NUMERICAL ALGORITHMS FOR THE ELECTRONIC STRUCTURE ANALYSIS

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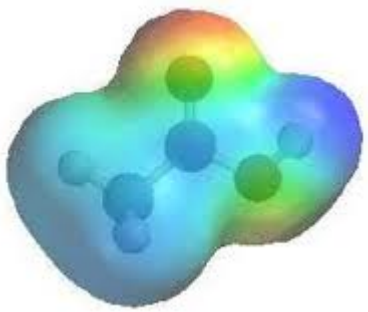
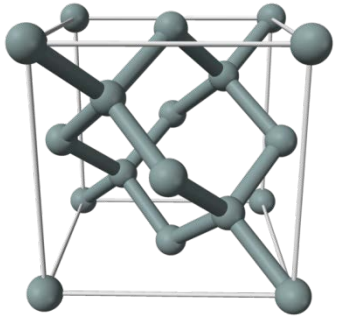
Electronic Structure of Matter and Modern Materials Design

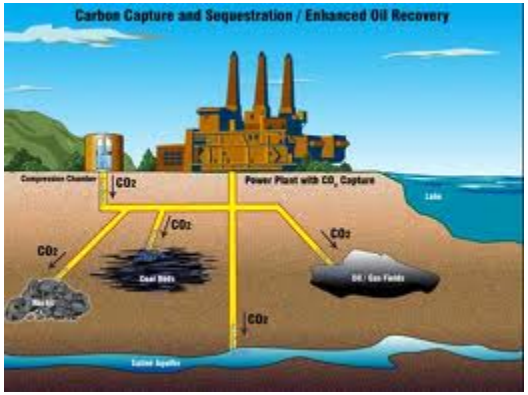
- Many-body Schrödinger's equation $H\Psi = \Psi E$





PV Solar Cells

Energy storage



Carbon capture

Electronic structure theory

Main goal: Given atomic positions $\{R_\alpha\}_{\alpha=1}^{M}$, Compute the ground state electron energy $E_e(\{R_\alpha\})$

Ground state electron wavefunction $\Psi_e(r_1, \cdots, r_N; \{R_\alpha\})$

$$\left(-\frac{1}{2}\sum_{i=1}^{N}\Delta_i - \sum_{\alpha=1}^{M}\sum_{j=1}^{N}\frac{Z_\alpha}{|r_i - R_\alpha|} + \frac{1}{2}\sum_{\substack{i,j=1,\\ i\neq j}}^{N}\frac{1}{|r_i - r_j|}\right)\Psi_e = E_e(\{R_\alpha\})\Psi_e$$

Curse of dimensionality

The fundamental laws necessary to the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficult lies only in the fact that application of these laws leads to equations that are too complex to be solved.

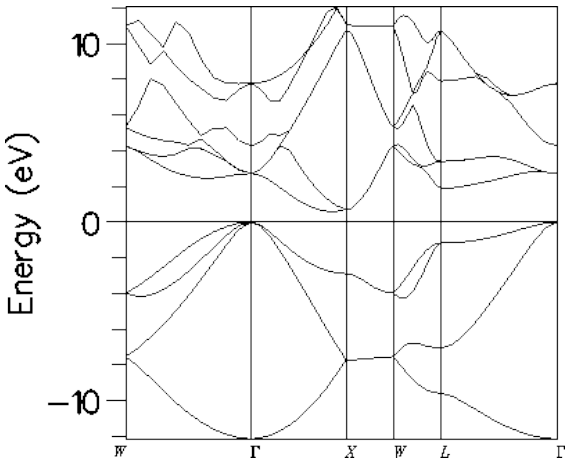
–P. Dirac, 1929

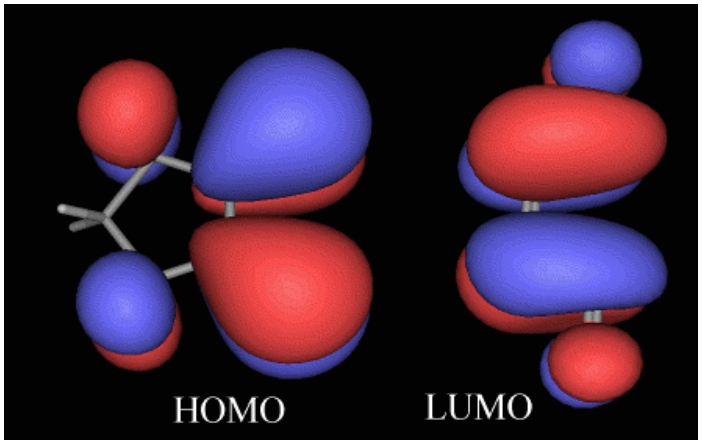
Approximation

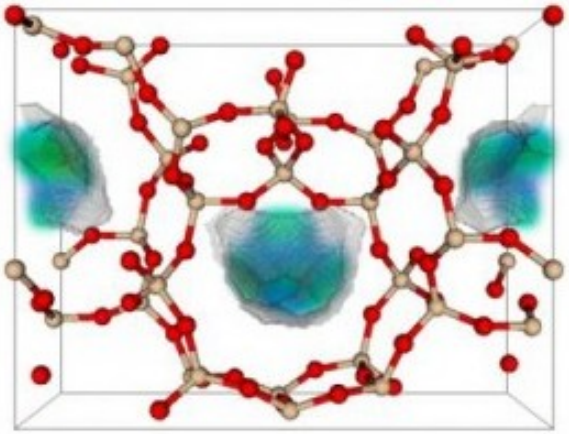
- Wavefunction methods
  - Hartree-Fock
  - Configuration interaction
  - Coupled cluster
  - MP2, MP3 etc.
- Density functional theory (DFT)
  - LDA
  - GGA
  - Perturbation (GW, Bathe-Salpeter)
  - Time-dependent DFT

What to compute?

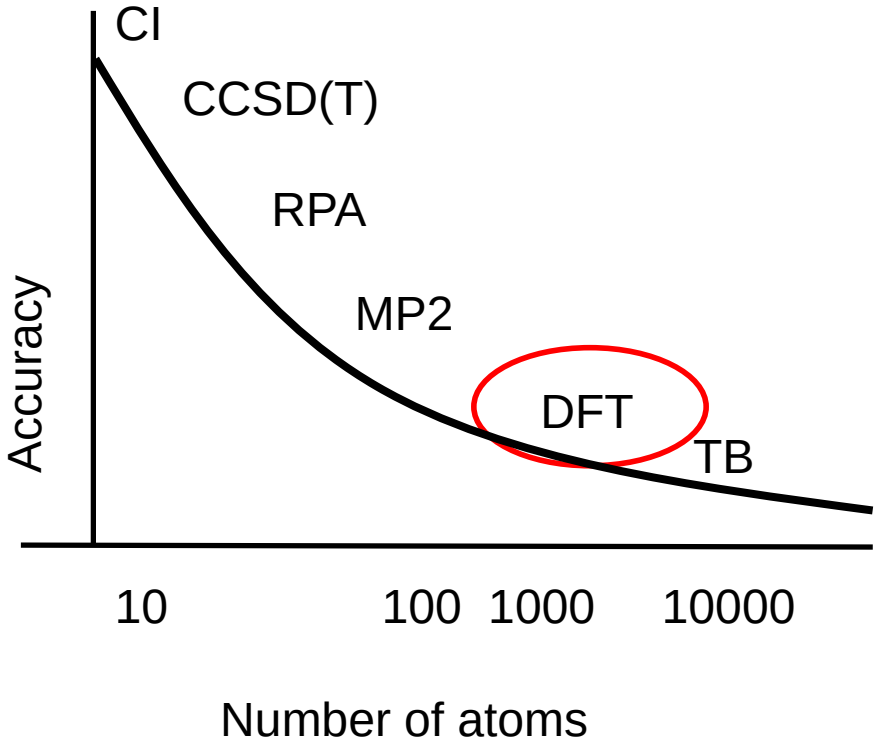
- Energy (binding, adsorption, absorption, vacancy, insertion, ionization etc.)
- Electron density
- Electron orbitals
- Geometry (atomic structure)
- Vibration (phonons)
- Transition states
- Dynamics
- Other observables (diffusion, electron mobility, dipole moment etc.)

