Imperial College London

THE THOMAS YOUNG CENTRE TyC

Linear Scaling Density-Functional Theory

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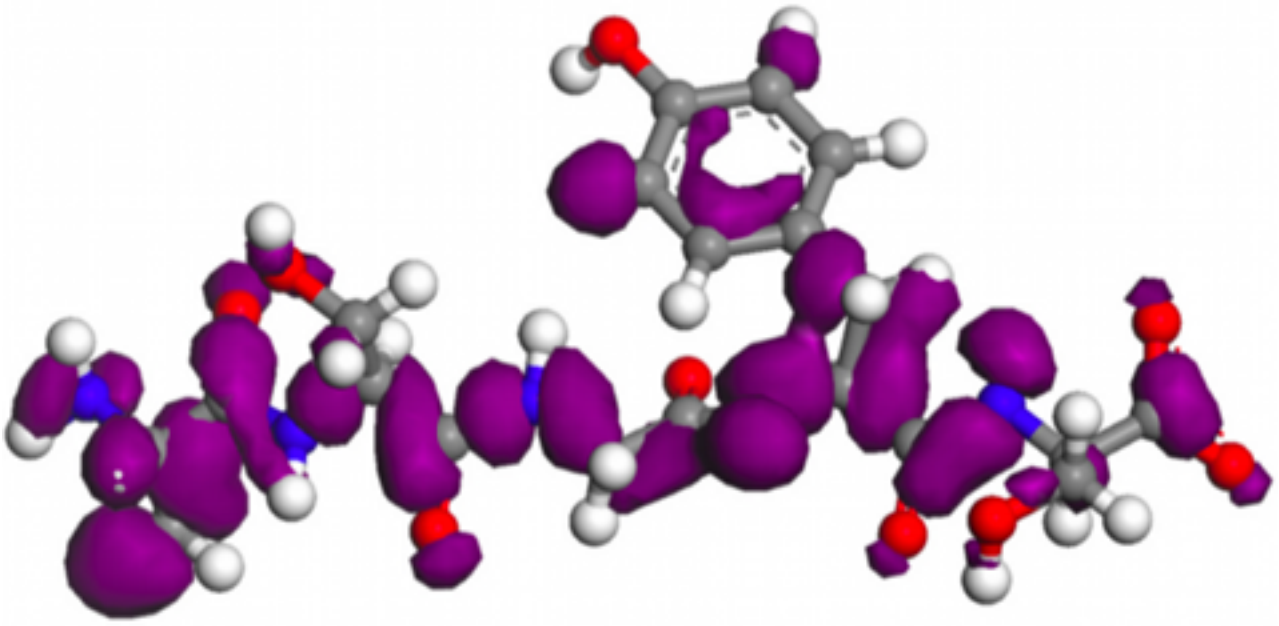
20+ years of *O*(*N*) DFT

