

Linear Scaling Density-Functional Theory



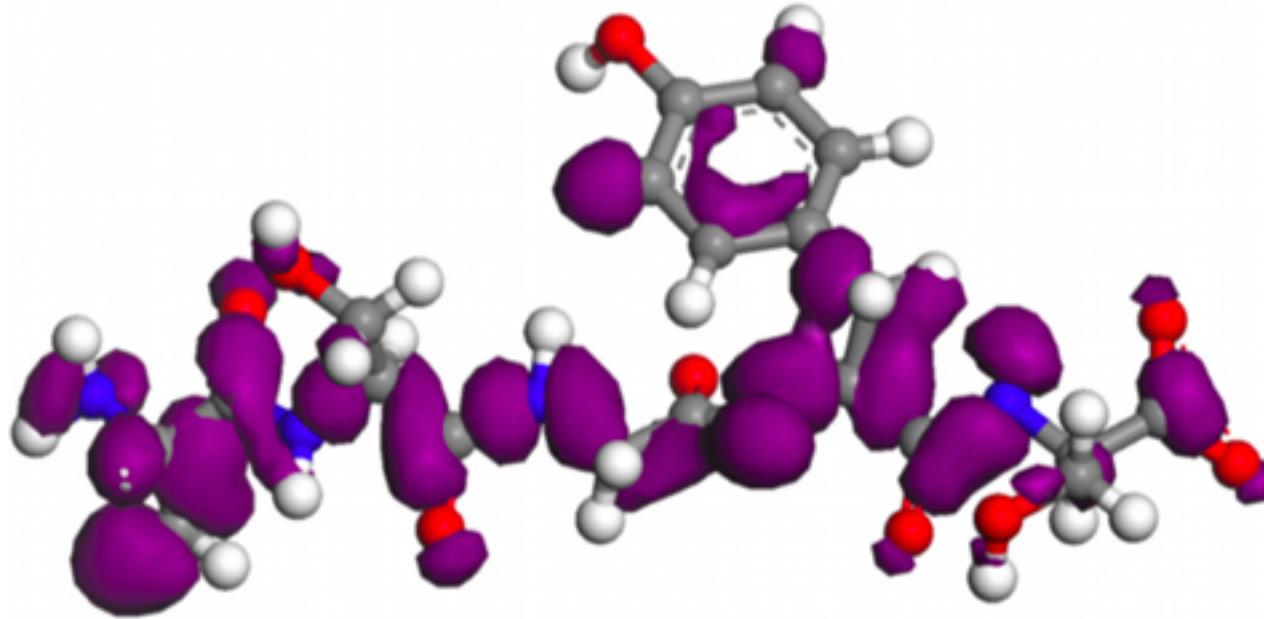
Peter Haynes

Departments of Physics and Materials, Imperial College London

20+ years of $O(N)$ DFT

- Divide & conquer: Yang, PRL **66**, 1438 (1991)
- Local orbitals: Galli & Parrinello, PRL **69**, 3547 (1992)
- Density-matrix: Li, Nunes & Vanderbilt, PRB **47**, 10891 (1993)
Hernández & Gillan, PRB **51**, 10157 (1995)
- Orbital minimization: Mauri, Galli & Car, PRB **47**, 9973 (1993)
Ordejón *et al.*, PRB **48**, 14646 (1993)
Kim *et al.*, PRB **52**, 1640 (1995)
- Orbital-free: Thomas, *Proc. Cambridge Philos. Soc.* **23**, 542 (1927)
Fermi, *Rend. Accad. Naz. Lincei* **6**, 602 (1927)
- Multiple scattering: Wang *et al.*, PRL **75**, 2867 (1995)
- Nearsightedness: Kohn, PRL **76**, 3168 (1996)
- Reviews: Goedecker, RMP **71**, 1085 (1999)
Bowler & Miyazaki, *Rep. Prog. Phys.* **75**, 036503 (2012)

Kohn-Sham equations

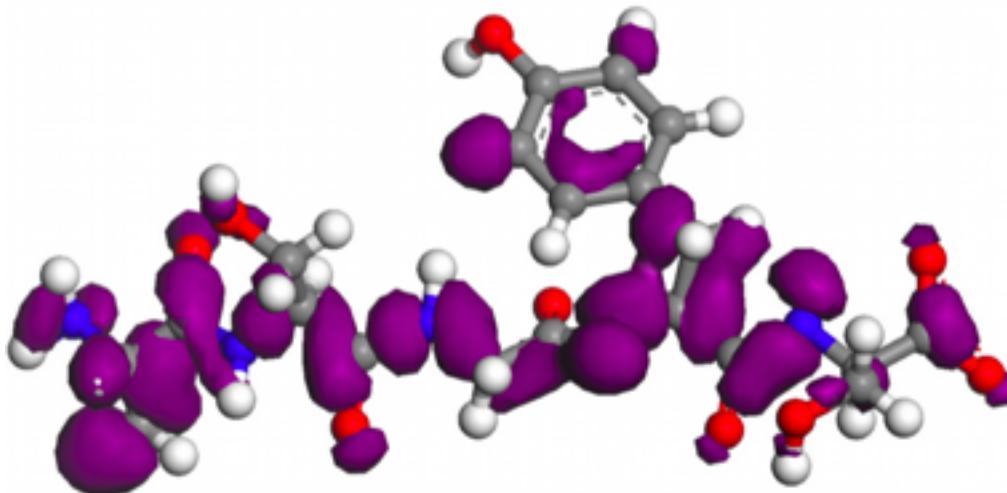


$$\left[-\frac{1}{2} \nabla^2 + V_{\sigma}^{\text{eff}} \right] \psi_{n\mathbf{k}\sigma} = \varepsilon_{n\mathbf{k}\sigma} \psi_{n\mathbf{k}\sigma}$$

- Computational effort scales as $O(N^3)$ where N is a measure of system-size (e.g. number of atoms)

The origin of the $O(N^3)$ scaling

- “Physicists”:
 - Typically employ large basis sets of simple functions e.g. plane waves
 - Computational effort dominated by FFTs
 - Asymptotic N^3 scaling from orthogonality constraint



The origin of the $O(N^3)$ scaling

- “Physicists”:
 - Typically employ large basis sets of simple functions e.g. plane waves
 - Computational effort dominated by FFTs
 - Asymptotic N^3 scaling from orthogonality constraint
- “Chemists”:
 - Typically employ small basis sets of more complicated functions e.g. contracted Gaussians
 - Computational effort dominated by building the Fock matrix

Simplifications

$$\left[-\frac{1}{2} \nabla^2 + V_{\sigma}^{\text{eff}} \right] \psi_{n\mathbf{k}\sigma} = \varepsilon_{n\mathbf{k}\sigma} \psi_{n\mathbf{k}\sigma}$$

Simplifications

$$\left[-\frac{1}{2} \nabla^2 + V_\sigma \right] \psi_{n\mathbf{k}\sigma} = \varepsilon_{n\mathbf{k}\sigma} \psi_{n\mathbf{k}\sigma}$$

- No self-consistency

Simplifications

$$\left[-\frac{1}{2}\nabla^2 + V\right] \psi_{n\mathbf{k}} = \varepsilon_{n\mathbf{k}} \psi_{n\mathbf{k}}$$

- No self-consistency
- No spin

Simplifications

$$\left[-\frac{1}{2}\nabla^2 + V\right] \psi_n = \varepsilon_n \psi_n$$

- No self-consistency
- No spin
- Sample Brillouin zone at Γ only

Simplifications

$$|\psi_n\rangle = \sum_k |\phi_k\rangle c_{kn} \quad \Rightarrow \quad \sum_j H_{ij} c_{jn} = c_{in} \varepsilon_n$$

- No self-consistency
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- (Localised) orthogonal basis set

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 - M basis functions $\rightarrow H$ is $M \times M$ matrix

$$H_{ij} = \langle \phi_i | \left(-\frac{1}{2} \nabla^2 + V \right) | \phi_j \rangle = \sum_n c_{in} \varepsilon_n c_{jn}^* \\ \rightarrow \text{full diagonalization } O(M^3)$$

Simplifications

$$|\psi_n\rangle = \sum_k |\phi_k\rangle c_{kn} \quad \Rightarrow \quad \sum_j H_{ij} c_{jn} = c_{in} \varepsilon_n$$

- No self-consistency
 - No spin
 - Sample Brillouin zone at Γ only
 - (Localised) orthogonal basis set
 - M basis functions $\rightarrow H$ is $M \times M$ matrix
 - N lowest states required
- \rightarrow iterative diagonalization $O(N^2M)$

Total energy methods

- Energy of the Kohn-Sham system:

$$E = \sum_n^{\text{occ}} \varepsilon_n$$

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- 1 for occupied states
 - 0 for unoccupied states

- Finite temperature:

$$f_n = f(\varepsilon_n) \quad f(\varepsilon) = \frac{1}{1 + \exp\left(\frac{\varepsilon - \mu}{k_B T}\right)}$$

Total energy methods

- Energy of the Kohn-Sham system:

$$E = \sum_n^{\text{all}} f_n \varepsilon_n$$

$$E = \text{tr} \left[\begin{pmatrix} \varepsilon_1 & 0 & 0 & \cdots & 0 \\ 0 & \varepsilon_2 & 0 & \cdots & 0 \\ 0 & 0 & \varepsilon_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & \varepsilon_N \end{pmatrix} \begin{pmatrix} f_1 & 0 & 0 & \cdots & 0 \\ 0 & f_2 & 0 & \cdots & 0 \\ 0 & 0 & f_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & f_N \end{pmatrix} \right]$$

Off-diagonal representation

$$E = \text{tr} \left[\begin{pmatrix} \varepsilon_1 & 0 & 0 & \cdots & 0 \\ 0 & \varepsilon_2 & 0 & \cdots & 0 \\ 0 & 0 & \varepsilon_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & \varepsilon_N \end{pmatrix} \begin{pmatrix} f_1 & 0 & 0 & \cdots & 0 \\ 0 & f_2 & 0 & \cdots & 0 \\ 0 & 0 & f_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & f_N \end{pmatrix} \right]$$

- Trace is invariant under similarity transformation:

$$c_{in} = \langle \phi_i | \psi_n \rangle \quad \Rightarrow \quad F_{ij} = \sum_n c_{in} f_n c_{jn}^*$$

$$\text{c.f. } H_{ij} = \sum_n c_{in} \varepsilon_n c_{jn}^*$$

Off-diagonal representation

$$E = \text{tr} \left[\begin{pmatrix} \varepsilon_1 & 0 & 0 & \cdots & 0 \\ 0 & \varepsilon_2 & 0 & \cdots & 0 \\ 0 & 0 & \varepsilon_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & \varepsilon_N \end{pmatrix} \begin{pmatrix} f_1 & 0 & 0 & \cdots & 0 \\ 0 & f_2 & 0 & \cdots & 0 \\ 0 & 0 & f_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & f_N \end{pmatrix} \right]$$

