemes:**

- Maximum entropy method[2] More
- Recursion method[3]: spectral measure corresponding to truncated tridiagonalisation of $\mathcal{H}$ More
  $\longrightarrow$ bond order potentials[4]
- Gauss quadrature More
  $\longrightarrow$ linear-scaling spectral Gauss quadrature[5]

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[1] [Silver, Roeder, Voter, Kress. J. Comput. Phys. 124 (1996)]
[2] [Mead, Papanicolaou. J. Math. Phys. 25 (1984)]
[3] [Haydock, Heine, Kelly. J. Phys. C 5 (1972), 8 (1975)]
[4] [Horsfield *et al.* Phys. Rev. B 53 (1996)]
[5] [Suryanarayana *et al.* J. Mech. Phys. Solids 61 (2013)]

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*where* $\lim_{N\to\infty} \gamma_N = \gamma > 0$, *and* $\gamma \sim g_{\mathrm{def}} + \beta^{-1}$.

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Numerics

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**Theorem (JT, Chen, Ortner (2022))**

*Fix N odd. There exist* $U \subset \mathbb{C}^N$ *and an analytic function* $\Theta_N\colon U \to \mathbb{C}$ *such that*

$$\left|E_\ell(\boldsymbol{r}) - \Theta_N\big(\mathcal{H}_{\ell\ell}, \dots, [\mathcal{H}^N]_{\ell\ell}\big)\right| \leq Ce^{-\eta_N N}$$

*where* $\lim_{N\to\infty} \eta_N = \eta > 0$, *and* $\eta \sim g + \beta^{-1}$.

*Now,*

- $\Theta_N$ *is a "universal" nonlinearity*
- *Eigenvalues in the gap* **do not** *affect the convergence rates*

However,

- Different $\Theta_N$ for different phases of the material
- Eigenvalues in the gap affect the convergence rate

Numerics

# Outline

# Conclusions

- $E(\boldsymbol{r}) = \sum_\ell E_\ell(\boldsymbol{r})$
  - Local pieces $\longrightarrow$ transferability
  - QM/MM schemes: size of the QM region $\sim \eta$

    *[e.g. Chen, Ortner. Multiscale Model. Simul., 2016]*
  - Thermodynamic limit problems

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- $E_\ell(\boldsymbol{r}) \approx \sum_{n=0}^{N} \sum_{\ell_1,\dots,\ell_n \neq \ell} V_{nN}\big(\boldsymbol{r}_{\ell\ell_1}, \dots, \boldsymbol{r}_{\ell\ell_n}\big)$,
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  - e.g. Linear Atomic Cluster Expansion (ACE)
- There exists $\Theta_N$ "universal" with

$$E_\ell(\boldsymbol{r}) \approx \Theta_N\big(\phi_1, \dots, \phi_N\big)$$

  where $\phi_n$ are linear body-ordered.
  - Nonlinear ACE

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*Body-Ordered Approximations of Atomic Properties*

Jack Thomas, Huajie Chen & Christoph Ortner

Also in the paper:

- Classical vacuum cluster expansion
  *[reasons for slow convergence]*
- Analysis of bond-order potentials (BOP),
  *[Recursion method with possibly different terminators]*
- (partial) Justification for linear-scaling spectral Gauss quadrature,
  *[Approximation of $\rho = F\big(\mathcal{H}[\rho]\big)$ with $\rho_N = F_N\big(\mathcal{H}[\rho_N]\big)$]*
- Truncation operators and connection to divide-and-conquer methods

# What we couldn't prove (yet?):

- Forces converge in the linear schemes

$$\left|\frac{\partial E_\ell}{\partial \boldsymbol{r}_k} - \frac{\partial E_\ell^N}{\partial \boldsymbol{r}_k}\right| \lesssim e^{-\gamma r_{\ell k}} e^{-\eta N}$$

- **But**, this is a lot less obvious in the nonlinear schemes
- True if $D_\ell$ has *"regular $n^{th}$ root asymptotic behaviour'*:

$$\lim_{n\to\infty} \left|p_n(z; D_\ell)\right|^{\frac{1}{n}} = e^{g_{\mathrm{supp}\, D_\ell}(z)}$$

locally uniformly on $\mathbb{C} \setminus \mathrm{conv}\,\mathrm{supp}\, D_\ell$