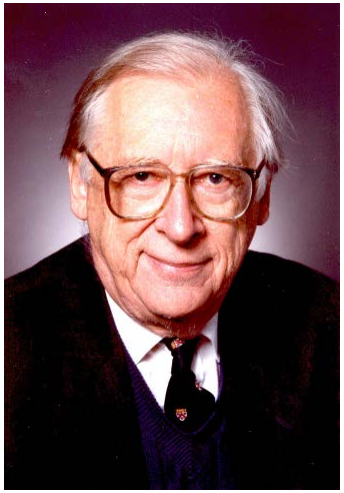






Pople diagram





John Pople,
Nobel Prize in
Chemistry, 1998

Density functional theory (DFT): best compromise between efficiency and accuracy. Most widely used electronic structure theory for condensed matter systems.

Density functional theory

Table 1. *Physical Review* Articles with more than 1000 Citations Through June 2003

Publication	# cites	Av. age	Title	Author(s)
PR **140**, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR **136**, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
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PR, Physical Review; PRB, Physical Review B; PRL, Physical Review Letters; RMP, Reviews of Modern Physics.

[S. Redner, Citation Statistics from 110 Years of Physical Review]

Density functional theory

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[S. Redner, Citation Statistics from 110 Years of Physical Review]

Self-consistent equations including exchange and **correlation effects**

W Kohn, LJ Sham - Physical Review, 1965 - APS

Abstract From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to **self-consistent ...**

Cited by 32998 Related articles All 27 versions Import into BibTeX Saved More

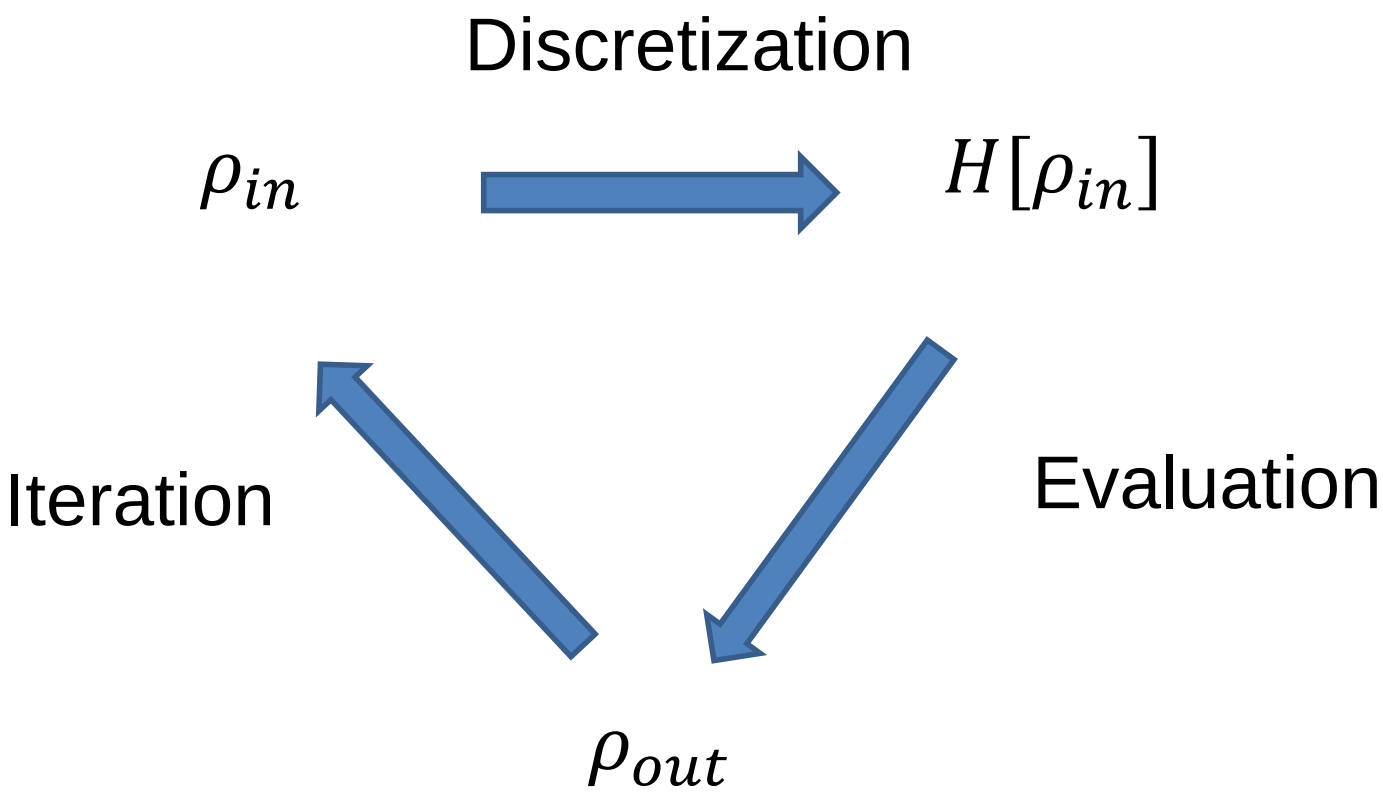
Kohn-Sham density functional theory

$$H[\rho]\psi_i(x) = \left(-\frac{1}{2}\Delta + \int dx' \frac{m(x') + \rho(x')}{|x - x'|} + V_{xc}[\rho]\right)\psi_i(x) = \varepsilon_i \psi_i(x)$$

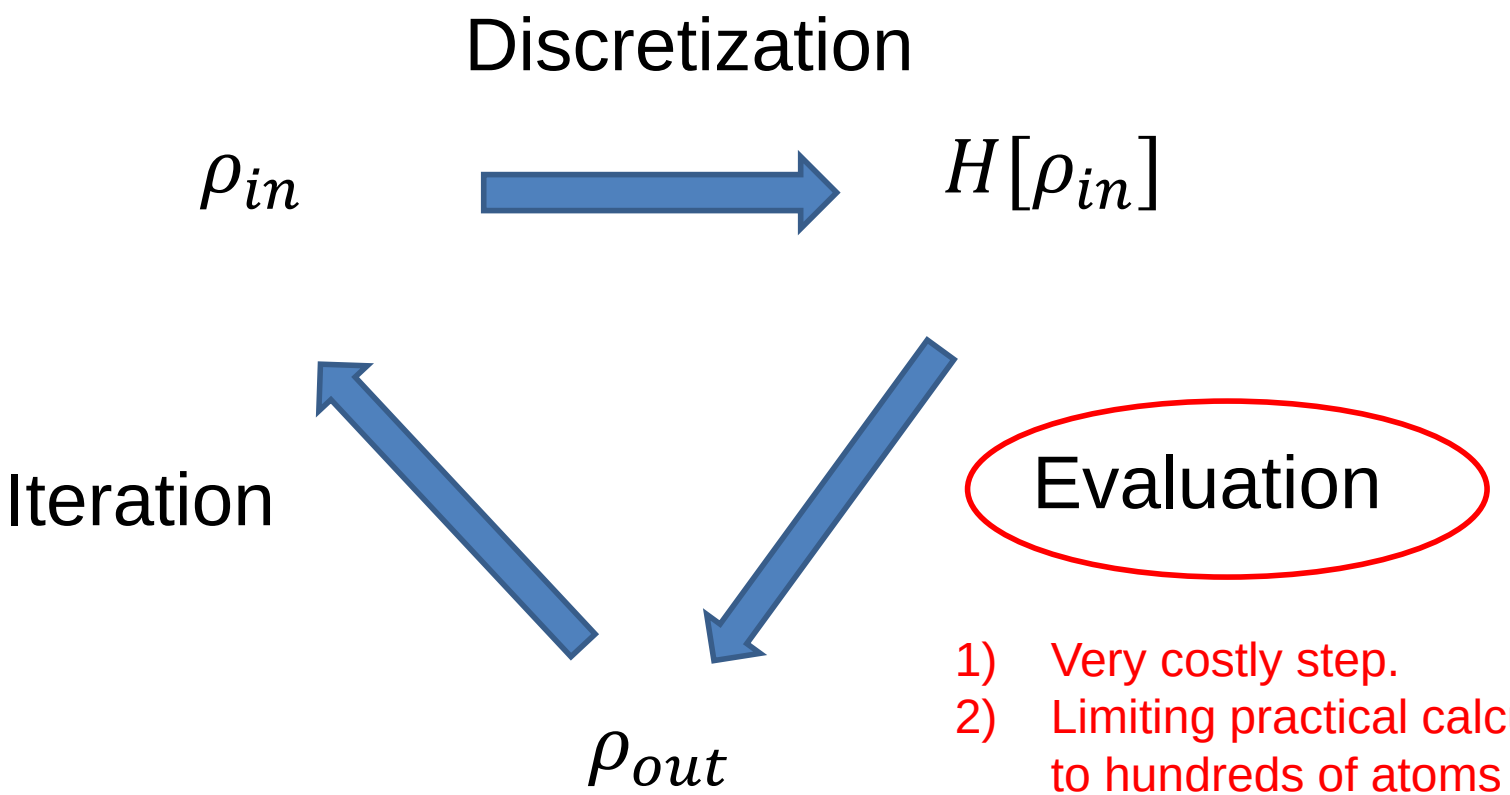
$$\rho(x) = 2\sum_{i=1}^{N/2} |\psi_i(x)|^2, \qquad \int dx\, \psi_i^*(x)\psi_j(x) = \delta_{ij}, \qquad \varepsilon_1 \leq \varepsilon_2 \leq \cdots$$