- Trace is invariant under similarity transformation:

$$c_{in} = \langle \phi_i | \psi_n \rangle \quad \Rightarrow \quad F_{ij} = \sum_n c_{in} f_n c_{jn}^*$$

$$E = \text{tr}(FH) = \sum_{ij}^n F_{ij} H_{ji}$$

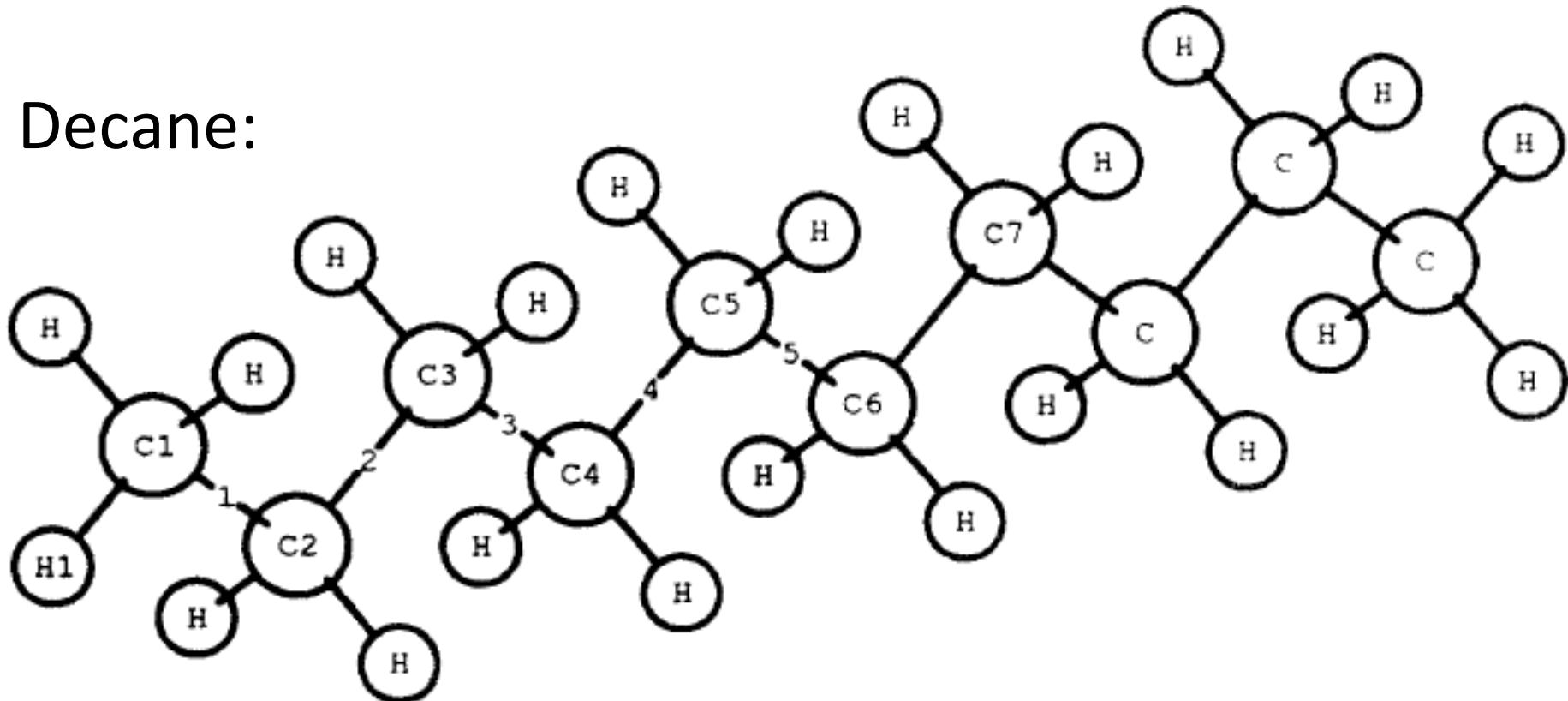
Density matrix

- F is the *single-particle* density matrix
 - F commutes with H (simultaneously diagonalizable)
 - Trace of F is the number of electrons (sum of occupation numbers)
 - At zero temperature F is idempotent: $F^2 = F$ (requires orthogonality and the Aufbau principle)
- Solving the Schrödinger equation is equivalent to finding the F that minimizes $E = \text{tr}(FH)$ subject to the above conditions

Nearsightedness

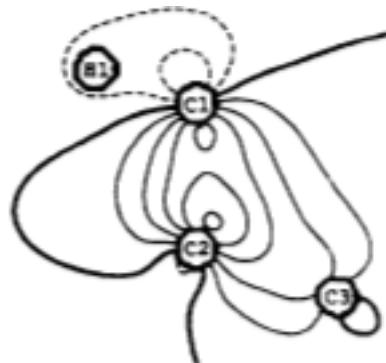
Hierse & Stechel, *Phys. Rev. B* 50, 17811 (1994)

Decane:

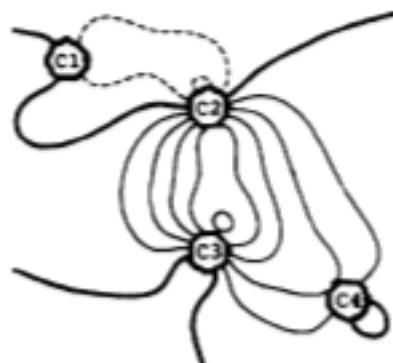


Nearsightedness

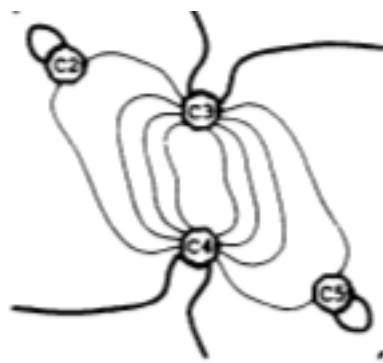
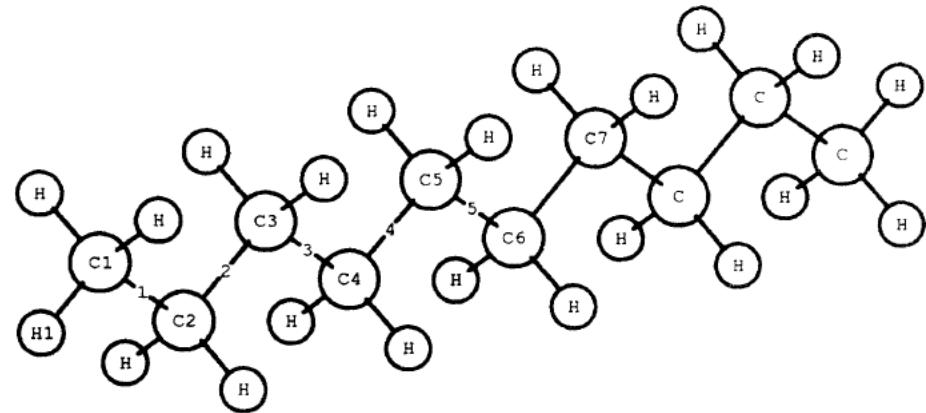
Hierse & Stechel, *Phys. Rev. B* 50, 17811 (1994)



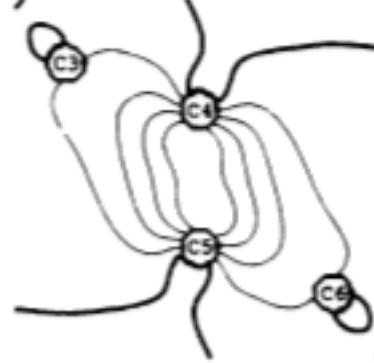
Bond 1



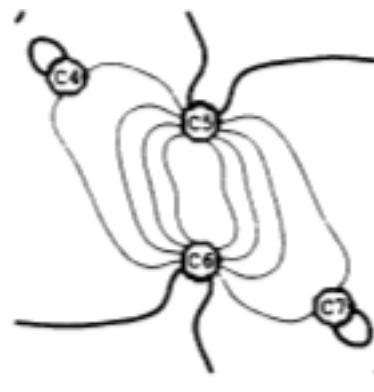
Bond 2



Bond 3



Bond 4



Bond 5

Nearsightedness

Hierse & Stechel, *Phys. Rev. B* 50, 17811 (1994)

TABLE I. Kohn-Sham energy errors for hydrocarbon systems, obtained from self-consistent iteration and/or orbital transfer.

System	$\Delta E_{KS}/\text{bond}$	How obtained
C_7H_{16}	0.555 meV	sc iteration
$C_{10}H_{22}$	0.661 meV	sc iteration
$C_{12}H_{26}$	0.703 meV	sc iteration
$C_{12}H_{26}$	0.707 meV	first guess (transfer from $C_{10}H_{22}$)
$C_{12}H_{26}$	0.725 meV	first guess (transfer from C_7H_{16})

Nearsightedness

- Implication for the density matrix:
 - In a local representation it is *sparse*
 - i.e. $F_{ij} \approx 0$ for distant basis functions ϕ_i and ϕ_j

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- In fact the density matrix decays exponentially:
 - Brouder *et al.*,
PRL 98, 046402 (2007)

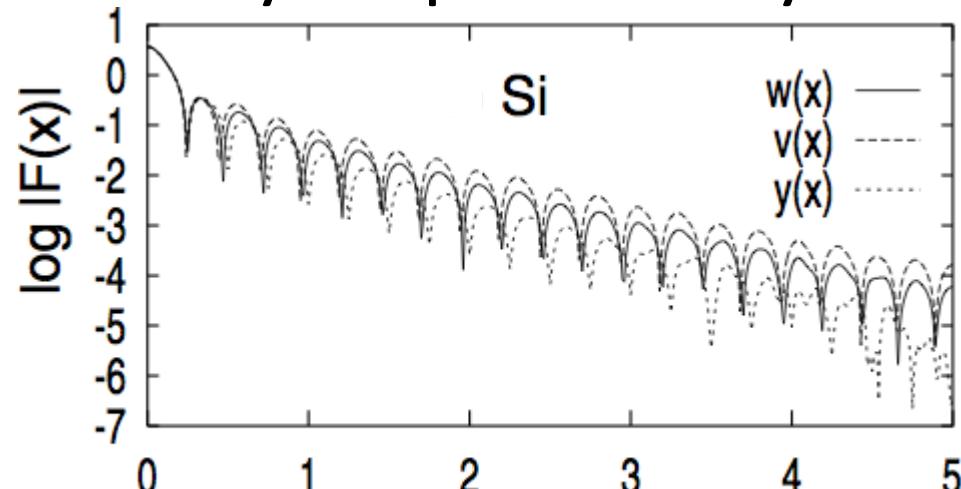


Figure from He & Vanderbilt, *PRL* 86, 5341 (2001) **x (unit cells)**

Nearsightedness

- Implication for the density matrix:
 - In a local representation it is *sparse*
 - i.e. $F_{ij} \approx 0$ for distant basis functions ϕ_i and ϕ_j
- In fact the density matrix decays exponentially
- Decay rate depends upon
 - Band gap
 - Basis quality