- "Proof"

$$\left|\frac{\partial E_\ell}{\partial \boldsymbol{r}_k} - \frac{\partial E_\ell^N}{\partial \boldsymbol{r}_k}\right| \lesssim \left[\sum_{n=0}^{\infty} \sum_{l=0}^{n} \|p_l\|^2_{L^\infty(\mathscr{C})} e^{-\eta_1 n}\right] e^{-\eta_2 N} e^{-\gamma\, r_{\ell k}}$$

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# $\Sigma = [-1, a] \cup [b, 1]$

Define $g_\Sigma(z) := \mathrm{Re}\, G_\Sigma(z)$ where

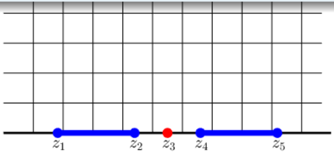
## Green's function problem

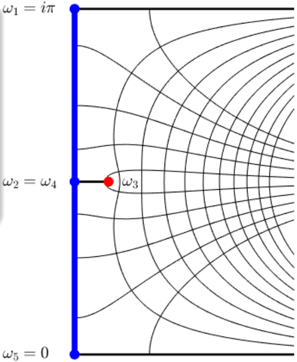
Find $g_\Sigma$ s.t.

- $\Delta g_\Sigma = 0$ on $\mathbb{C} \setminus \Sigma$,
- $g_\Sigma(z) \sim \log|z|$ as $z \to \infty$,
- $g_\Sigma = 0$ on $\Sigma$.

## $z_3 \in [a, b]$ s.t. $G_\Sigma(a) = G_\Sigma(b)$

$$z_3 = \frac{\displaystyle\int_a^b \frac{\zeta}{\sqrt{\zeta+1}\sqrt{\zeta-a}\sqrt{\zeta-b}\sqrt{\zeta-1}}\mathrm{d}\zeta}{\displaystyle\int_a^b \frac{1}{\sqrt{\zeta+1}\sqrt{\zeta-a}\sqrt{\zeta-b}\sqrt{\zeta-1}}\mathrm{d}\zeta}$$



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for some $z_3 \in [a, b]$

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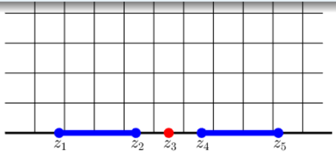


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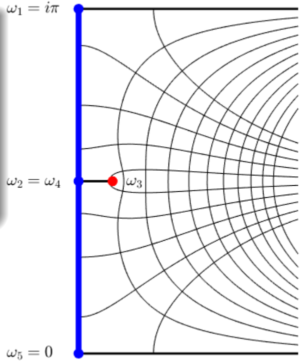
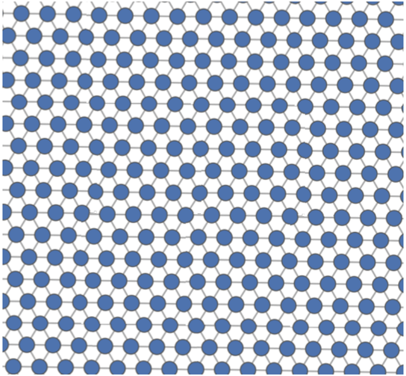
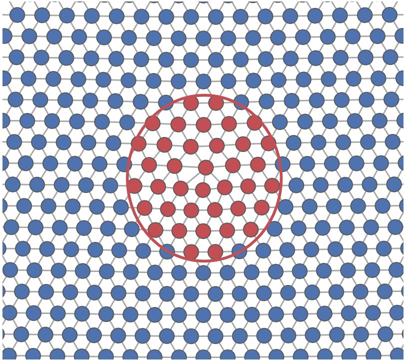