- 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

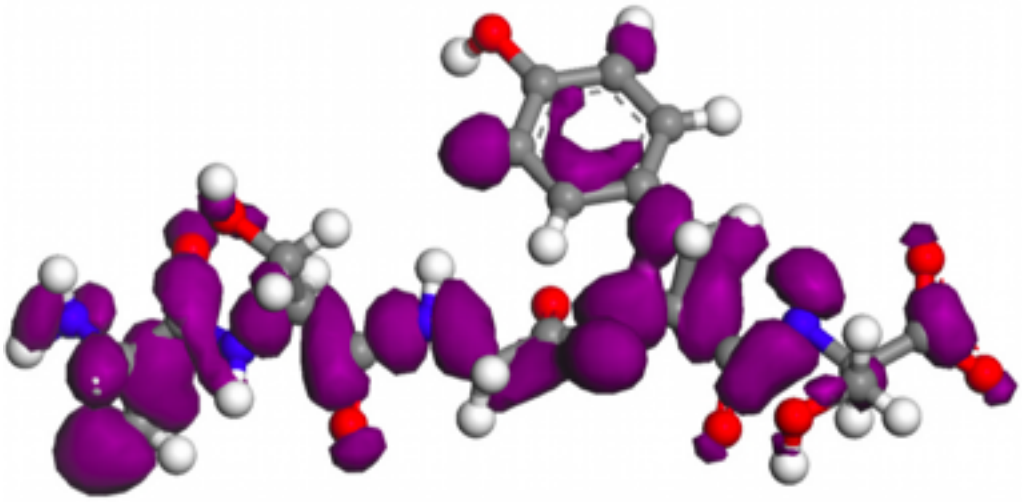


$$\left[-\frac{1}{2}\nabla^2 + V_\sigma^{\mathrm{eff}}\right]\psi_{n\mathbf{k}\sigma} = \varepsilon_{n\mathbf{k}\sigma}\psi_{n\mathbf{k}\sigma}$$

- 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

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

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- 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

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

- 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
- No spin
- Sample Brillouin zone at Γ only
- (Localised) orthogonal basis set

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- No spin
- Sample Brillouin zone at Γ only
- (Localised) orthogonal basis set
  - *M* basis functions → H is *M* x *M* matrix

$$H_{ij} = \langle \phi_i | \left(-\tfrac{1}{2}\nabla^2 + V \right) | \phi_j \rangle = \sum_n c_{in} \varepsilon_n c^*_{jn}$$

→ 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 → H is *M* x *M* matrix
  - *N* lowest states required

  → 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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$$E = \sum_{n}^{\text{all}} f_n \varepsilon_n$$

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  - 1 for occupied states
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Total energy methods

- Energy of the Kohn-Sham system:

$$E = \sum_{n}^{\text{all}} f_n \varepsilon_n$$

- Introduce occupation numbers f_n:
  - 1 for occupied states
  - 0 for unoccupied states
- Finite temperature:

$$f_n = f(\varepsilon_n) \qquad f(\varepsilon) = \frac{1}{1 + \exp\left(\frac{\varepsilon - \mu}{k_\mathrm{B} T}\right)}$$

Total energy methods

- Energy of the Kohn-Sham system:

$$E = \sum_{n}^{\text{all}} f_n \varepsilon_n$$

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

Off-diagonal representation

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

- Trace is invariant under similarity transformation:

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

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

Off-diagonal representation

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

- Trace is invariant under similarity transformation:

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

$$E = \mathrm{tr}(FH) = \sum_{ij} F_{ij} H_{ji}$$

Density matrix

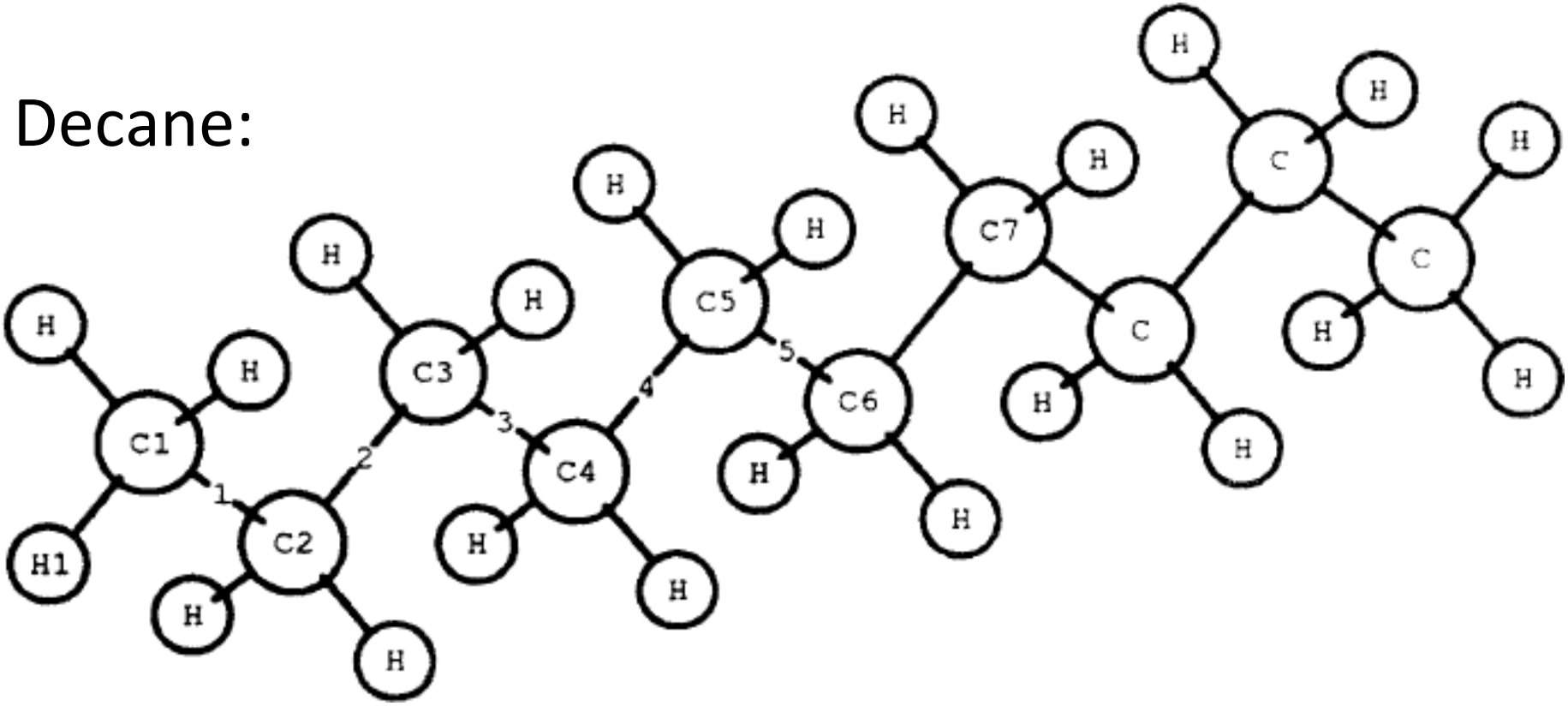
- F is the *single-particle* density matrix
  - F commutes with H (simultaneously diagonalizable)
  - Trace of F is the number of electrons (sum of occupation numbers)
  - At zero temperature F is idempotent: $F^2 = F$ (requires orthogonality and the Aufbau principle)

- Solving the Schrödinger equation is equivalent to finding the F that minimizes $E = \mathrm{tr}(FH)$ subject to the above conditions

Nearsightedness

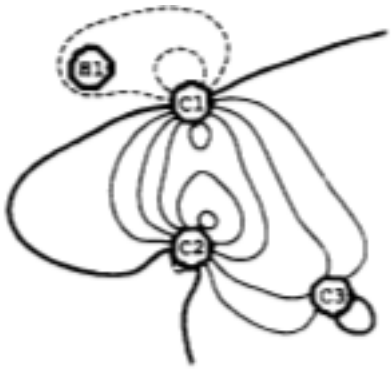
Hierse & Stechel, *Phys. Rev. B* **50**, 17811 (1994)

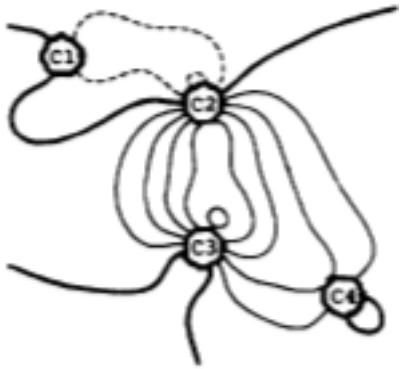
Decane:

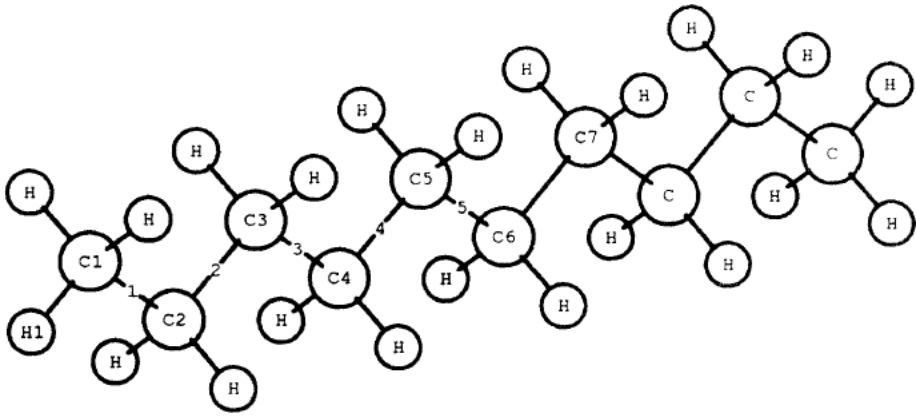


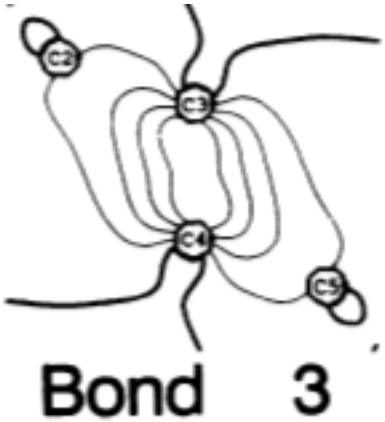
Nearsightedness

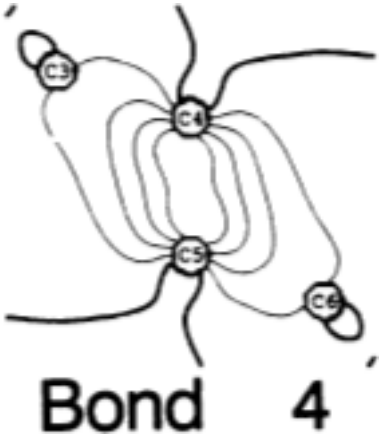
Hierse & Stechel, *Phys. Rev. B* **50**, 17811 (1994)

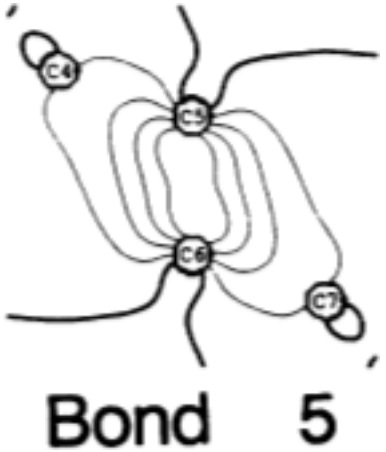












Nearsightedness

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	ΔE_{KS}/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)
  - See also Lecture 10, p. 41 (Frank Neese)