Divide and conquer

Yang, *Phys. Rev. Lett.* **66**, 1438 (1991)

Yang & Lee, *J. Chem. Phys.* **103**, 5674 (1995)

Divide and conquer

- Consider subvolumes of the whole system
- Calculate contributions to the density (matrix)

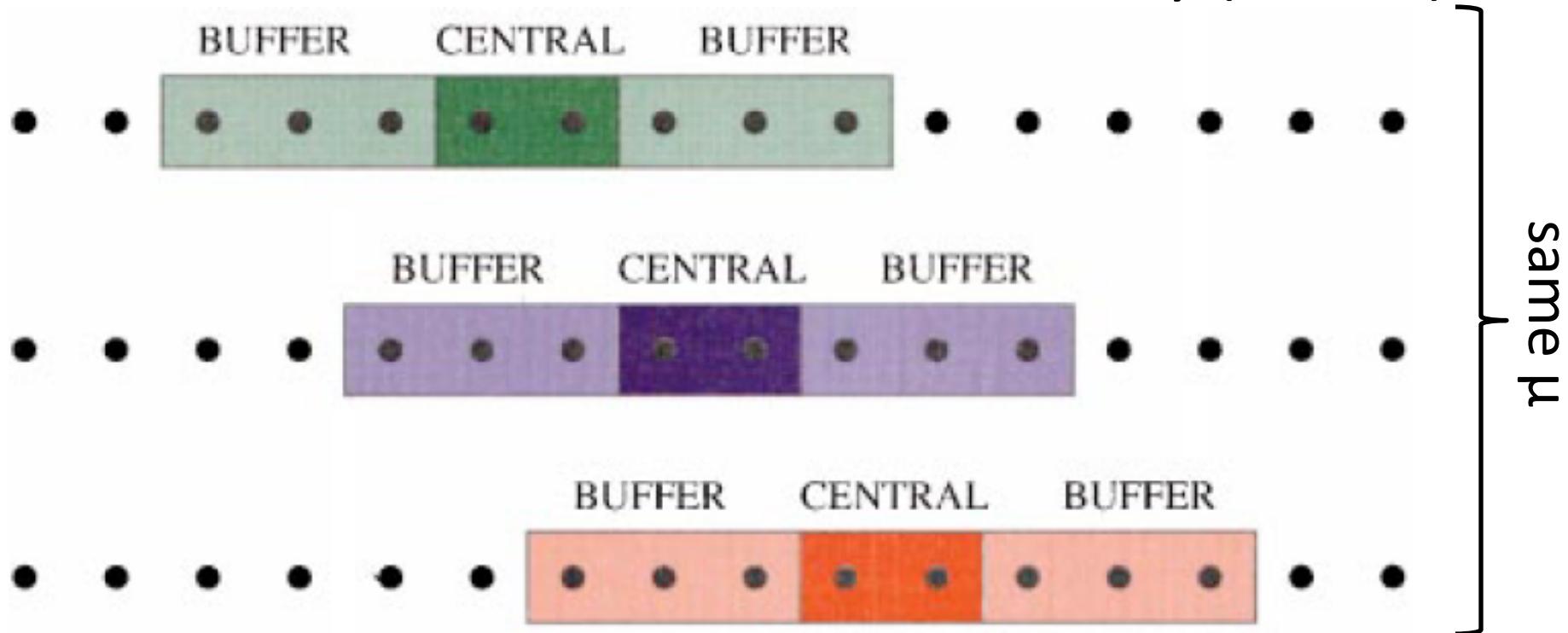


Figure from Goedecker, *Rev. Mod. Phys.* **71**, 1085 (1999)

Divide and conquer

- Trim the corners:

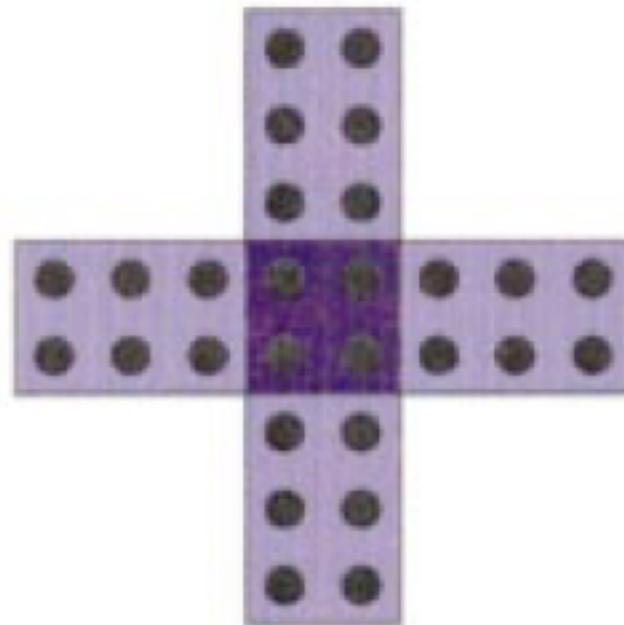
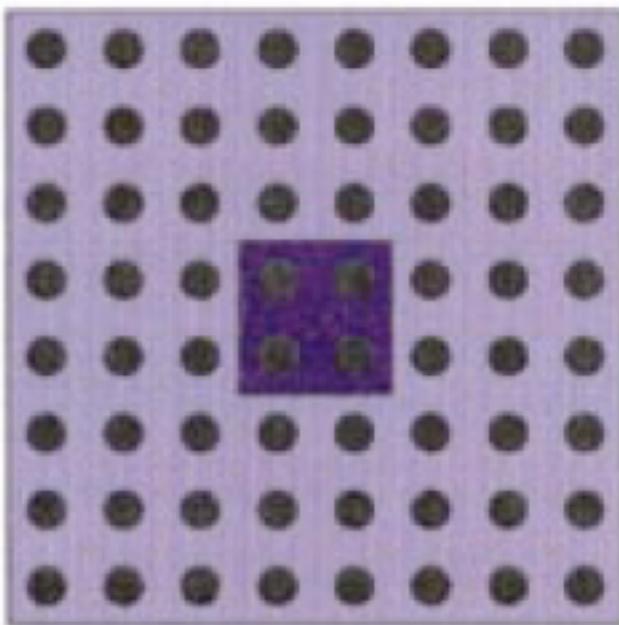


Figure from Goedecker, *Rev. Mod. Phys.* **71**, 1085 (1999)

Divide and conquer

- Combine the pieces:

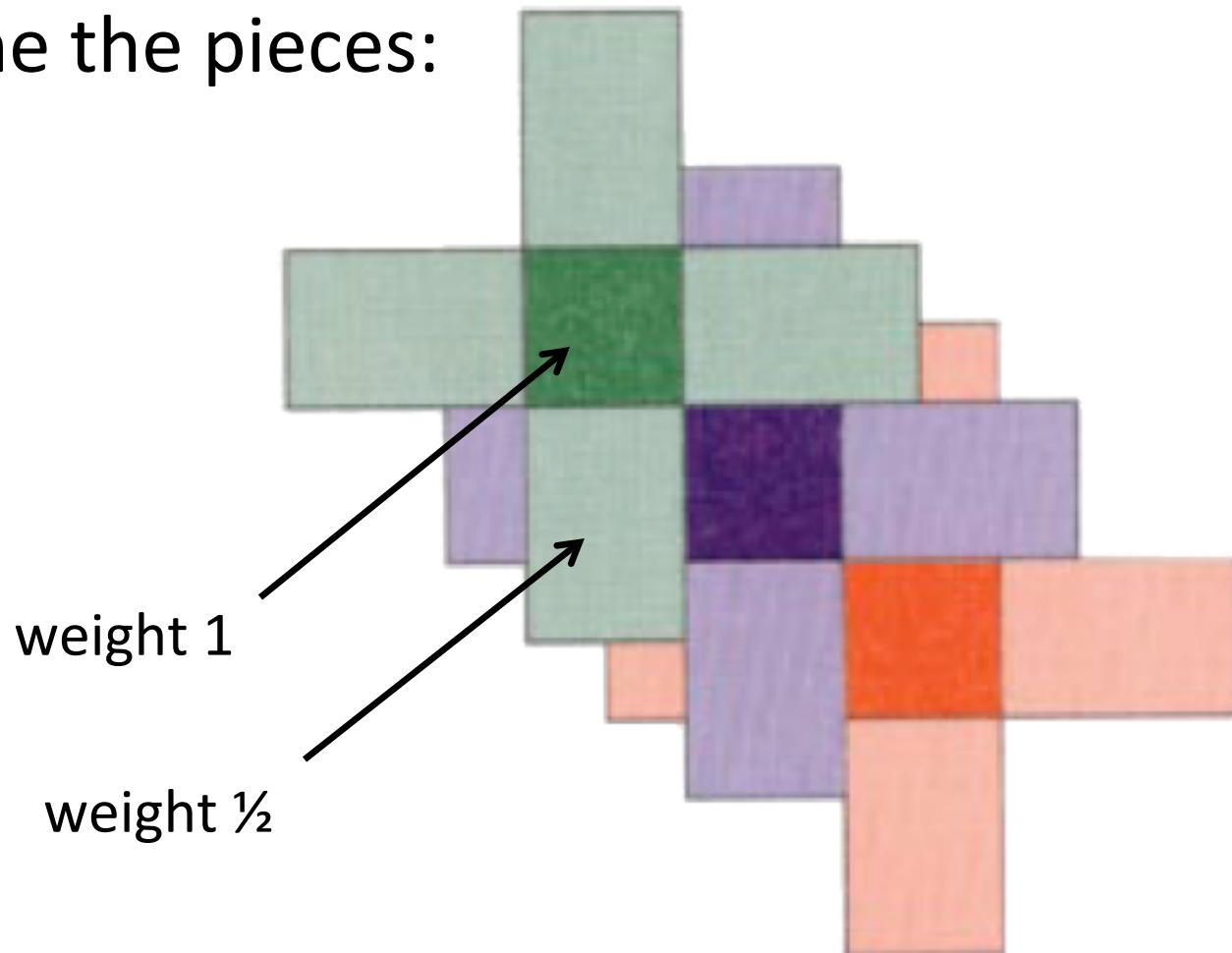


Figure from Goedecker, *Rev. Mod. Phys.* **71**, 1085 (1999)

Fermi operator expansion

Goedecker & Colombo, *Phys. Rev. Lett.* **73**, 122 (1994)

Goedecker & Teter, *Phys. Rev. B* **51**, 9455 (1995)

Compatibility

- Need to find F that commutes with H
- Any matrix M always commutes with:
 - The identity I
 - Itself i.e. M
 - Any power of itself e.g. M^2, M^3 etc.