# Spectrum of the Hamiltonian

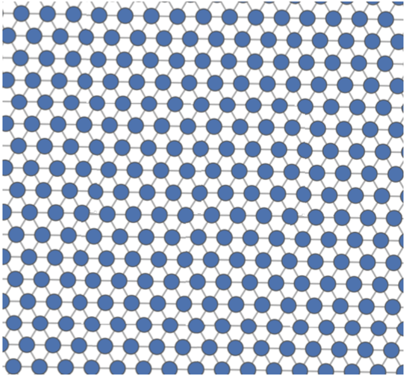
$\boldsymbol{r} =$ 

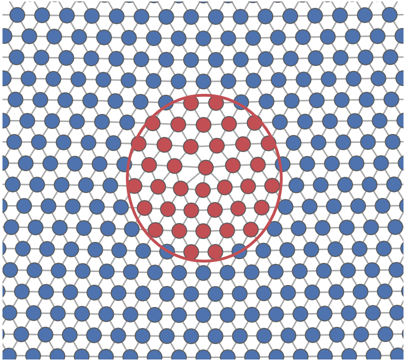
$\boldsymbol{r}^{\text{def}} =$ 

# Spectrum of the Hamiltonian

$$\{\ell \colon |\boldsymbol{r}_\ell^{\mathrm{def}}| \le R_{\mathrm{def}}\} \quad \text{finite}$$

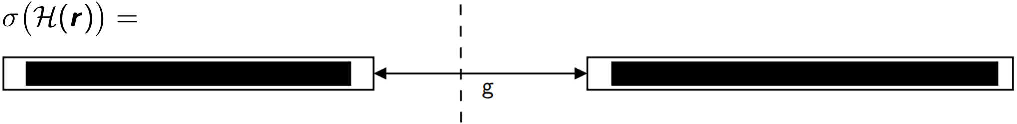
$$\sup_{\ell \colon |\boldsymbol{r}_\ell| > R_{\mathrm{def}}} |\boldsymbol{r}_\ell^{\mathrm{def}} - \boldsymbol{r}_\ell| \le \delta$$

$\boldsymbol{r} =$ 

$\boldsymbol{r}^{\mathrm{def}} =$ 

# Spectrum of the Hamiltonian: Insulators

$$\sigma\big(\mathcal{H}(\boldsymbol{r})\big) =$$

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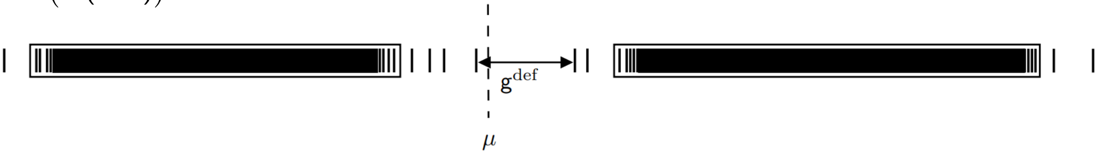

# Spectrum of the Hamiltonian: Insulators

**Locality:**

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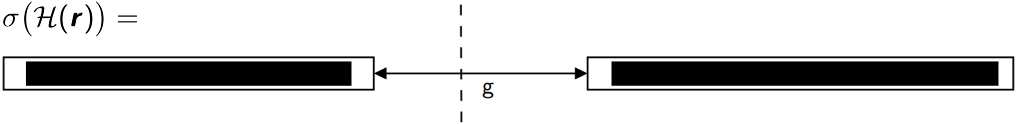
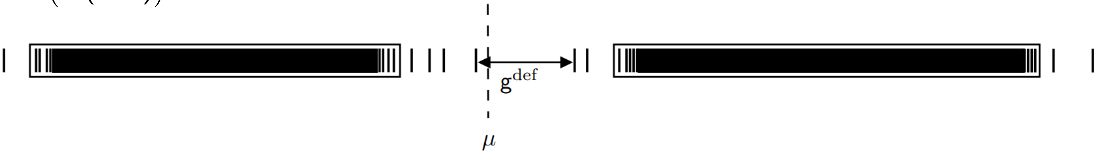



Back

$$\sigma\big(\mathcal{H}(\boldsymbol{r}^{\mathrm{def}})\big) =$$



# Spectrum of the Hamiltonian: Insulators

**Locality:**

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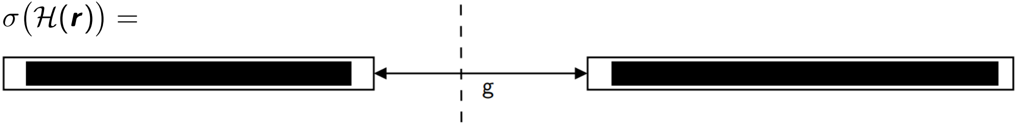