- Efficient: Always solve an equation in R^3, regardless of the number of electrons N.
- Accurate: Exact ground state energy for exact $V_{xc}[\rho]$, [Hohenberg-Kohn,1964], [Kohn-Sham, 1965]
- Best compromise between efficiency and accuracy. Most widely used electronic structure theory for condensed matter systems and molecules
- Nobel Prize in Chemistry, 1998

Self Consistent Field Iteration



Self Consistent Field Iteration



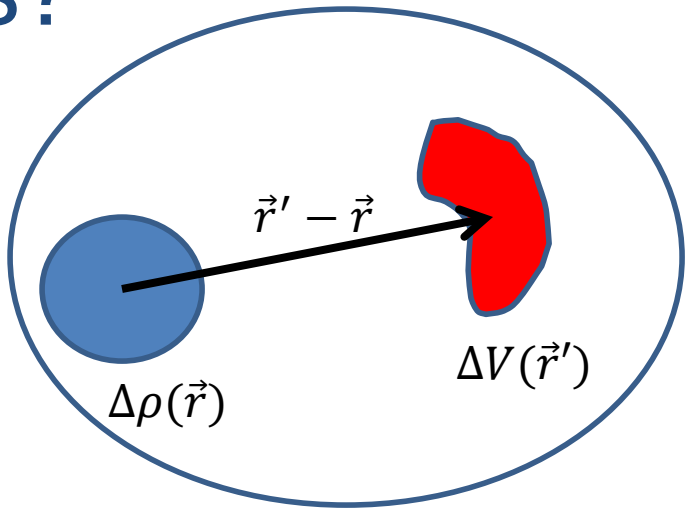
1) Very costly step.
2) Limiting practical calculations to hundreds of atoms
3) Almost always treated by solving a linear eigenvalue problem

Cubic scaling of KSDFT

$$\begin{array}{cc} & \overbrace{\qquad\qquad\qquad\qquad}^{O(N)} \\ O(N) & \left[\begin{pmatrix} X & X & X & X \\ X & X & X & X \\ X & X & X & X \\ X & X & X & X \\ X & X & X & X \\ X & X & X & X \end{pmatrix}\right. \end{array}$$

- KS orbitals (eigenfunctions) are delocalized in the global domain.
- N atoms. $O(N)$ grid points. $O(N)$ KS orbitals.
- Orthogonalization of an $O(N) \times O(N)$ matrix $\Rightarrow$ $O(N^3)$ scaling, regardless of what eigensolver is being used.
- Conclusion: DO NOT directly treat KS orbitals that are delocalized in the global domain.

Evaluation: Alternatives?



- Linear scaling algorithms
  - Near-sightedness [Kohn, PRL 1996] [Benzi-Boito-Razouk, SIAM Rev. 2013]
  - Truncation based algorithm:
    hard to balance efficiency and accuracy
  - Only applicable to insulators.

[Bowler and Miyazaki, Rep. Prog. Phys 2012]
"…The second challenge is that of metallic systems: there is no clear route to linear-scaling solution for systems with low or zero gaps and extended electronic structure…"

- Difficult task:
  - Accurate and efficient
  - Applicable to insulators, semiconductors and metals

Alterative solution?

Linear scaling methods

- Truncation (KS orbital, 1-dm). Near-sightedness.
- Costly for metals (large preconstant)
- Complicated user-interface (select truncation region)

[Yang, 1991], [Kohn, 1996].
Review: [Goedecker, 1999].
[Bowler-Miyazaki, 2012].

What we propose

- No truncation. Not based on near-sightedness.
- Applicable to insulator, semiconductor and metal.
- Black-box user-inteface.
- Scales at most $O(N^2)$.
- Localized basis and relatively small number of basis functions per atom.

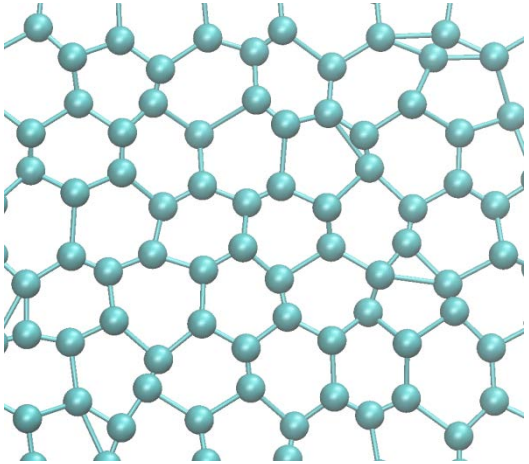
Outline

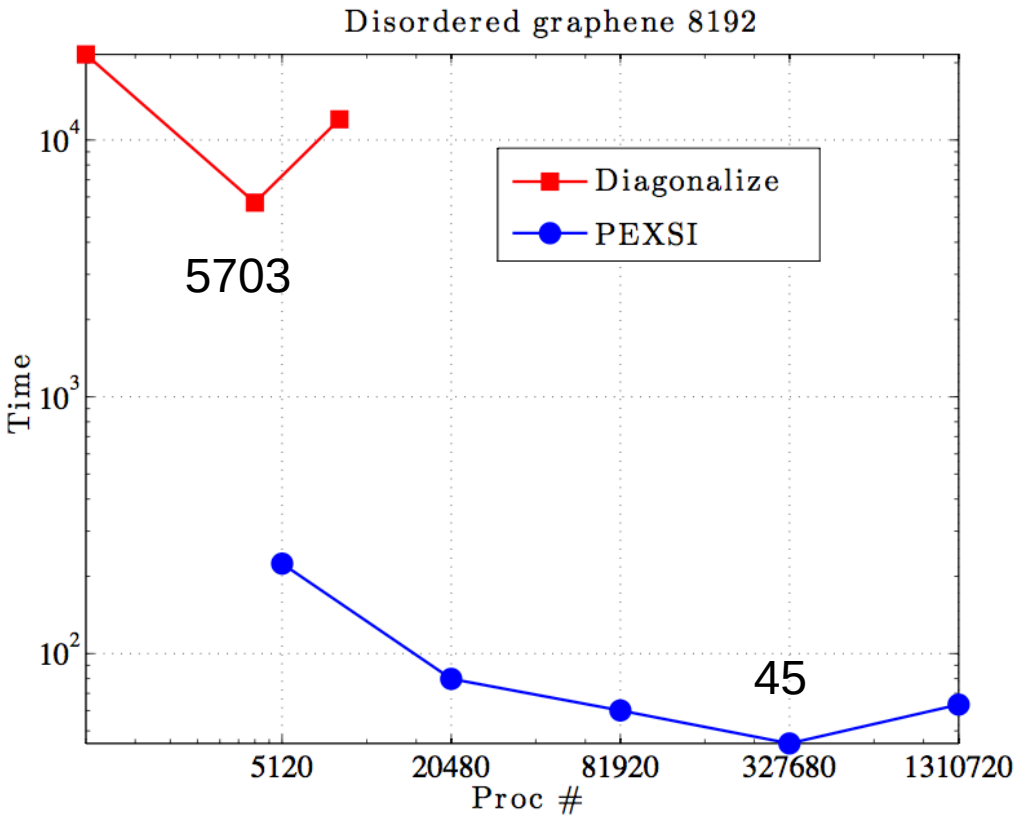
PEXSI: Pole EXpansion and Selected Inversion