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- Any matrix M always commutes with:
 - The identity I
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 - Any power of itself e.g. M^2, M^3 etc.
- Expand F as a polynomial in H i.e.

$$F \approx c_0 I + c_1 H + c_2 H^2 + \dots + c_n H^n$$

- Coefficients are those from a power series expansion of the Fermi-Dirac distribution

Chebyshev polynomials

$$T_n(x) = \cos(n \arccos x)$$

$$T_0(x) = 1$$

$$T_1(x) = x$$

$$T_{j+1}(x) = 2xT_j(x) - T_{j-1}(x)$$

- Defined on $[-1,1]$
- Bounded between ± 1

Chebyshev polynomials

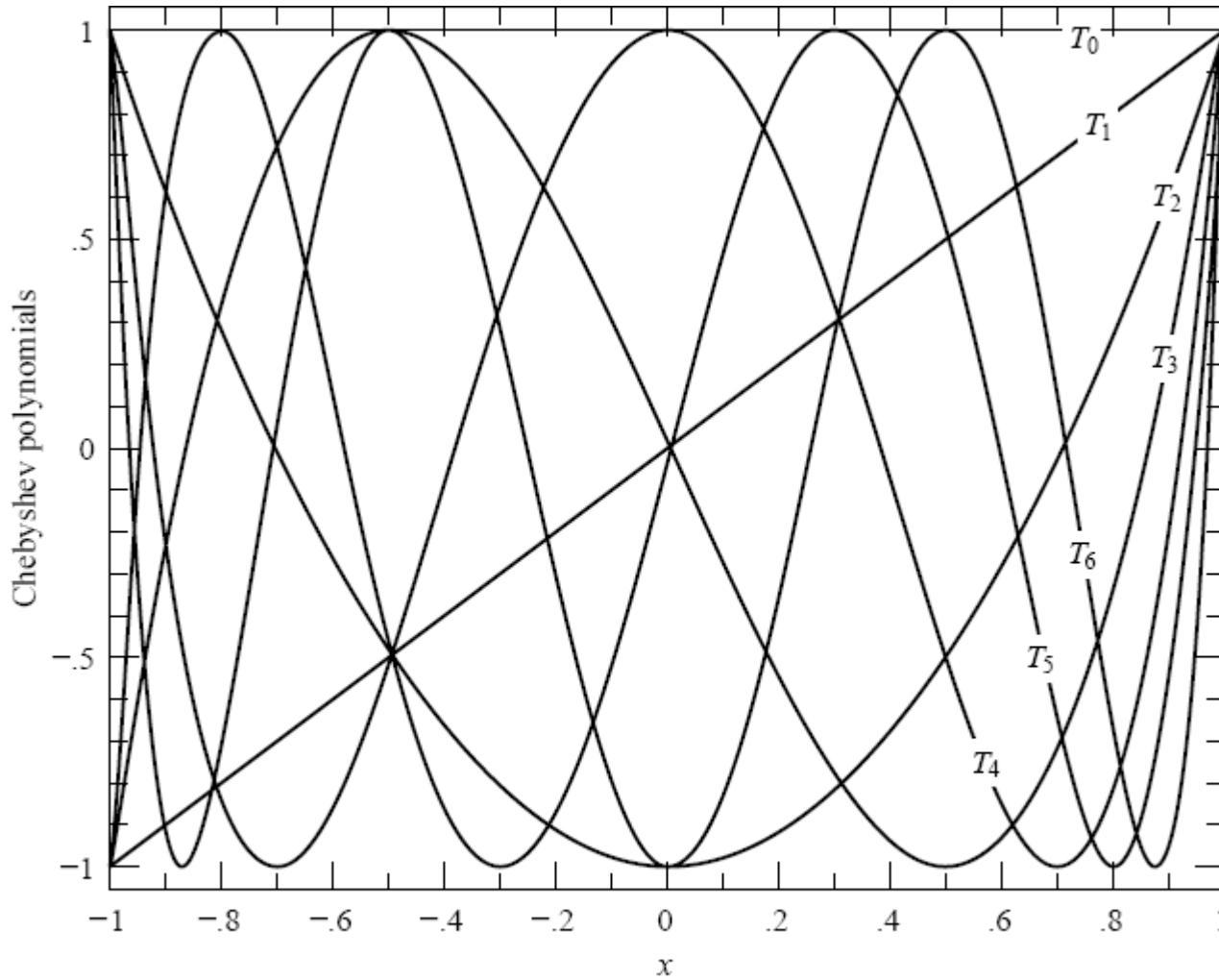


Figure 5.8.1. Chebyshev polynomials $T_0(x)$ through $T_6(x)$. Note that T_j has j roots in the interval $(-1, 1)$ and that all the polynomials are bounded between ± 1 .

Press et al., Numerical Recipes,
Cambridge University Press
(1986-92)

Chebyshev expansion

- Scale and shift the Hamiltonian so eigenvalues lie on [-1,1]:

$$F \approx \frac{1}{2}c_0 I + \sum_{j=1}^n c_j T_j(H)$$

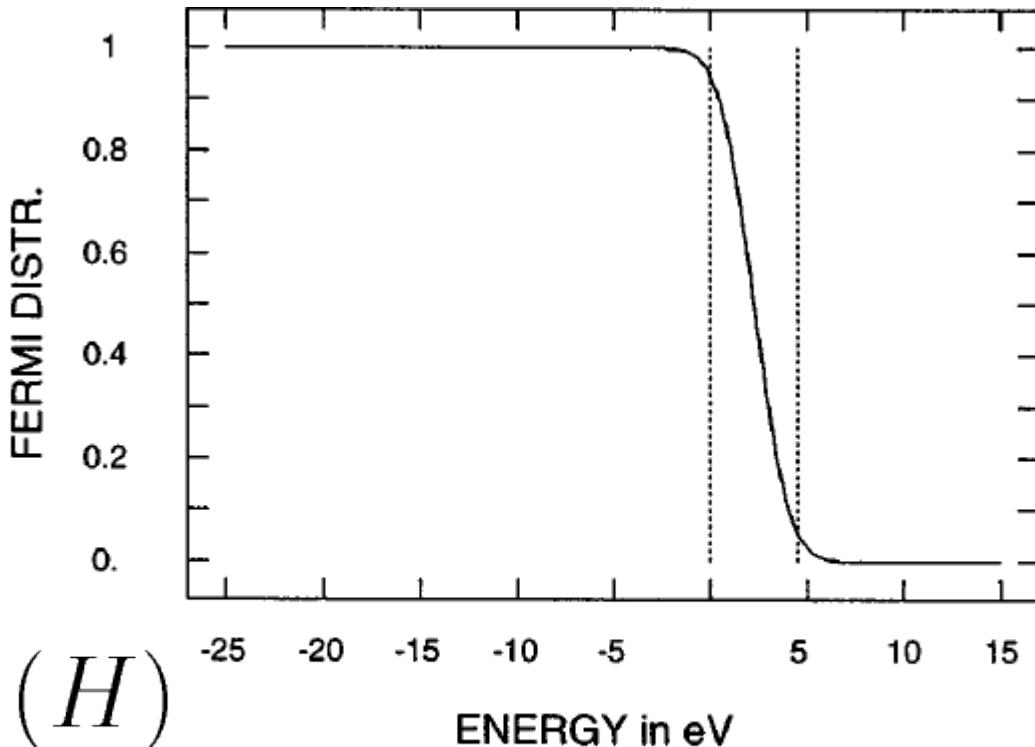


FIG. 7. The Fermi distribution as obtained by a Chebyshev fit of degree 40 in the case of a diamond structure. The band gap is in between the two vertical lines.

Figure from Goedecker,
Rev. Mod. Phys. **71**, 1085 (1999)

Fermi operator expansion

- Region over which expansion changes from 0 to 1 is the energy resolution $\Delta\varepsilon$ (gap)
- Smaller energy resolution requires higher order expansion
- Use finite temperature distribution to avoid Gibbs oscillation
- In practice use error functions instead (decay faster to 0 and 1 away from gap)
- Rational expansion also possible

Density matrix minimization

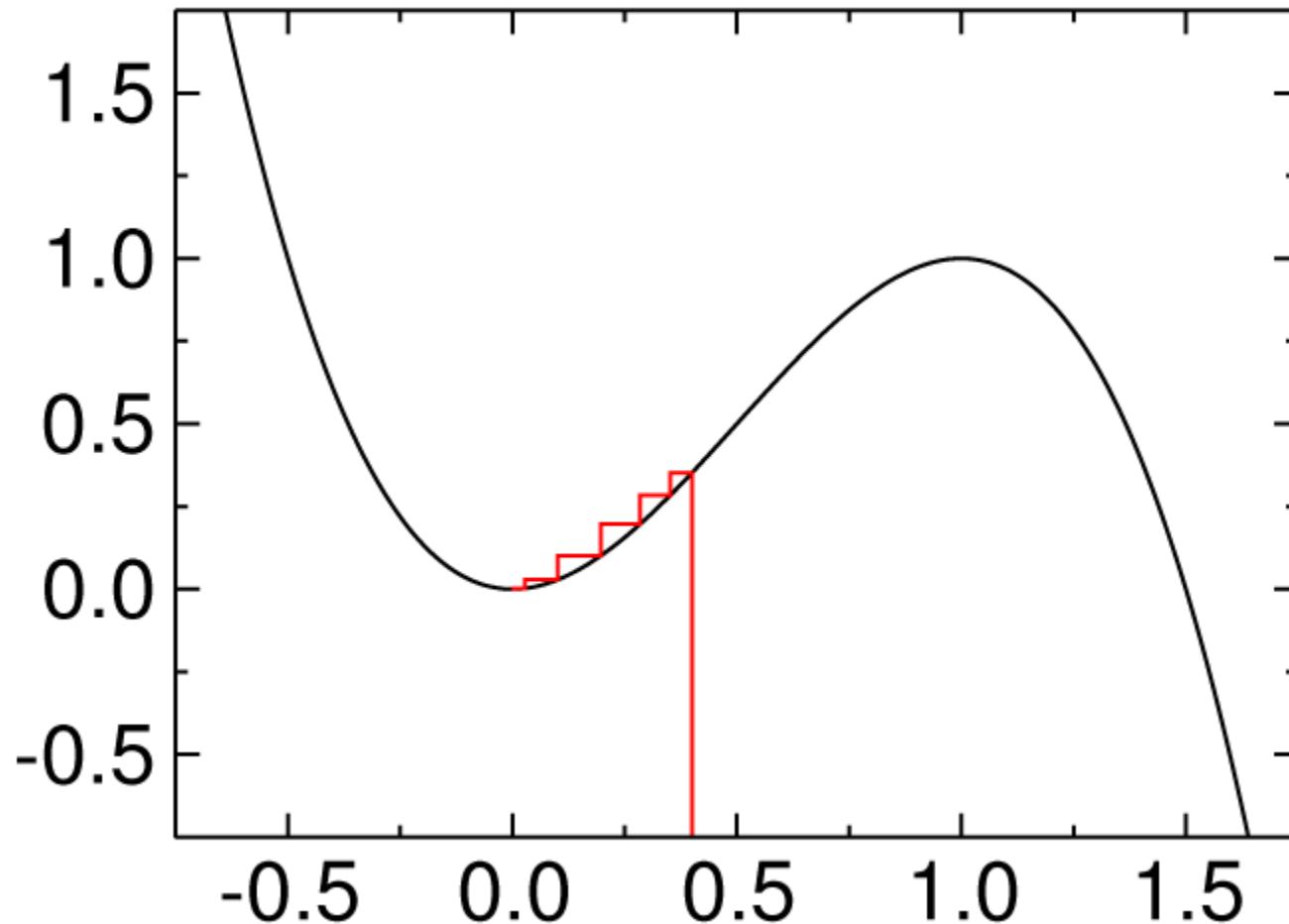
McWeeny, *Rev. Mod. Phys.* **32**, 335 (1960)