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Back

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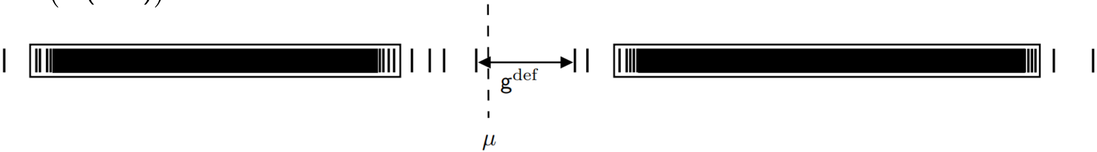

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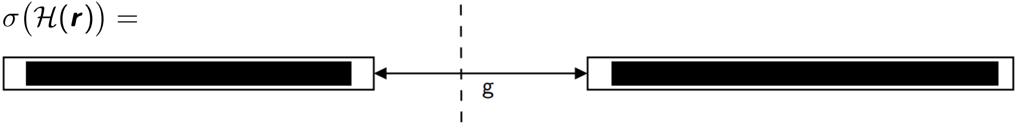


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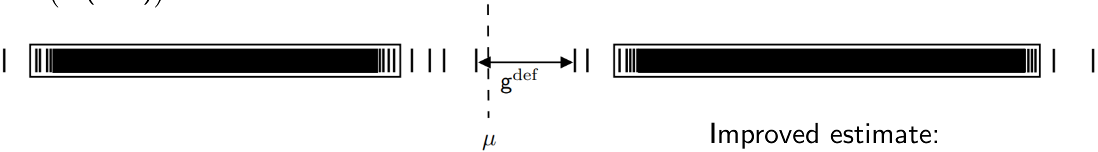


Improved estimate:

$\eta \sim \mathrm{g} \gg \mathrm{g}^{\mathrm{def}}$

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# Green's Functions for Multiply Connected Domains via Conformal Mapping*

Mark Embree[†]
Lloyd N. Trefethen[†]

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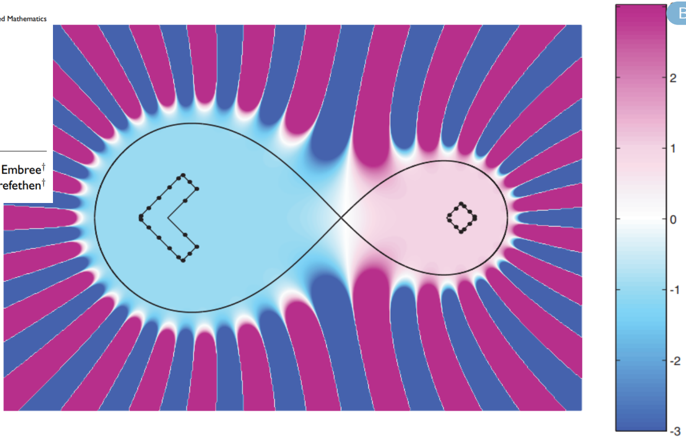


**Fig. 8** *Illustration of the overconvergence phenomenon of Theorem 2(b) and Theorem 4. On the same two-polygon region as in Figure 3, a polynomial $p(z)$ is sought that approximates the values $-1$ on the hexagon and $+1$ on the square. For this figure, $p$ is taken as the degree-29 near-best approximation defined by interpolation in 30 pre-images of roots of unity in the unit circle under the conformal map $z = \Phi^{-1}(w)$ (eqs. (8) and (9)); a similar plot for the exactly optimal polynomial would not look much different. The figure shows* $\mathrm{Re}\,p(z)$ *by a blue-red color scale together with the polygons, the interpolation points, and the figure-8-shaped critical level curve of the Green's function. Not just on the polygons themselves, but throughout the two lobes of the figure-8,* $\mathrm{Re}\,p(z)$ *comes close to the constant values* $-1$ *and* $+1$. *Outside, it grows very fast.*

# Vacuum cluster expansion

$E\colon \bigcup_{J=0}^{\infty} \left\{ \{ \boldsymbol{r}_1, \ldots, \boldsymbol{r}_J \} \subset \mathbb{R}^3 \right\} \to \mathbb{R}$

Back

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V_N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) &= \sum_{K \subseteq \{\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N\}} (-1)^{N-|K|} E(K)
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Exact for $N = J$.

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Convergence? Rate of convergence? Not clear!