- Pole Expansion
- Selected Inversion
- How it works in practice

PEXSI at work

Disordered graphene
8192 atoms





Speed up: 127

KSDFT: Matrix point of view

$$\rho(x) = 2\sum_{i=1}^{N/2} |\psi_i(x)|^2$$

$$= \begin{pmatrix} \psi_1(x) & \dots & \psi_{N_t}(x) \end{pmatrix} \begin{pmatrix} \chi(\varepsilon_1 - \mu) & & \\ & \ddots & \\ & & \chi(\varepsilon_{N_t} - \mu) \end{pmatrix} \begin{pmatrix} \psi_1(x) \\ \vdots \\ \psi_{N_t}(x) \end{pmatrix}$$

$$= \{\chi(H[\rho] - \mu I)\}_{x,x}$$

- μ : Chemical potential such that $\#\{\sigma(H) \leq \mu\} = N/2$
- χ : Heaviside function satisfying $\chi(x) = \begin{cases} 2, & x \leq 0, \\ 0, & x > 0 \end{cases}$

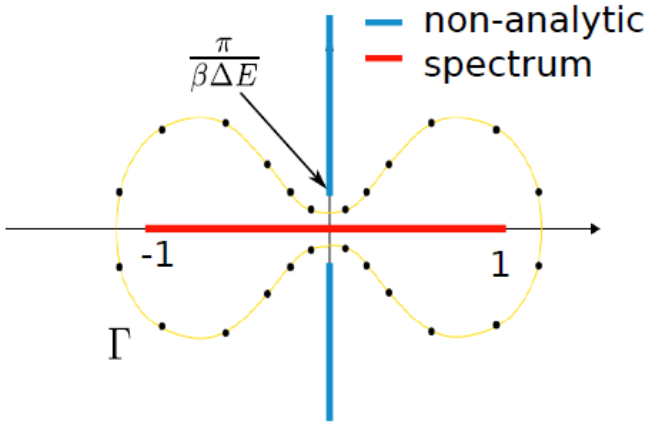
$$\rho = \operatorname{diag} \chi(H[\rho] - \mu I)$$

Pole expansion

- [LL, Lu, Ying and E, 2009] $Q \sim O(\log(\beta \Delta E))$

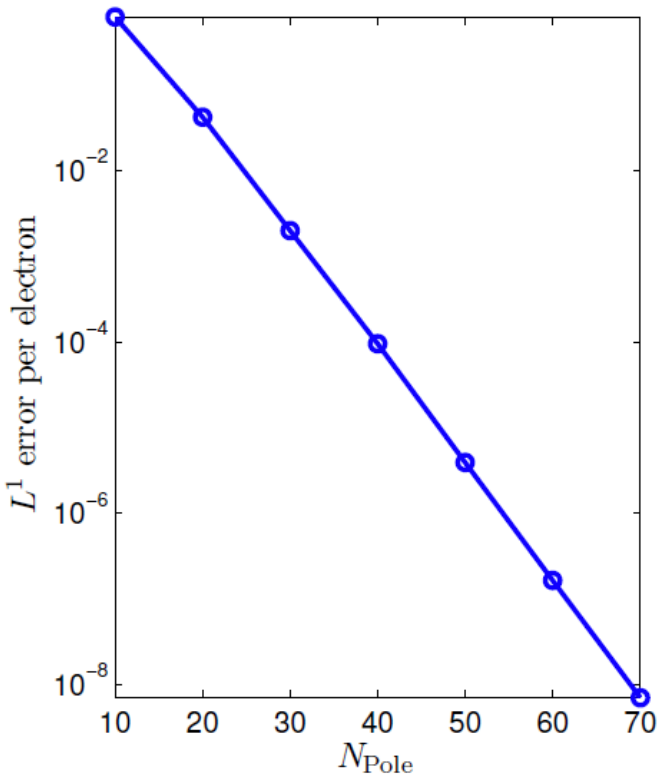
$$\rho \approx \mathrm{diag} \sum_{i=1}^{Q} \frac{\omega_i}{H - z_i I}$$

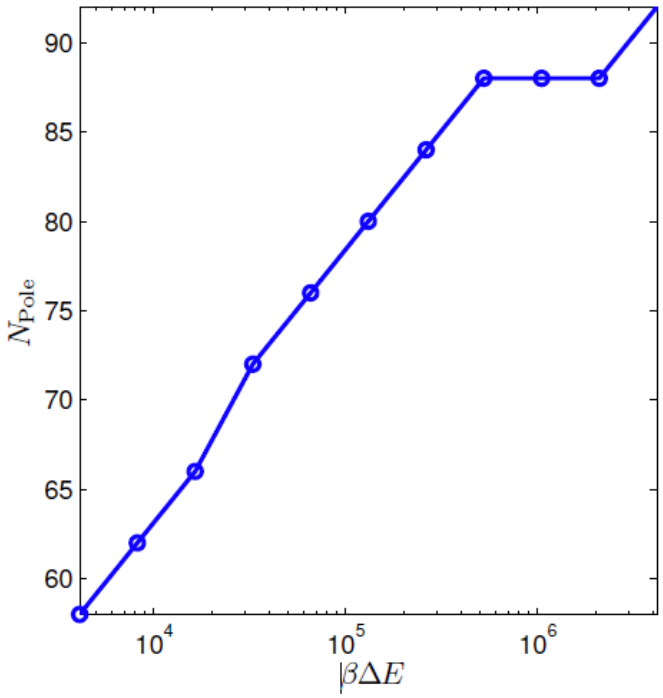
- $z_i, \omega_i \in \mathbb{C}$ are complex shifts and complex weights
- Cauchy contour integral technique



Numerical result

H: Tight binding model on a 2D grid





Outline

PEXSI: Pole EXpansion and Selected Inversion

- Pole Expansion
- Selected Inversion
- How it works in practice

Selected inversion

$$\rho \approx \mathrm{diag} \sum_{i=1}^{Q} \frac{\omega_i}{H - z_i I}$$

- All the diagonal elements of an inverse matrix.
- H is a sparse matrix, but $(H - z_i I)^{-1}$ is a full matrix.
- Naïve approach: $O(N^3)$.
- Need selected inversion.