Li, Nunes & Vanderbilt, *Phys. Rev. B* **47**, 10891 (1993)

Daw, *Phys. Rev. B* **47**, 10895 (1993)

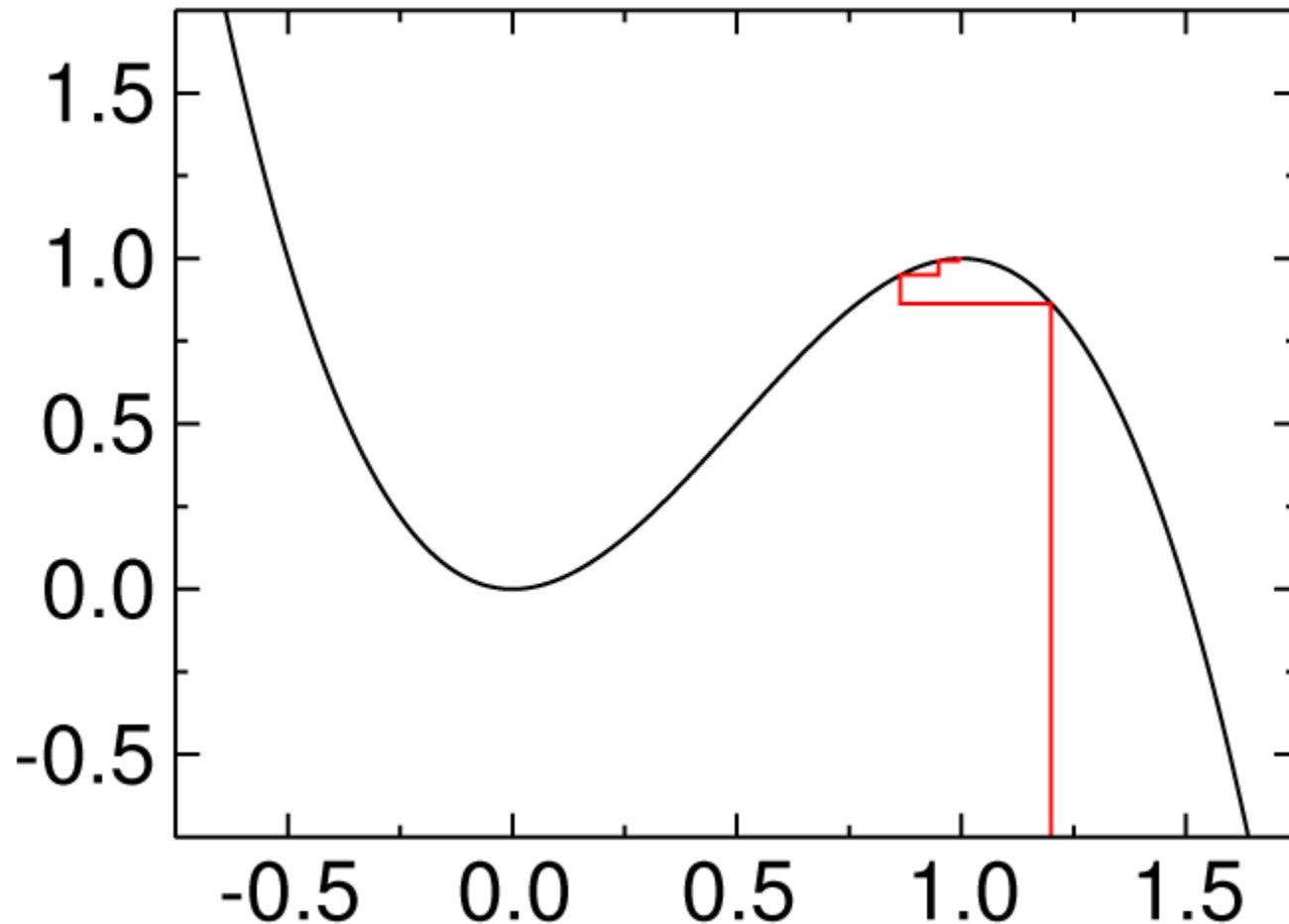
Purifying transformation

$$y = 3x^2 - 2x^3 \quad \Rightarrow \quad x_{k+1} = y(x_k)$$



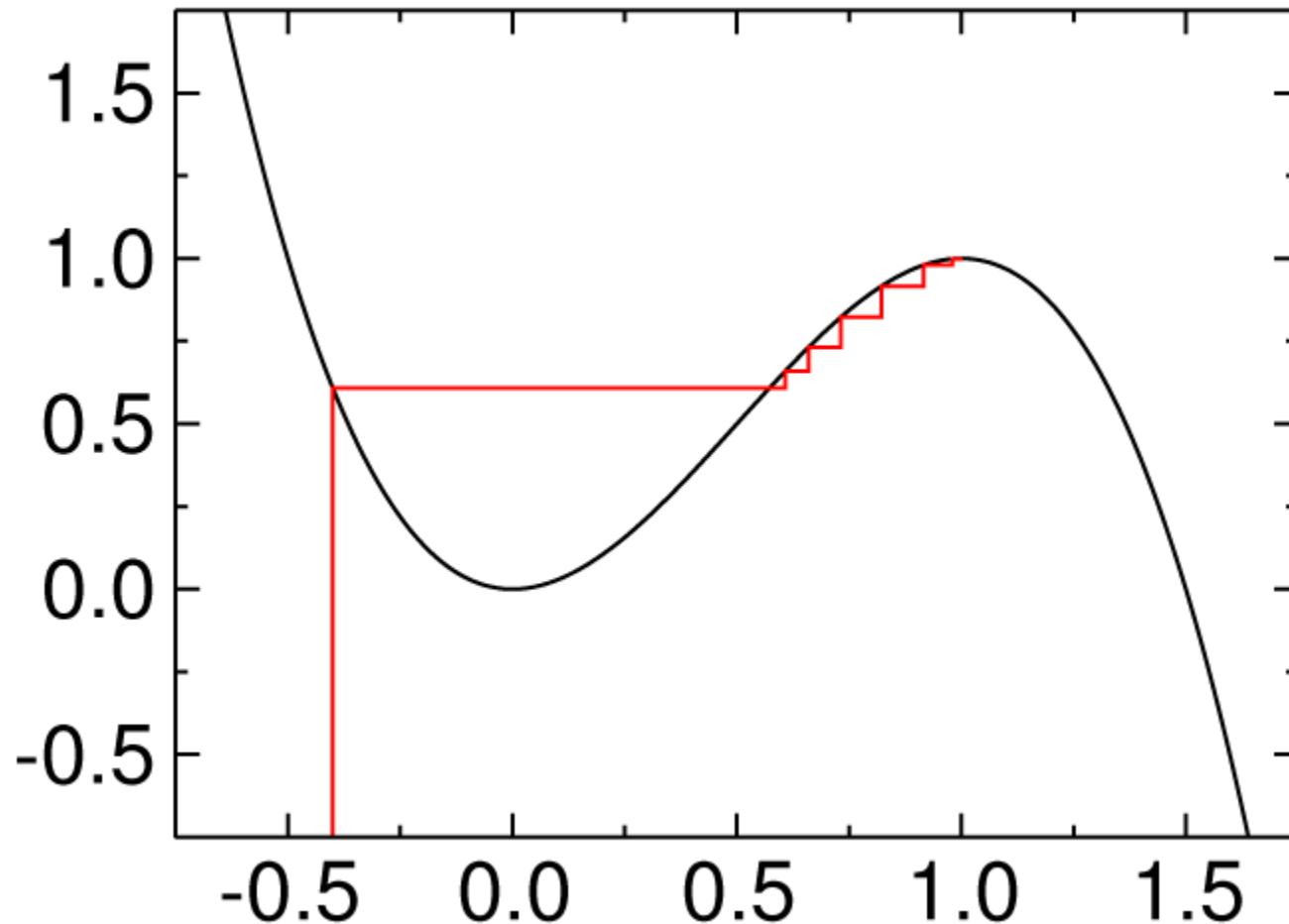
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Purifying transformation