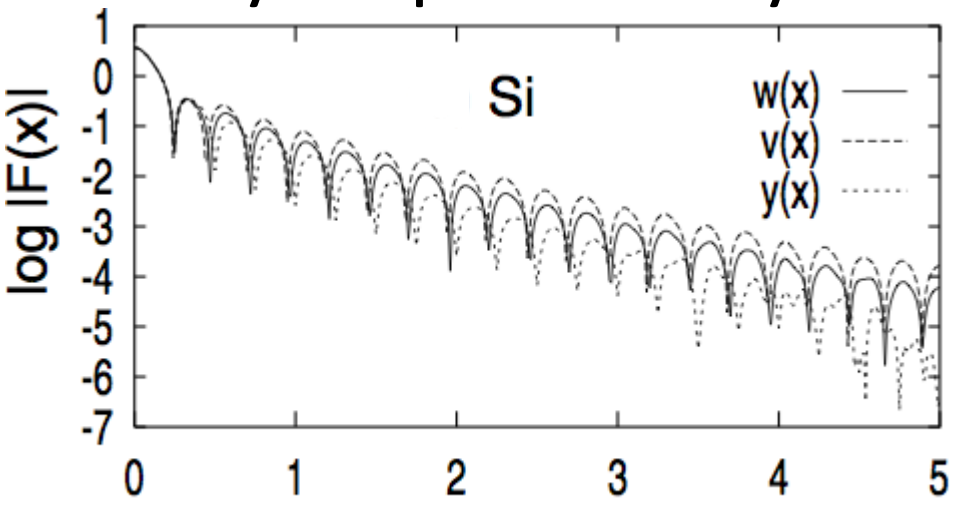


Figure from He & Vanderbilt, *PRL* **86**, 5341 (2001)

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)

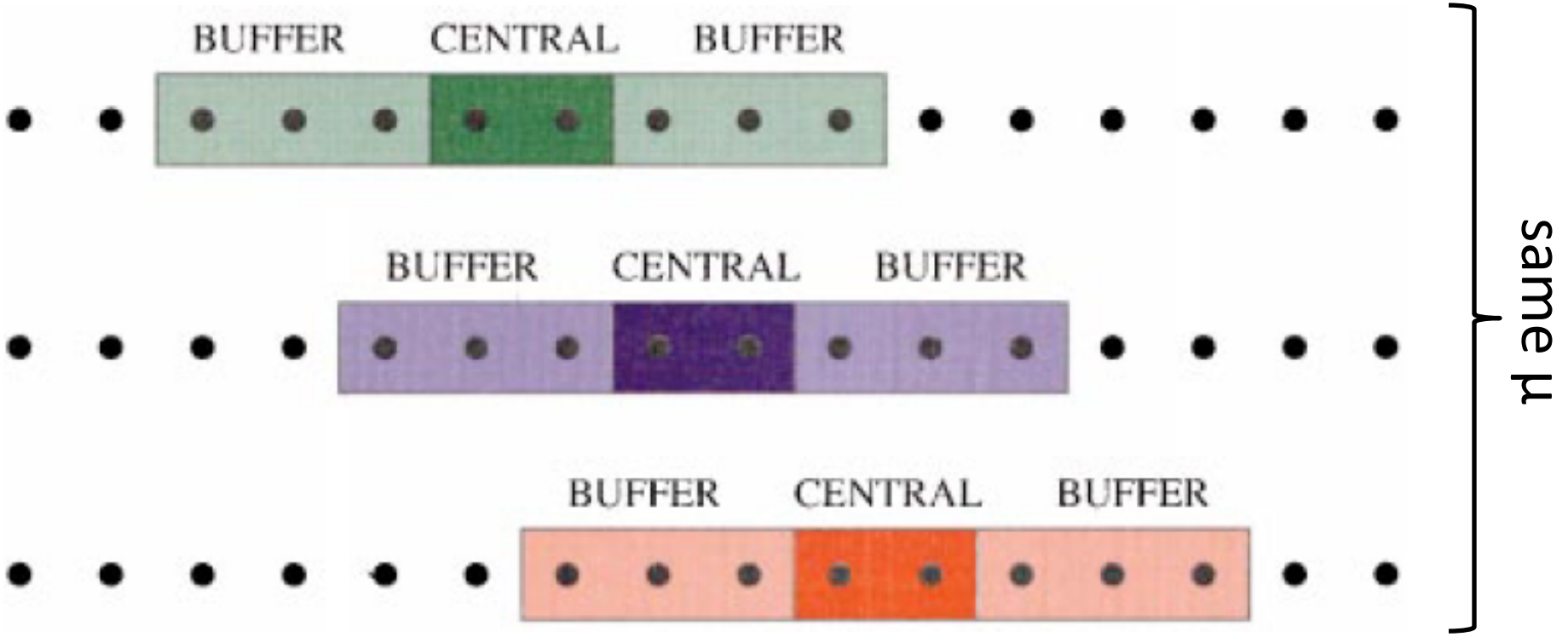


Figure from Goedecker, *Rev. Mod. Phys.* **71**, 1085 (1999)