*"An intuitive explanation for this slow convergence is that we are building an interaction law for a condensed or possibly even crystalline phase material from clusters in vacuum where the bonding chemistry is significantly different."*

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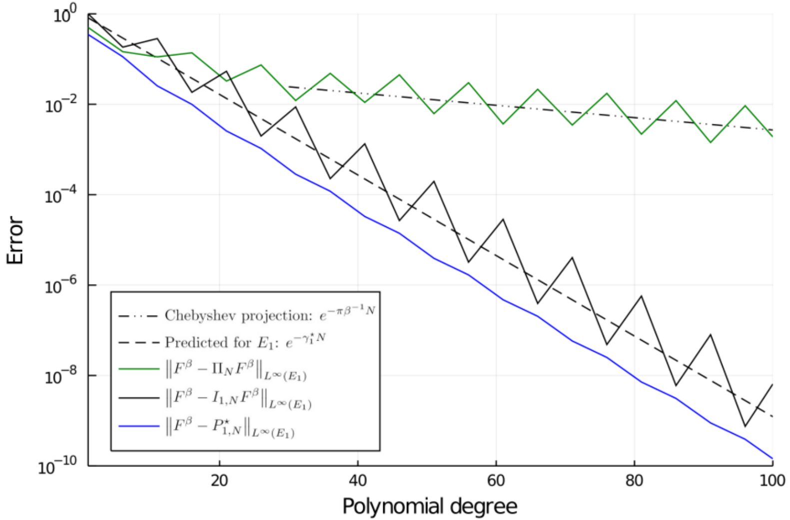
**Instead:**

Replace $V_n$ with $V_{nN}$

*"An intuitive explanation for this slow convergence is that we are building an interaction law for a condensed or possibly even crystalline phase material from clusters in vacuum where the bonding chemistry is significantly different."*

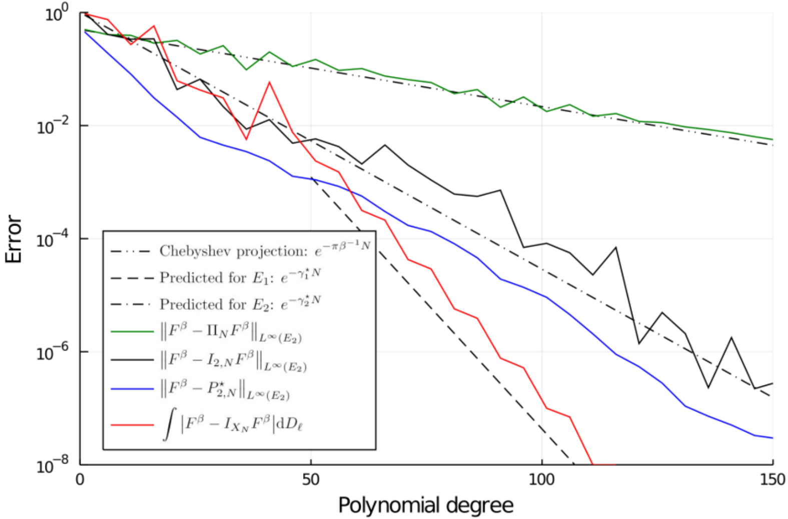
# Numerical experiments: “defect-free”

- Approximation domain $E_1 = [-1, -0.2] \cup [0.2, 1]$



# Numerical experiments: with defect

- Approximation domain $E_2 = E_1 \cup [-0.06, -0.03]$

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# Maximum entropy method

- Fix $[a, b] \supset \sigma(\mathcal{H})$, maximise

$$S(P) := -\int_a^b \big[P(x)\log P(x) - P(x)\big]\mathrm{d}x + \sum_{n=0}^{N} \lambda_n \Big( \int_a^b x^n P(x)\mathrm{d}x - [\mathcal{H}^n]_{\ell\ell} \Big)$$

- Leads to

$$P_N(x) = e^{-\sum_{n=0}^{N} \lambda_n x^n} \qquad \text{s.t. first } N \text{ moments}$$

- Moreover, if $\{(\mathcal{H}^n)_{\ell\ell}\}$ is completely monotone, then $\exists! P$.