- Apply it to the density matrix:

$$F_{k+1} = 3F_k^2 - 2F_k^3$$

- Iteration converges to 0 or 1 as long as:

$$f_n \in \left(\frac{1-\sqrt{5}}{2}, \frac{1+\sqrt{5}}{2} \right)$$

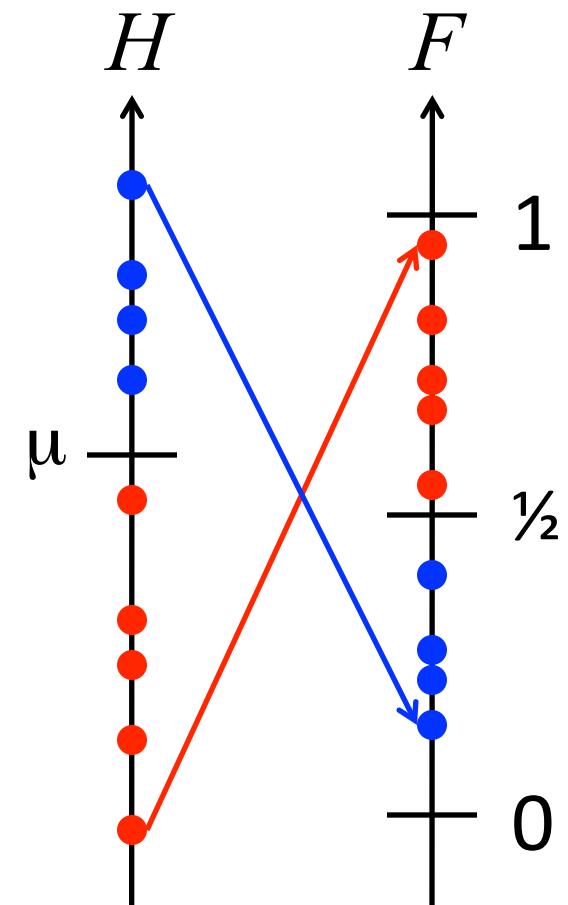
- Converges without “flipping” if:

$$f_n \in \left[\frac{1-\sqrt{3}}{2}, \frac{1+\sqrt{3}}{2} \right]$$

Canonical purification

Palser & Manolopoulos, *Phys. Rev. B* 58, 12704 (1998)

- Start with Hamiltonian
- Shift, invert and scale so eigenvalues lie in $[0,1]$
- Apply purification transformation until convergence achieved



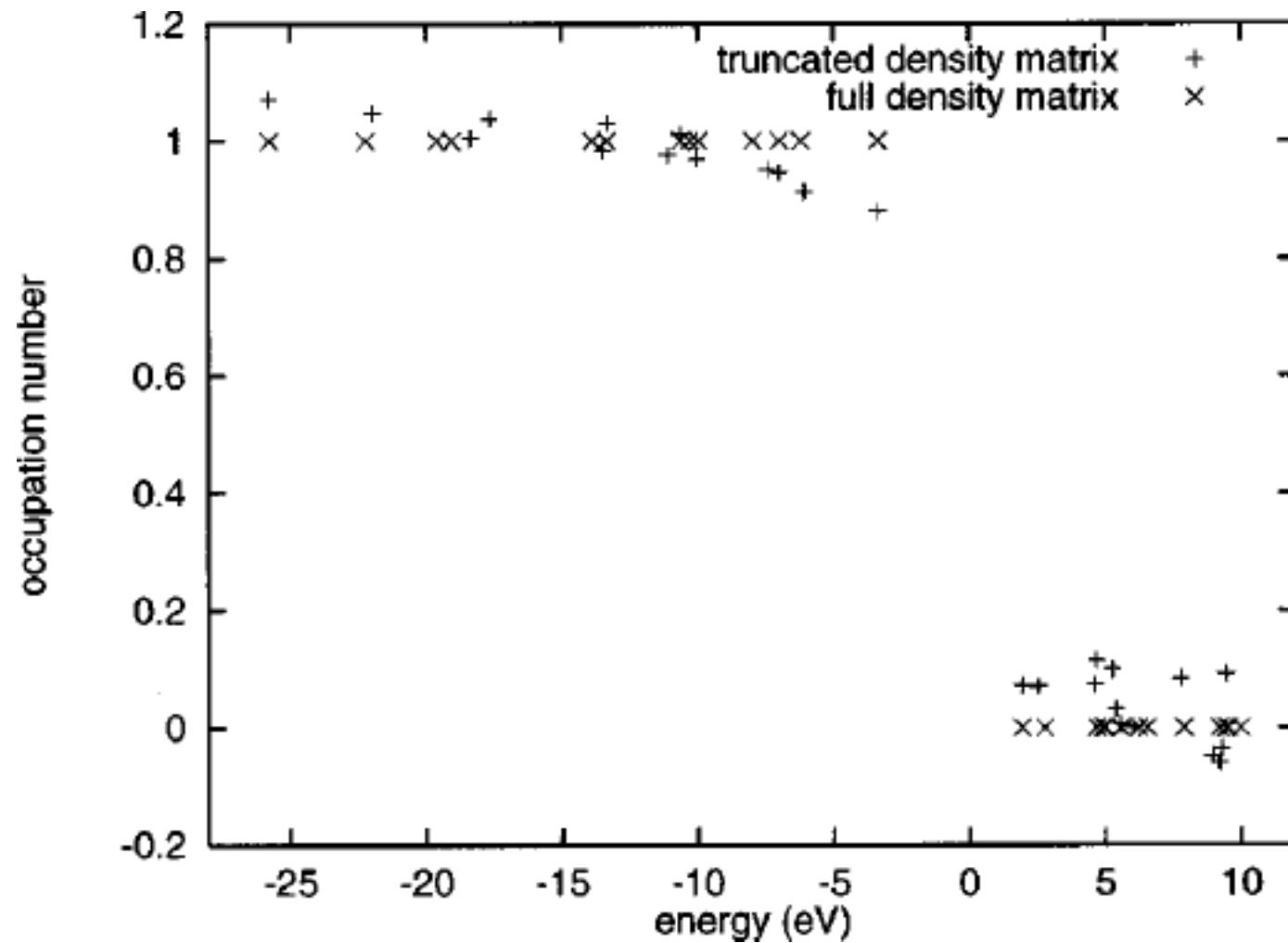
Li-Nunes-Vanderbilt

- Define a purified density matrix P

$$P = 3F^2 - 2F^3$$

- Minimize $E = \text{tr}(PH)$ with respect to F
- Truncate F to obtain linear scaling
- Variational method

Li-Nunes-Vanderbilt



Goedecker, Rev. Mod. Phys. 71,
1085 (1999)

Orbital minimization

Mauri *et al.*, *Phys. Rev. B* **47**, 9973 (1993)

Ordejón *et al.*, *Phys. Rev. B* **48**, 14646 (1993)

Mauri & Galli, *Phys. Rev. B* **50**, 4316 (1994)

Ordejón *et al.*, *Phys. Rev. B* **51**, 1456 (1995)

Kim *et al.*, *Phys. Rev. B* **52**, 1640 (1995)

Orbital minimization

- Works with Wannier functions rather than density matrix
- Imposes the orthogonality constraint by expanding the inverse overlap matrix about the identity:

$$\begin{aligned} S^{-1} &= [I - (I - S)]^{-1} \\ &= I + (I - S) + (I - S)^2 + \dots \\ &\approx 2I - S \end{aligned}$$

Orbital minimization

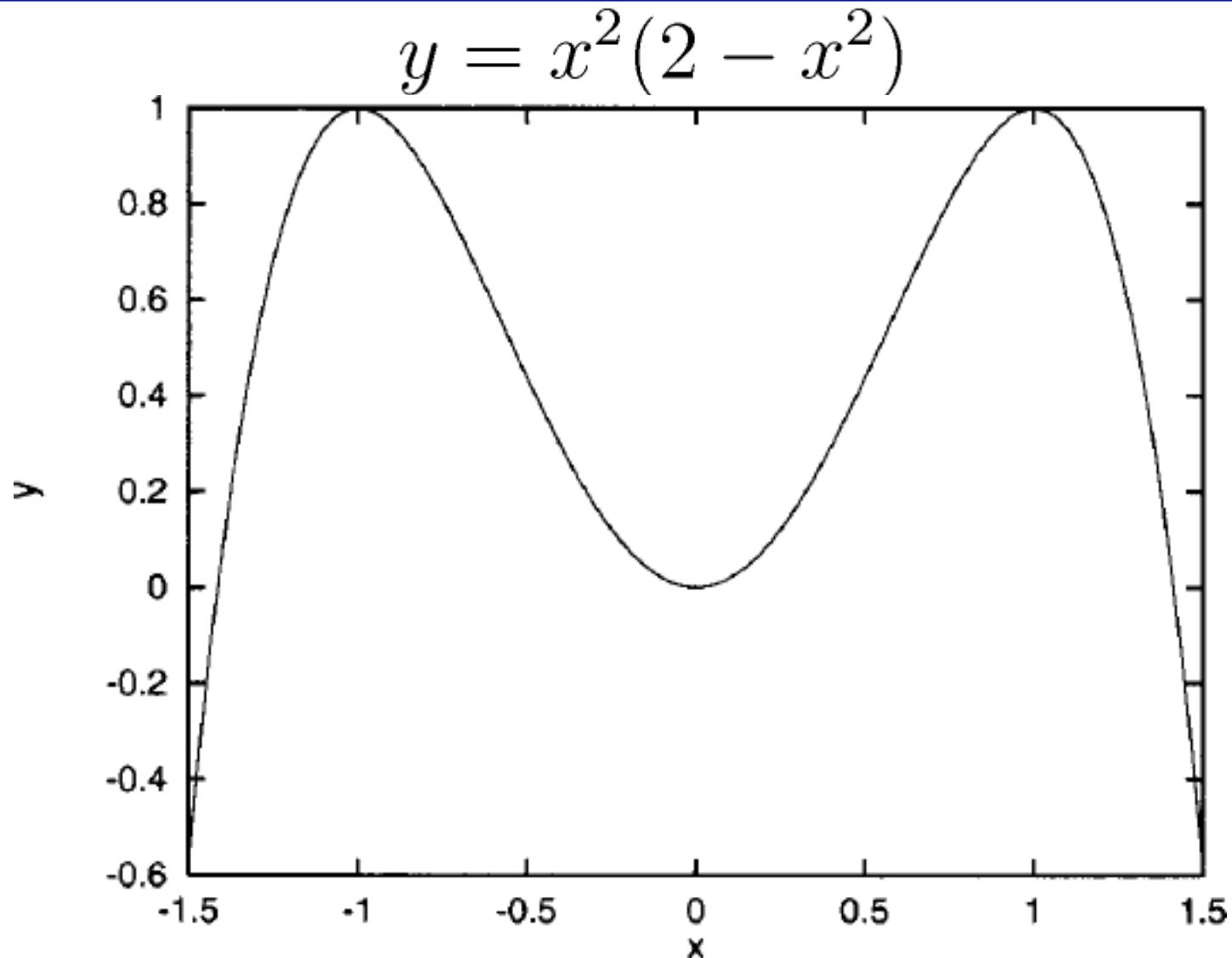
- Leads to a generalized functional:

$$\Omega = 2 \sum_n \sum_{ij} c_{in}^* H'_{ij} c_{jn} - \sum_{nm} \sum_{ij} c_{in}^* H'_{ij} c_{jm} \sum_k c_{km}^* c_{kn}$$

– where $H' = H - \mu I$

- Quartic in the coefficients c
- Solve for localized orbitals to obtain linear scaling

Orbital minimization



Orbital minimization

- With localization constraints:
 - Large number of iterations required
 - Atom-centred Wannier functions can break symmetry
 - Local minimum so runaway solutions possible
 - Problems conserving electron number
 - Generally considered more challenging than density-matrix minimization

Yang, *Phys. Rev. B* **56**, 9294 (1997)

Orbital-free DFT (metals!)