Selected inversion: basic idea

- LDL^T factorization

$$A = \begin{pmatrix} A_{11} & A_{21}^T \\ A_{21} & \hat{A}_{22} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ L_{21} & I \end{pmatrix} \begin{pmatrix} A_{11} & 0 \\ 0 & S_{22} \end{pmatrix} \begin{pmatrix} 1 & L_{21}^T \\ 0 & I \end{pmatrix}$$

$$L_{21} = A_{21} A_{11}^{-1}, \qquad S_{22} = \hat{A}_{22} - A_{21} L_{21}^T$$

- Inversion

$$A^{-1} = \begin{pmatrix} A_{11}^{-1} + L_{21}^T S_{22}^{-1} L_{21} & -L_{21}^T S_{22}^{-1} \\ -S_{22}^{-1} L_{21} & S_{22}^{-1} \end{pmatrix}$$

Observation:

If L_{21} is sparse, $L_{21}^T S_{22}^{-1} L_{21}$ only require rows and columns of S_{22}^{-1} corresponding to the sparsity pattern of L_{21}.

Recursive relation

$$S_{22} = \begin{pmatrix} A_{22} & A_{32}^T \\ A_{32} & \hat{A}_{33} \end{pmatrix}$$

$$A = \begin{pmatrix} 1 & 0 \\ L_{21} & I \end{pmatrix} \boxed{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & L_{32} & I \end{pmatrix} \begin{pmatrix} A_{11} & 0 & 0 \\ 0 & A_{22} & 0 \\ 0 & 0 & \hat{A}_{33} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & L_{32}^T \\ 0 & 0 & I \end{pmatrix}} \begin{pmatrix} 1 & L_{21}^T \\ 0 & I \end{pmatrix}$$

$$A^{-1} = \begin{pmatrix} A_{11}^{-1} + L_{21}^T S_{22}^{-1} L_{21} & -L_{21}^T S_{22}^{-1} \\ -S_{22}^{-1} L_{21} & \boxed{\begin{matrix} A_{22}^{-1} + L_{32}^T S_{33}^{-1} L_{32} & -L_{32}^T S_{33}^{-1} \\ -S_{33}^{-1} L_{32} & S_{33}^{-1} \end{matrix}} \end{pmatrix}$$

Selected inversion

- $A = LDL^T$: A^{-1} restricted to the non-zero pattern of L is "self-contained": Only compute $\left\{A_{ij}^{-1} \middle| L_{ij} \neq 0 \; or \; L_{ji} \neq 0\right\}$.

- Exact method with exact arithmetic.

- For KS Hamiltonian discretized by local basis set, the cost of selected inversion is $O(N)$ for 1D systems, $O(N^{1.5})$ for 2D systems, and $O(N^2)$ for 3D systems.

- Combined with pole expansion: At most $O(N^2)$ scaling for solving Kohn-Sham problem.

- Idea of selected inversion dates back to [Erisman and Tinney, 1975], [Takakashi et al 1973]; For electronic structure [LL-Lu-Ying-Car-E, 2009]; For quantum transport [Li, Darve et al, 2008, 2012]

SelInv: Numerical results

SelInv: a selected inversion package for general sparse symmetric matrix written in FORTRAN.
[LL-Yang-Meza-Lu-Ying-E, 2011]

Problems from Harwell-Boeing Test Collection and the University of Florida Matrix Collection.

problem	n	selected inversion time	direct inversion time	speedup
bcsstk14	1,806	0.01 sec	0.13 sec	13
bcsstk24	3,562	0.02 sec	0.58 sec	29
bcsstk28	4,410	0.02 sec	0.88 sec	44
bcsstk18	11,948	0.24 sec	5.73 sec	24
bodyy6	0.19,366	09 sec	5.37 sec	60
crystm03	24,696	0.78 sec	26.89 sec	34
wathen120	36,441	0.34 sec	48.34 sec	142
thermal1	82,654	0.44 sec	95.06 sec	216
shipsec1	140,874	17.66 sec	3346 sec	192
pwtk	217,918	14.55 sec	5135 sec	353
parabolic_fem	525,825	20.06 sec	7054 sec	352
tmt_sym	726,713	13.98 sec	$>$ 3 hours	$>$ 772
ecology2	999,999	16.04 sec	$>$ 3 hours	$>$ 673
G3_circuit	1,585,478	218.7 sec	$>$ 3 hours	$>$ 49

Parallel PEXSI

- Distributed memory parallel selected inversion. Highly scalable to 1024~4096 procs. C++ implementation. [Jacquelin-LL-Yang, submitted]

- Parallel PEXSI: two level parallism:
  e.g. 80 poles × 1024 procs per pole = 81920 procs.

- The parallel PEXSI package is integrated with SIESTA, one of the most popular electronic structure software using atomic orbitals. [LL-Garcia-Huhs-Yang, JPCM 2014]

Parallel PEXSI

http://www.pexsi.org

PEXSI

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Main Page

Welcome to the documentation of PEXSI (current version: v0.7.1)

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  - Solving Kohn-Sham density functional theory: II

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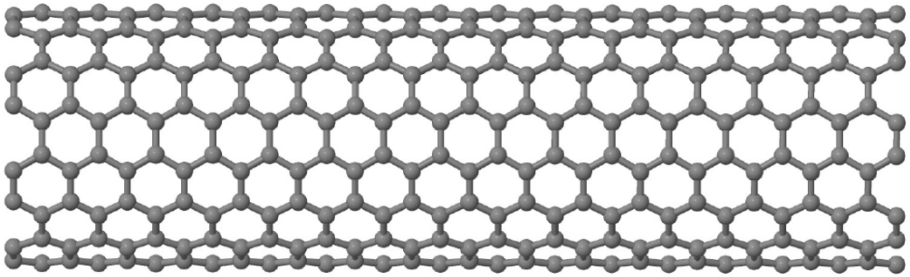
Accuracy of the pole expansion

# Poles	$E_{\text{PEXSI}} - E_{\text{ref}}$ (eV)	MAE Force (eV/Angstrom)
20	5.868351108	0.400431
40	0.007370583	0.001142
60	0.000110382	0.000026
80	0.000000360	0.000002