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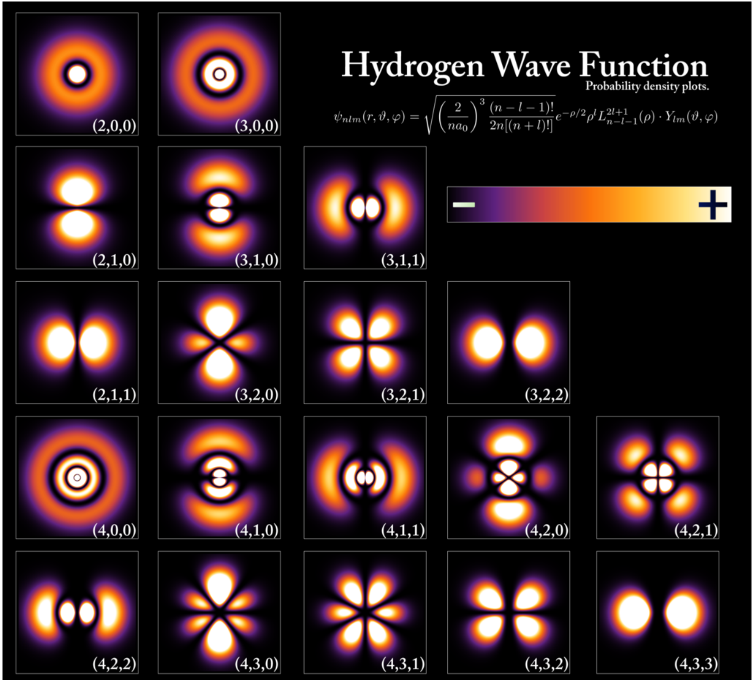
Hydrogen Wave Function
Probability density plots.
$\psi_{nlm}(r,\vartheta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) \cdot Y_{lm}(\vartheta,\varphi)$
(2,0,0)
(3,0,0)
(2,1,0)
(3,1,0)
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Back

# Nonlinear schemes: Recursion method

- Let $\{p_n\}$ orthogonal polynomials with respect to $D_\ell$:

$$b_{n+1}p_{n+1}(x) = (x - a_n)p_n(x) - b_n p_{n-1}(x) \qquad \text{[Lanczos recursion]}$$

define

$$T_N := \begin{pmatrix} a_0 & b_1 & & \\ b_1 & a_1 & \ddots & \\ & \ddots & \ddots & b_N \\ & & b_N & a_N \end{pmatrix} = \Big( \int p_i(x) x p_j(x) \mathrm{d}D_\ell(x) \Big)_{0 \le i,j \le N},$$

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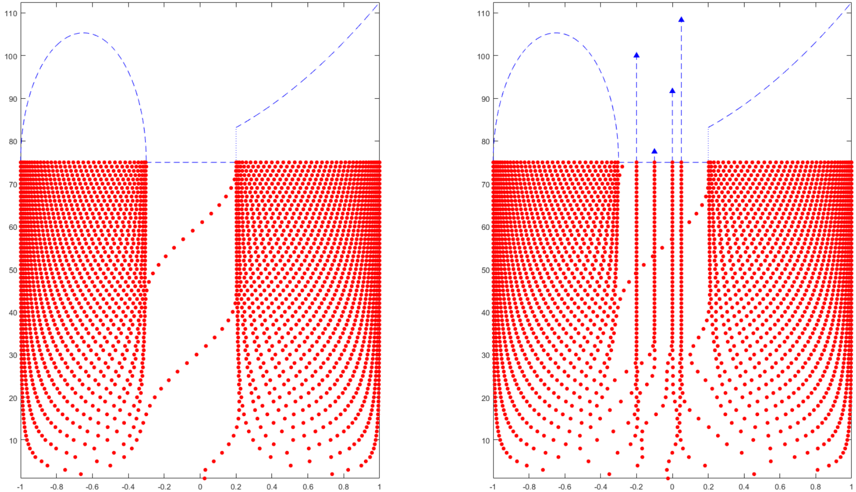


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supp$(D_\ell^N)$ "nice enough"

- Can show that $E_\ell^N = \Theta\big(\mathcal{H}_{\ell\ell}, \dots, (\mathcal{H}^{2N+1})_{\ell\ell}\big)$ where $\Theta\colon \mathbb{C}^{2N+1} \to \mathbb{C}$ is analytic in open neighbourhoods of "admissible moment sequences"