Wang and Carter, in *Theoretical Methods in Condensed Phase Chemistry*, edited by S.D. Schwartz (Kluwer, Dordrecht, 2000), p. 117

Orbital-free DFT

- Aim to improve upon Thomas-Fermi:

$$T_s[n] = \frac{3}{10} (3\pi^2)^{2/3} \int n(\mathbf{r})^{5/3} d^3r$$

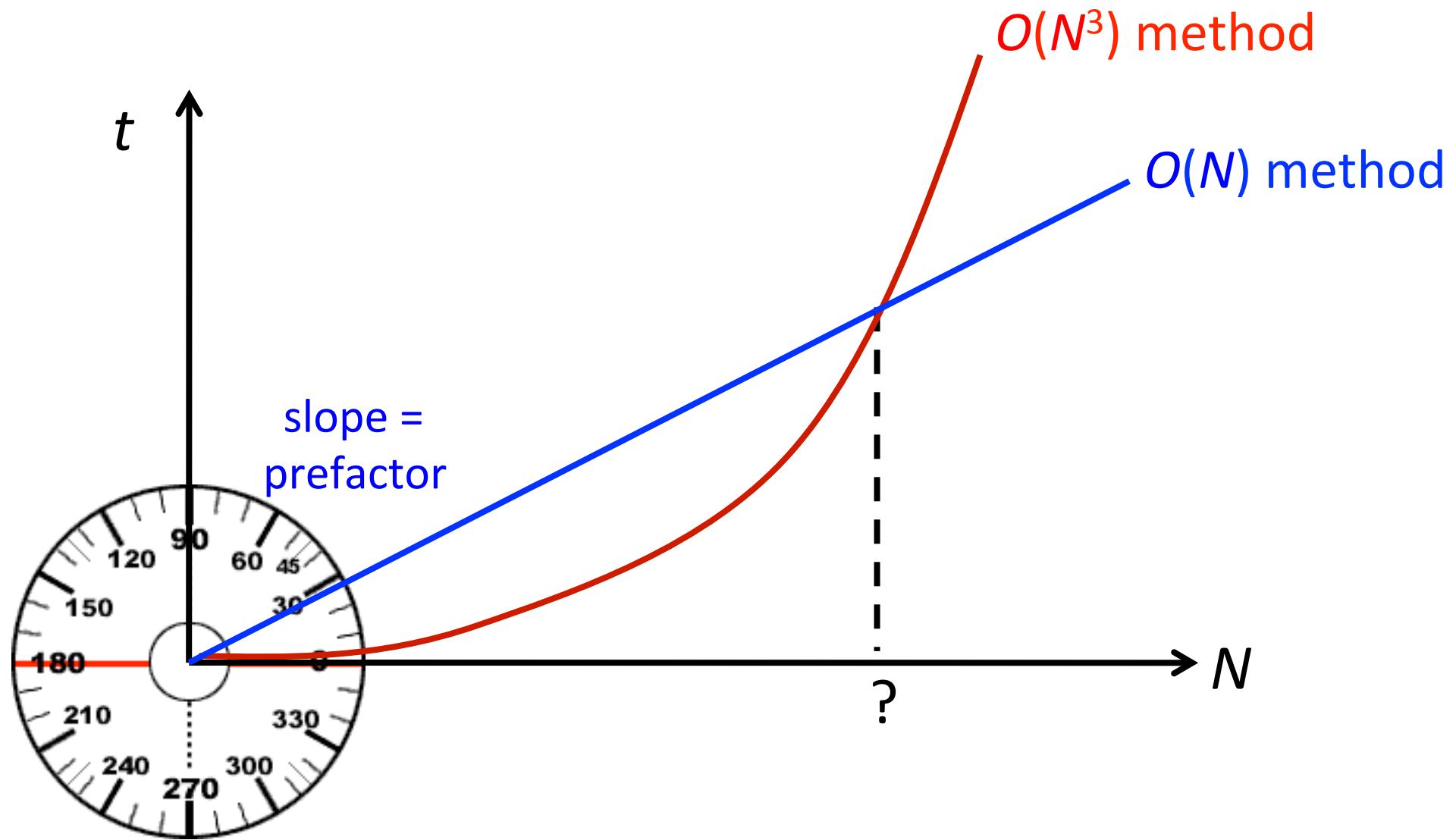
- von Weizsäcker: *Z. Phys.* **96**, 431 (1935)

$$+ \frac{\lambda}{8} \int \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})} d^3r$$

- Linear response of the electron gas (Lindhard)
- Angular momentum dependence via a muffin-tin construction:

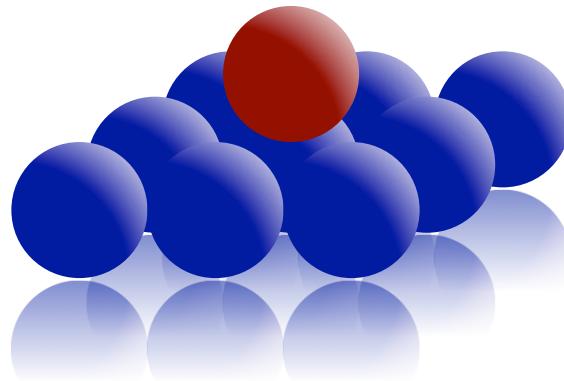
Ke *et al.*, *Phys. Rev. Lett.* **111**, 066402 (2013)

What's the cross-over?



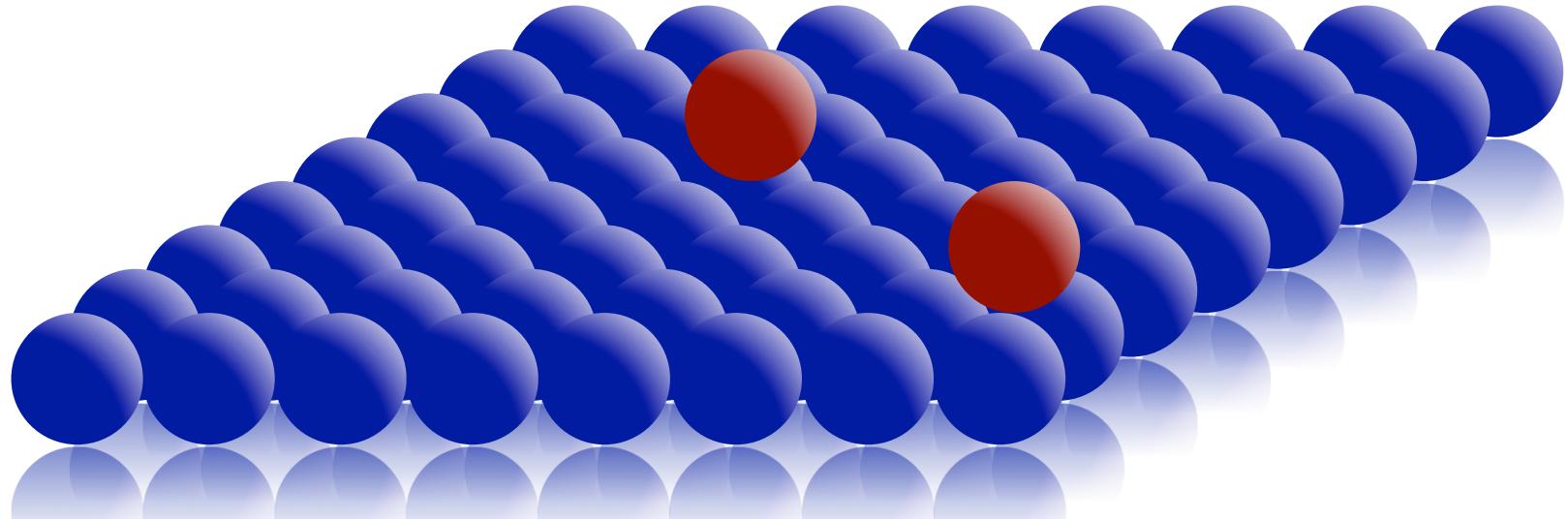
1. The possibilities are endless

- Explosion of phase space:
 - arrangement of adatoms on a surface
 - distribution of defects in bulk
 - time-scales for protein folding



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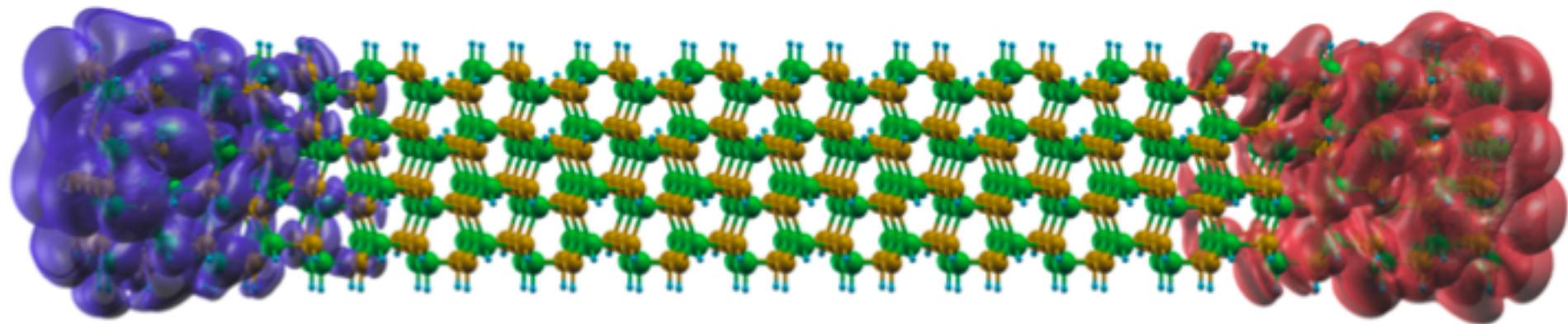
2. Energy and forces are not enough

- That is all most $O(N)$ codes output
 - but vastly more information is generated
 - e.g. optimized local orbitals (Wannier functions)
- Importance of link to experiment

So what is linear-scaling DFT good for?