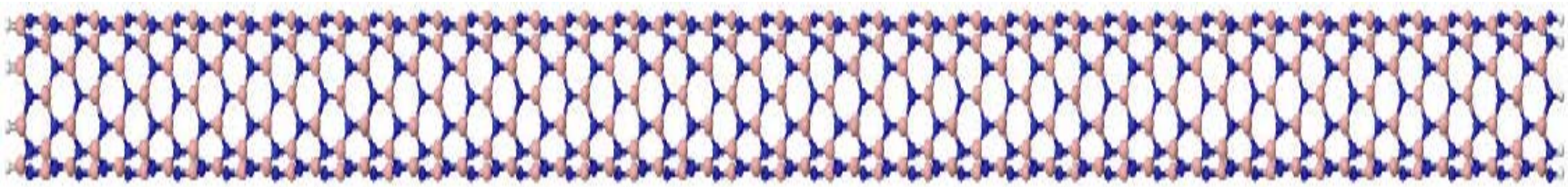


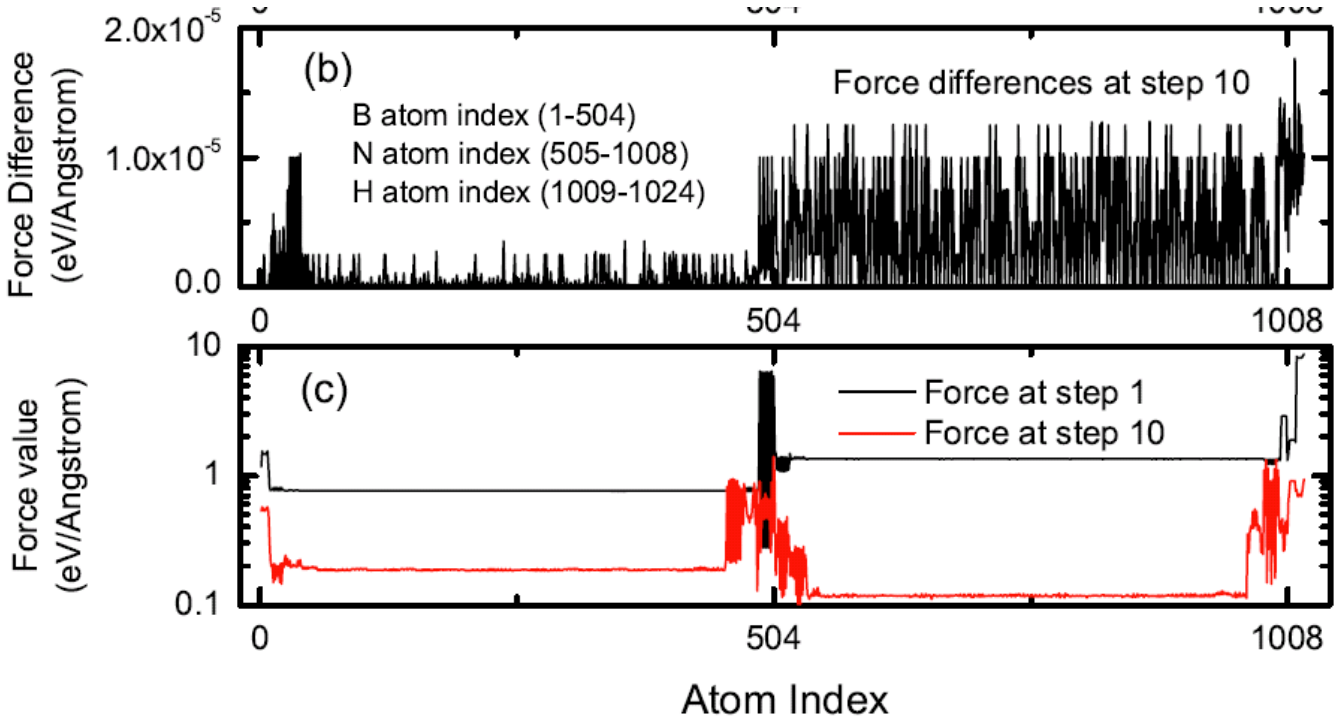
Carbon Nanotube (metallic)

Atomic orbitals

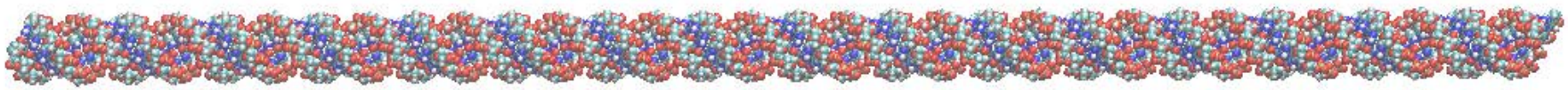
Geometry optimization: BNNT

Truncated Boron Nitride Nanotube (BNNT). 504 B atoms, 504 N atoms, 16 H atoms

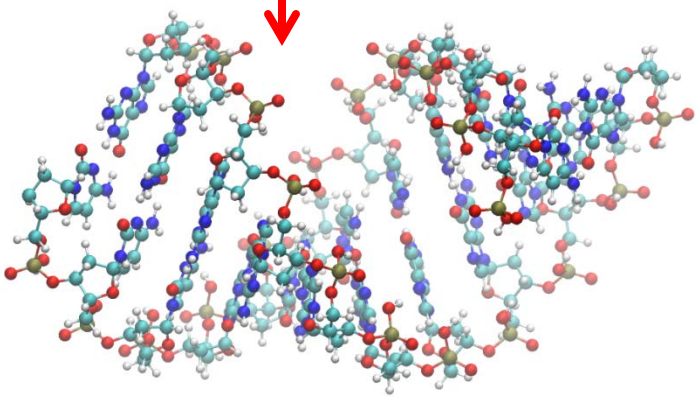




DNA



DNA molecule 11440 atoms (16 cells)



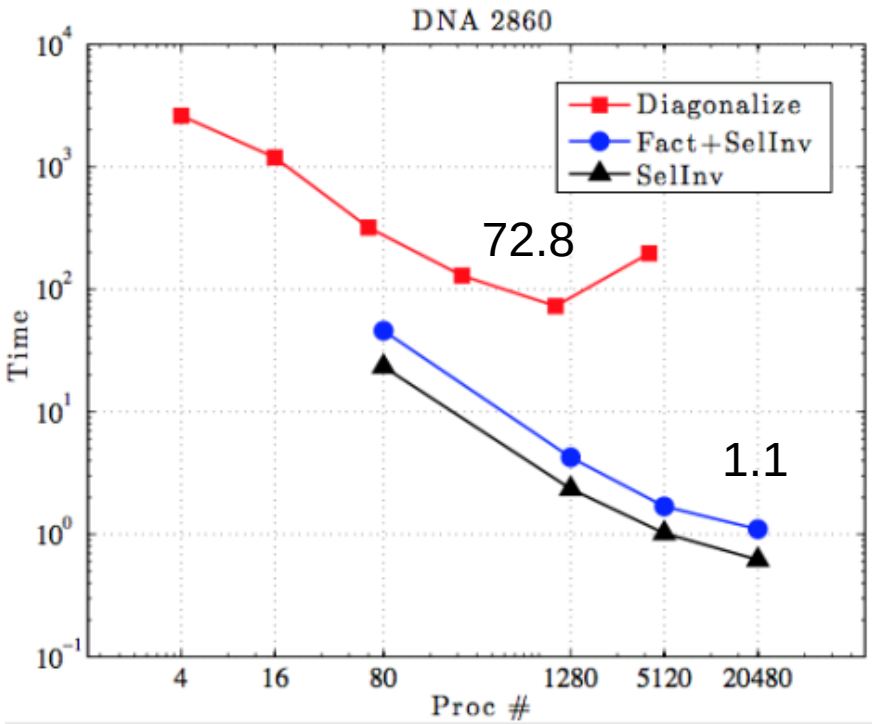
715 atoms (1 cell)

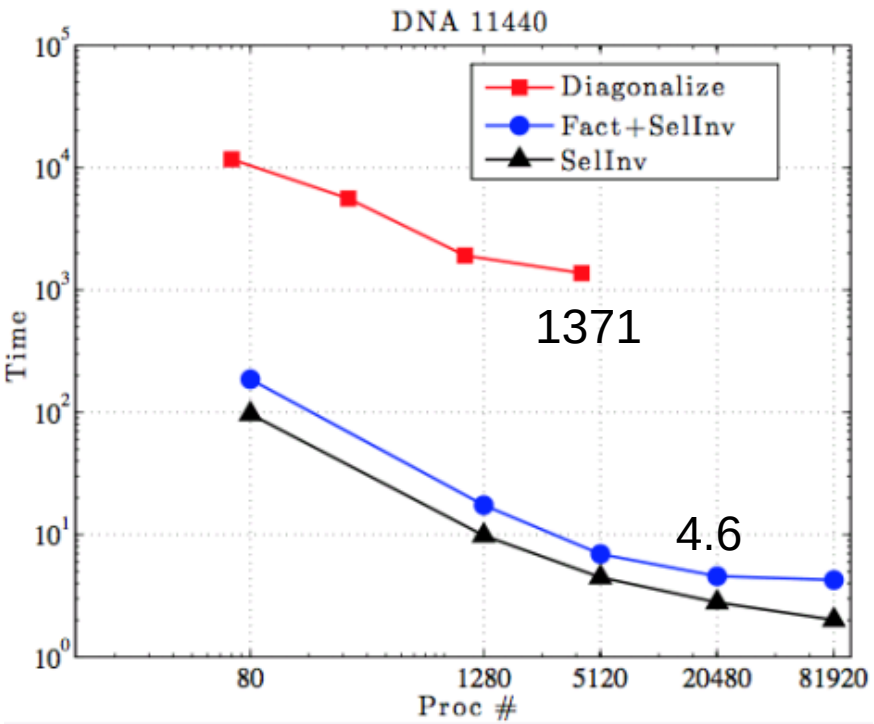
Number of atoms	Equivalent cells	Matrix dimension
715	1	7183
2860	4	28732
11440	16	114928
45760	64	459712

Atomic orbital basis set generated by SIESTA [Soler et al, 2002]

Double-zeta polarized basis set.