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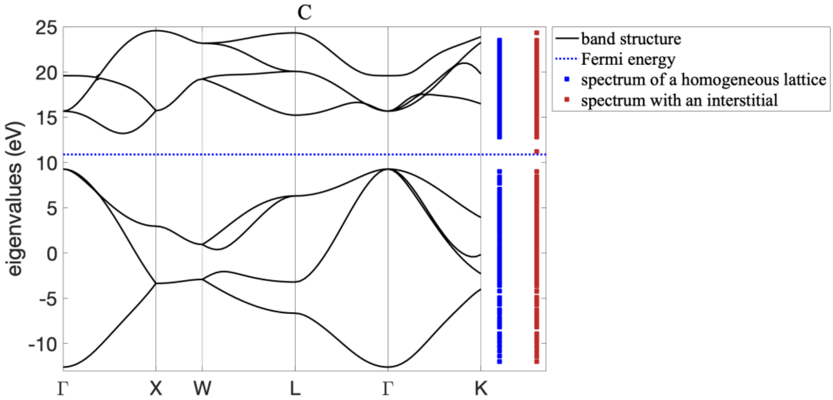
# Numerical Experiments




*[Ortner, JT, Chen. ESAIM: M2AN, 2020]*

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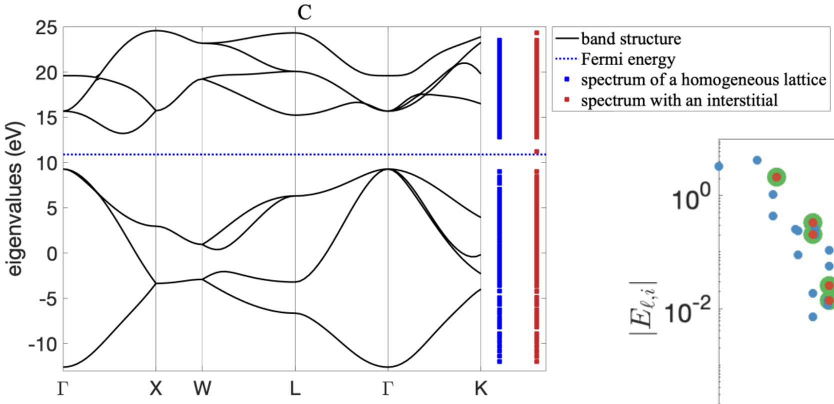


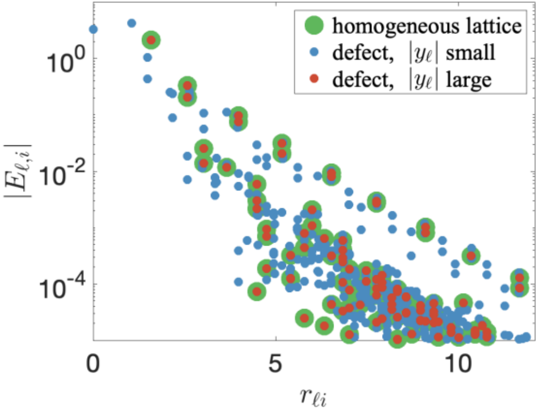


(a) Decay of site energy derivatives.

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[Ortner, JT, Chen. ESAIM: M2AN, 2020]

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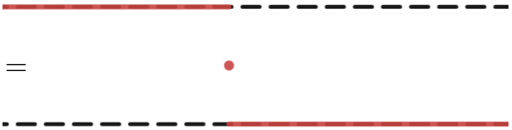

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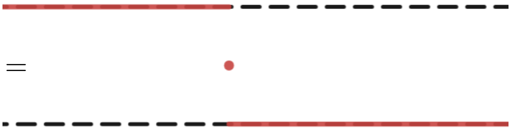

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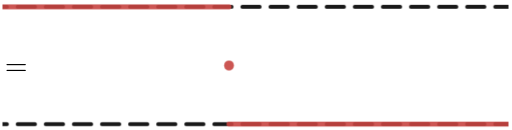