1. Specific systems that exploit the advantages of the method

Phil Avraam, Nicholas Hine, Paul Tangney, PDH

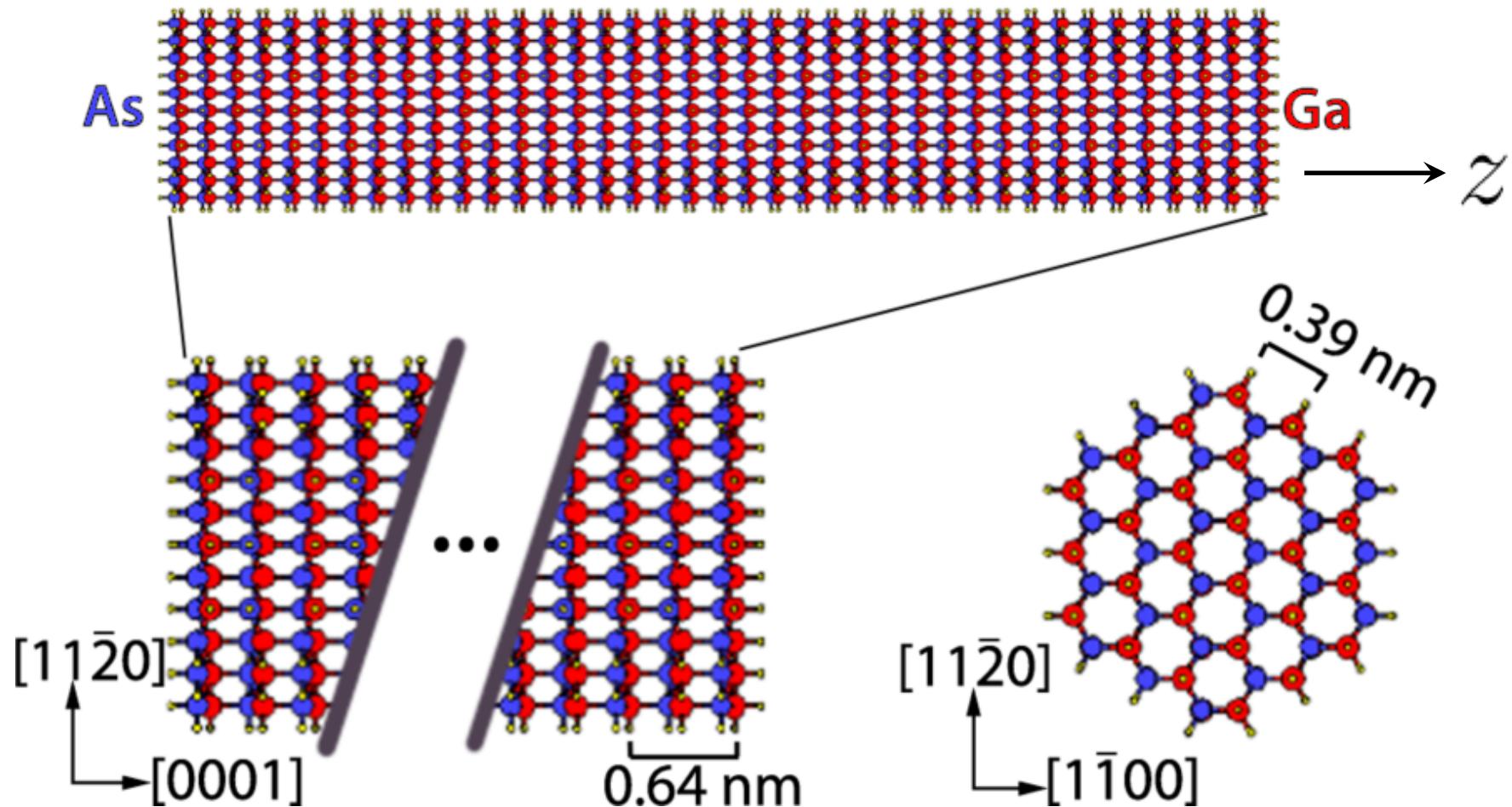


Phys. Rev. B **83**, 241402(R) (2011)

Phys. Rev. B **85**, 115404 (2012)

Model polar nanorod

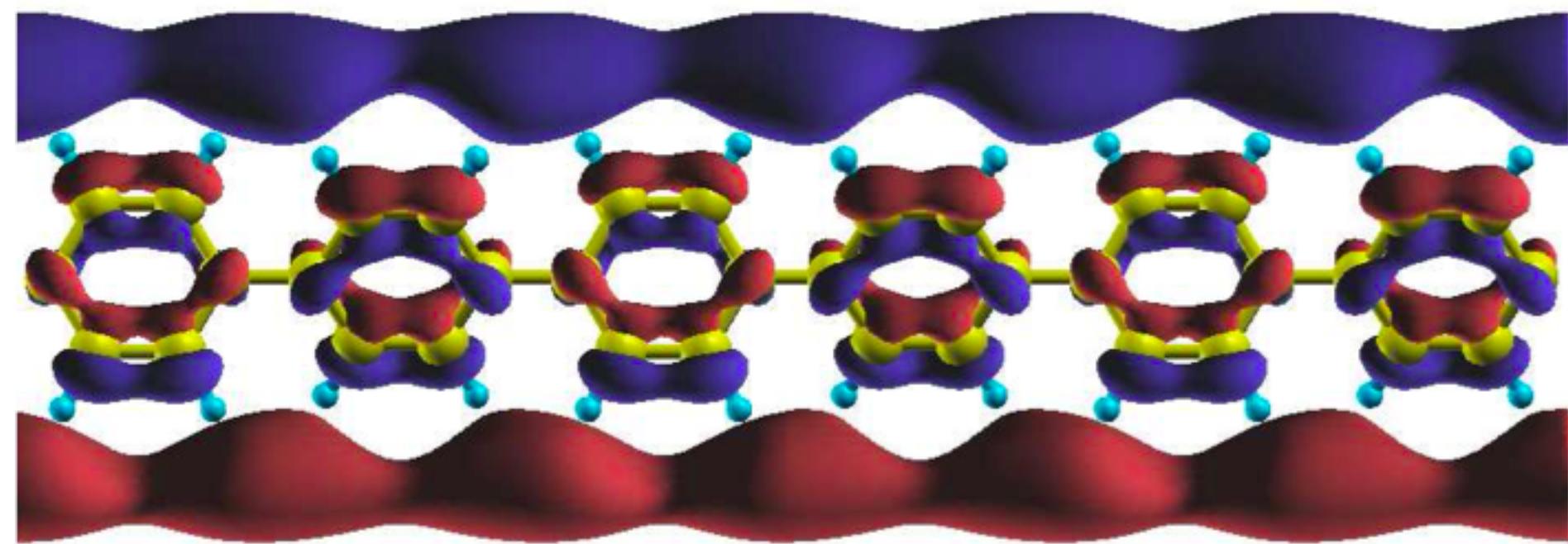
Variety of surface terminations: bare, H, “pseudo-atoms”



Correct treatment of electrostatics: *Hine et al., J. Chem. Phys. 135, 204103 (2011)*

2. Theoretical spectroscopy?

Laura Ratcliff, Nicholas Hine, Tim Zuehlsdorff, PDH

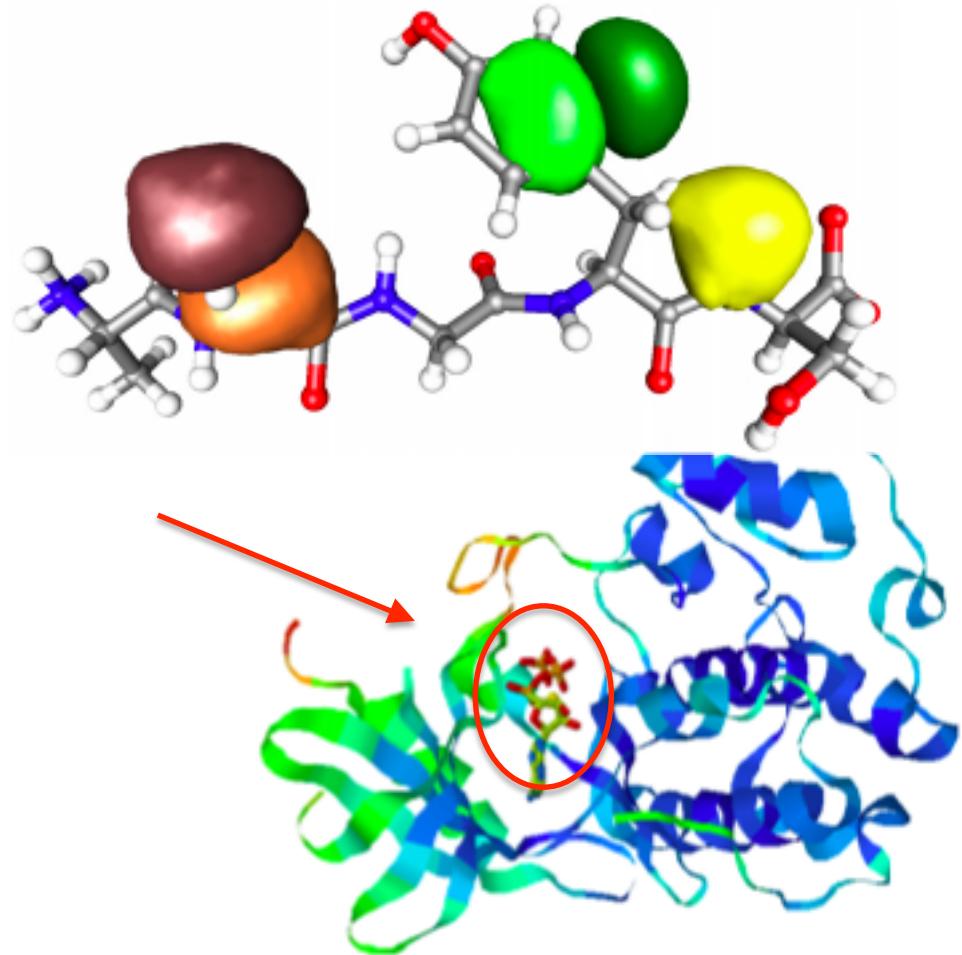


Phys. Rev. B **84**, 165131 (2011)

J. Chem. Phys. **139**, 064104 (2013)

3. As one part of a multiscale strategy

- Local orbitals enable more flexible boundary conditions
- Vary accuracy in space
- Easier to embed in a larger simulation



More information

David Bowler and Tsuyoshi Miyazaki
“ $O(N)$ methods in electronic structure calculations”
Rep. Prog. Phys. **75**, 036503 (2012)

Stefan Goedecker
“Linear scaling electronic structure methods”
Rev. Mod. Phys. **71**, 1085 (1999)