Comparing PEXSI with diagonalization





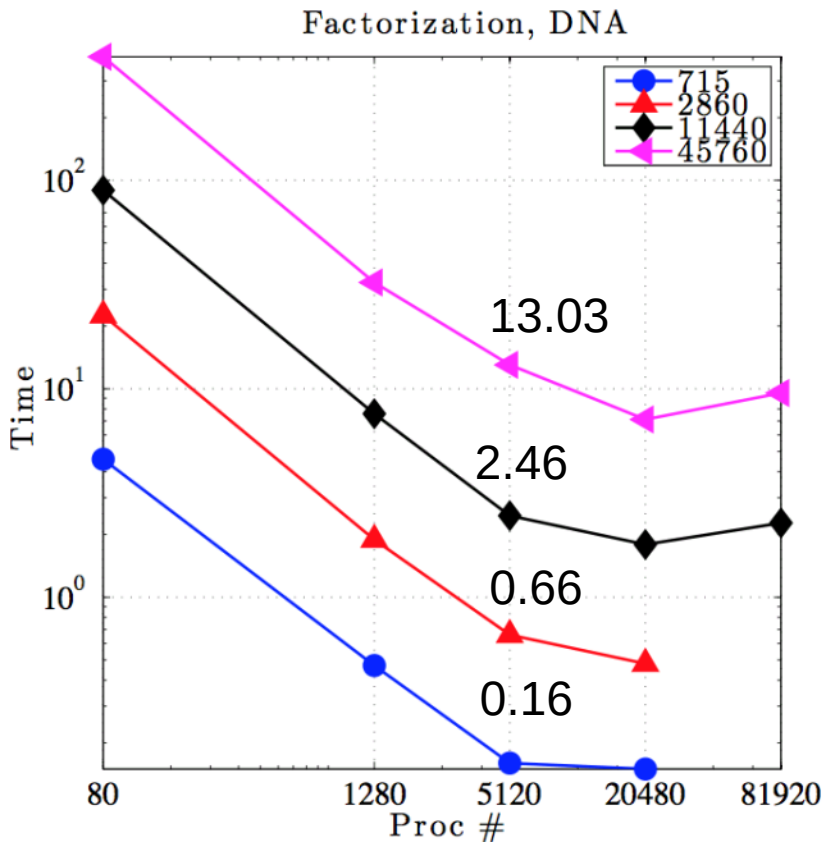
Speed-up: 66

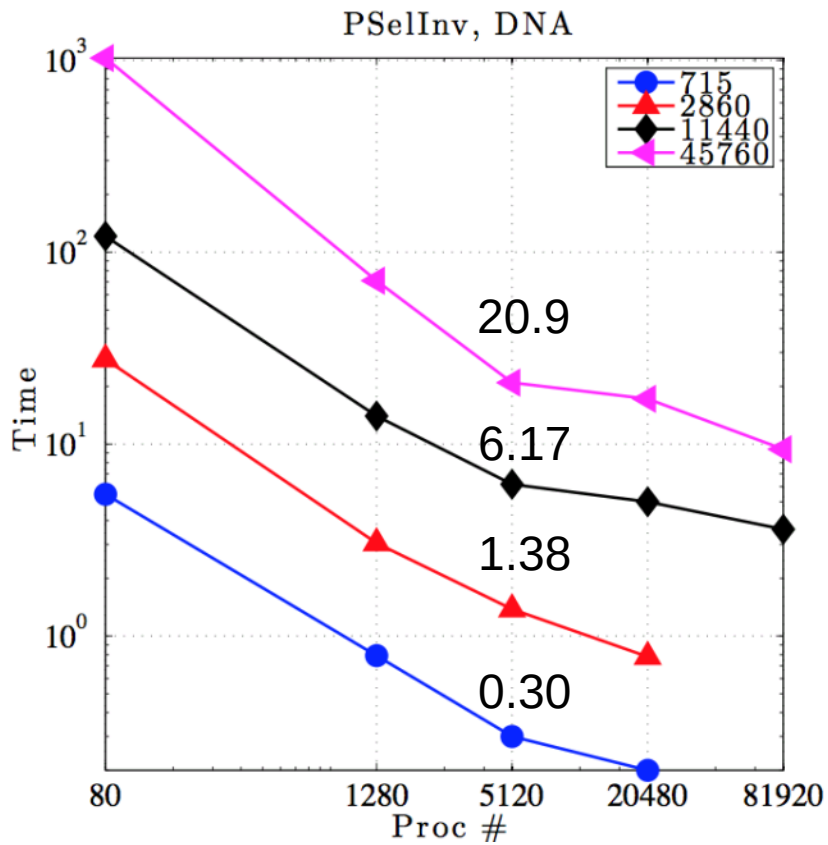
Speed-up: 298

(Partial) diagonalization routine: `pdsyevr` in ScaLAPACK [Vömel, 2010]

Parallelization of PEXSI benefited from two-level parallelism: 80 poles used

Strong and Weak scaling

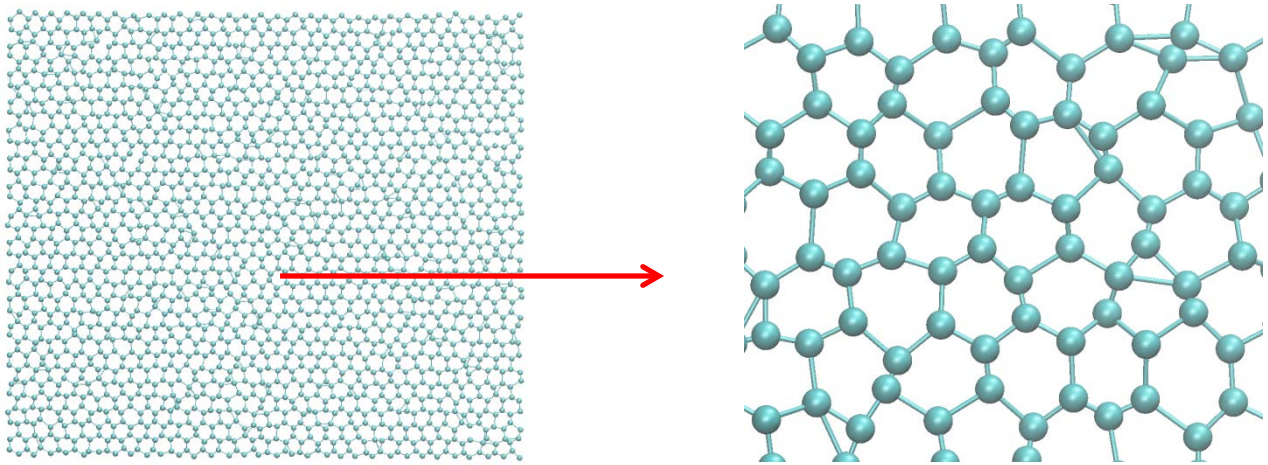




80 poles used.