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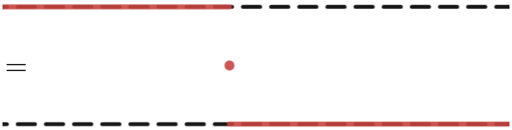
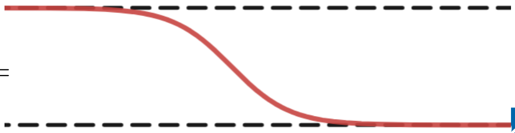
- Energy

$$E^{KS}[\rho] = \sum_n F(\lambda_n)\lambda_n + \dots$$

$F =$ 

$F^\beta =$ 

# DFT

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- Schrödinger eq. $\rightsquigarrow$ *Kohn–Sham equations*

$$\mathcal{H}^{\mathrm{KS}}\psi_n := \left(-\frac{1}{2}\Delta + V_{\mathrm{eff}}(x;\rho)\right)\psi_n(x) = \lambda_n\psi_n(x), \qquad \rho(x) = \sum_n F(\lambda_n)\left|\psi_n(x)\right|^2$$

$$V_{\mathrm{eff}}(x;\rho) := \int \frac{\rho(y)}{|x-y|}\mathrm{d}y - \sum_m \frac{Z_m}{|x-\boldsymbol{r}_m|} + V_{\mathrm{xc}}(x;\rho),$$

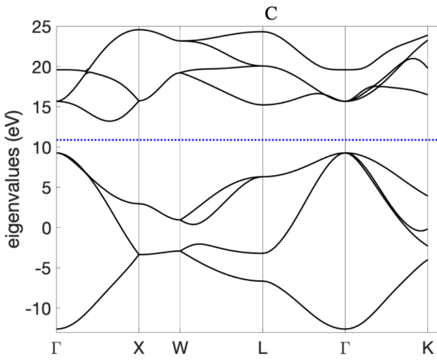
- Energy

$$E^{KS}[\rho] = \sum_n \lambda_n F(\lambda_n) - \int \rho(x) V_{\mathrm{eff}}(x;\rho)$$
$$+ E_{\mathrm{xc}}[\rho] + \frac{1}{2}\int\int \frac{\rho(x)\rho(y)}{|x-y|}\mathrm{d}x\mathrm{d}y - \sum_m Z_m \int \frac{\rho(x)}{|x-\boldsymbol{r}_m|}\mathrm{d}x + E_{ZZ}$$

# Aside: Metals at zero temperature

Periodic systems:

$$F(\mathcal{H})_{ij} = \sum_n \int_{\boldsymbol{k}\in\mathcal{B}} F(\varepsilon_{n,\boldsymbol{k}})[u^\star_{n,\boldsymbol{k}}]_i [u_{n,\boldsymbol{k}}]_j e^{-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)} \mathrm{d}\boldsymbol{k}$$

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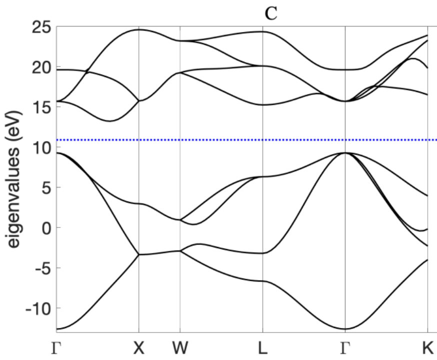
Decay rate depends on the curvature of the Fermi surface ($\mathcal{S} := \{\varepsilon_{n,\boldsymbol{k}} = \varepsilon_{\mathrm{F}}\}$):

e.g. Free electron gas: $|F(\mathcal{H})_{ij}| \lesssim r_{ij}^{-\frac{d+1}{2}}$

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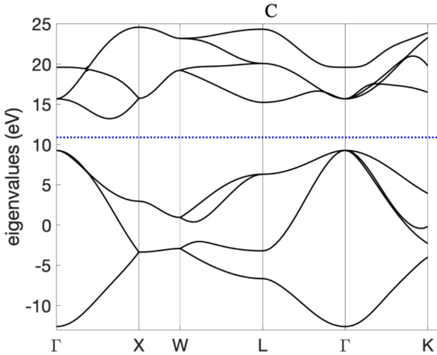


More generally, $\mathcal{S}$ has $1 \leq k \leq d-1$ non-zero principal curvatures at points with normal in the direction $\pm(\boldsymbol{r}_i - \boldsymbol{r}_j)$ then

$$F(\mathcal{H})_{ij} \lesssim r_{ij}^{-[\frac{k}{2}+1]}$$

Periodic Table of Fermi Surfaces

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