quasi-1D system: $O(N)$ scaling

Disordered Graphene



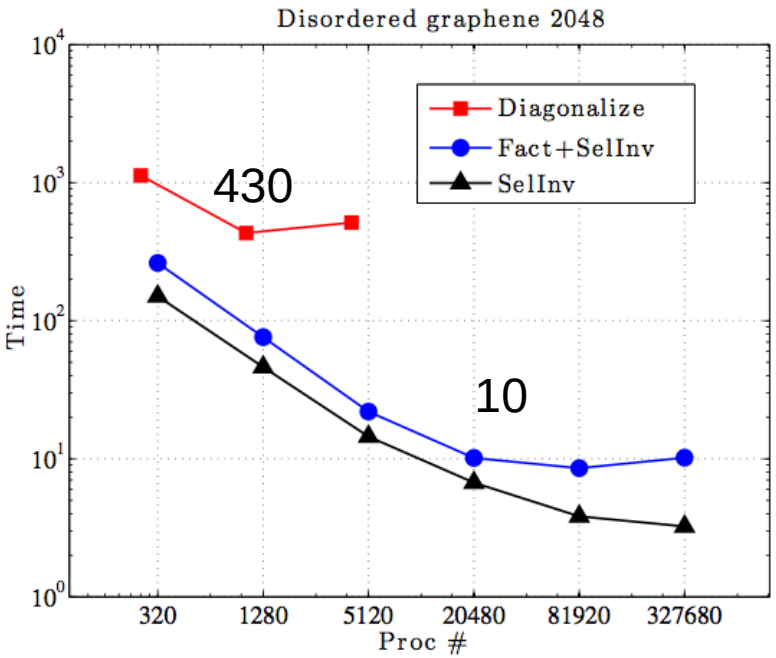
2048 atoms (1x1)

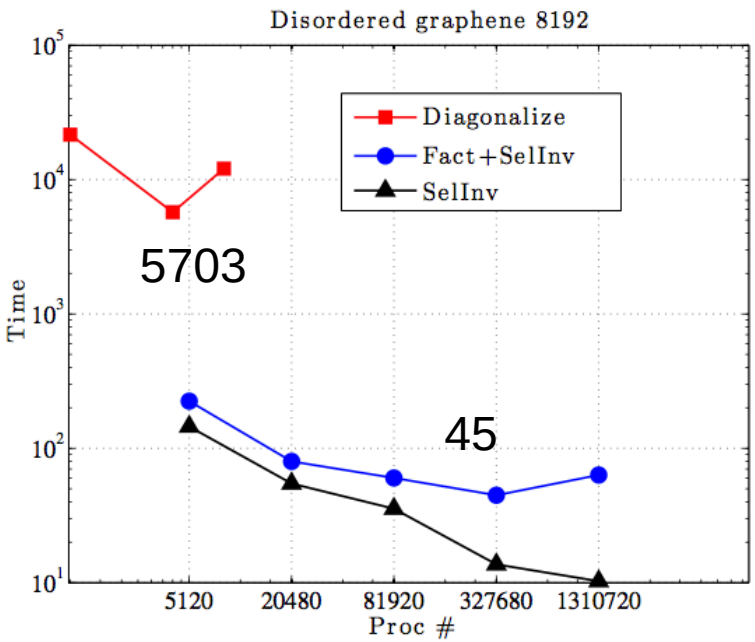
Number of atoms	Equivalent cells	Matrix dimension
2048	1×1	81,920
8192	2×2	327,680
32768	4×4	1,310,720

Discretized by the adaptive local basis functions.
[LL-Lu-Ying-E, JCP, 2012]

40 basis / atom to get 1meV/atom accuracy in the energy.

Comparing PEXSI with diagonalization





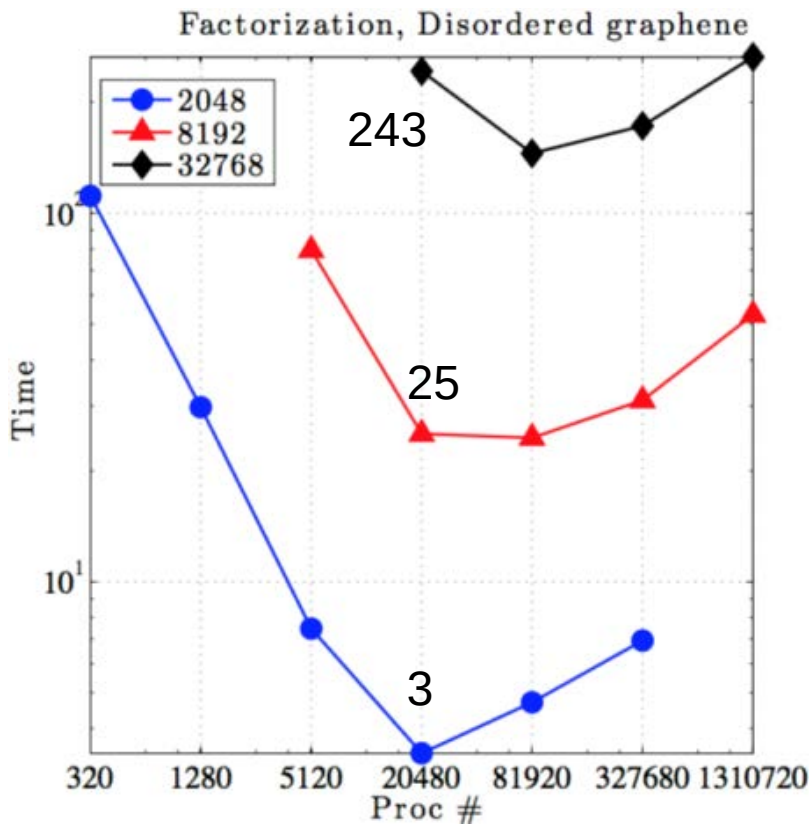
Speed up: 43

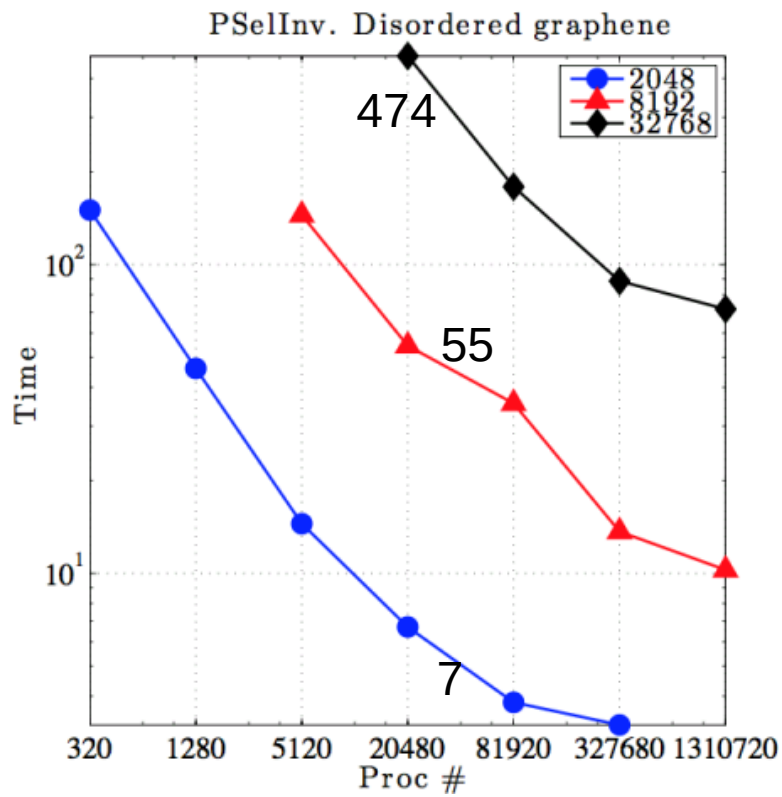
Speed up: 127

(Partial) diagonalization routine: `pdsyevr` in ScaLAPACK [Vömel, 2010]

Parallelization of PEXSI benefited from two-level parallelism: 80 poles used

Strong and Weak scaling





80 poles used.

quasi-2D system: $O(N^{1.5})$ scaling

Conclusion

- Pole Expansion and Selected Inversion (PEXSI) method for KSDFT at large scale.
- Based on the sparsity of Hamiltonian and overlap matrix. Require local basis set with small number of basis per atom (such as NAO and GTO, not applicable to PW)
- Accurate calculation of density, total energy, free energy and force (no truncation) for insulating and metallic systems.
- $O(N)$ for quasi-1D system, $O(N^{1.5})$ for quasi-2D system, and $O(N^2)$ for 3D bulk systems.
- Black-box: suitable for all codes localized basis set such atomic orbitals.

Acknowledgment and references

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Thank you for your attention!