Divide and conquer

- Trim the corners:

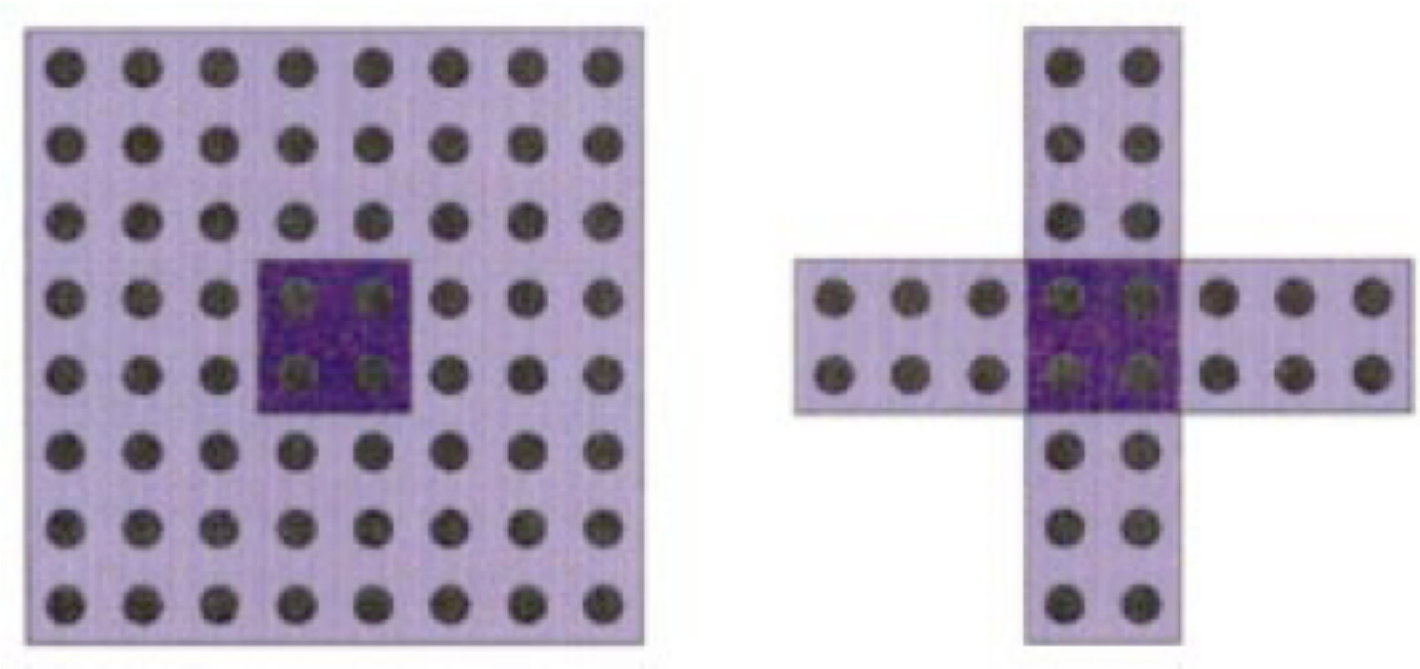


Figure from Goedecker, *Rev. Mod. Phys.* **71**, 1085 (1999)

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.

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.
- Expand F as a polynomial in H i.e.

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

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

Chebyshev polynomials

$$
\begin{aligned}
T_n(x) &= \cos(n \arccos x) \\
T_0(x) &= 1 \\
T_1(x) &= x \\
T_{j+1}(x) &= 2xT_j(x) - T_{j-1}(x)
\end{aligned}
$$

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

Chebyshev polynomials

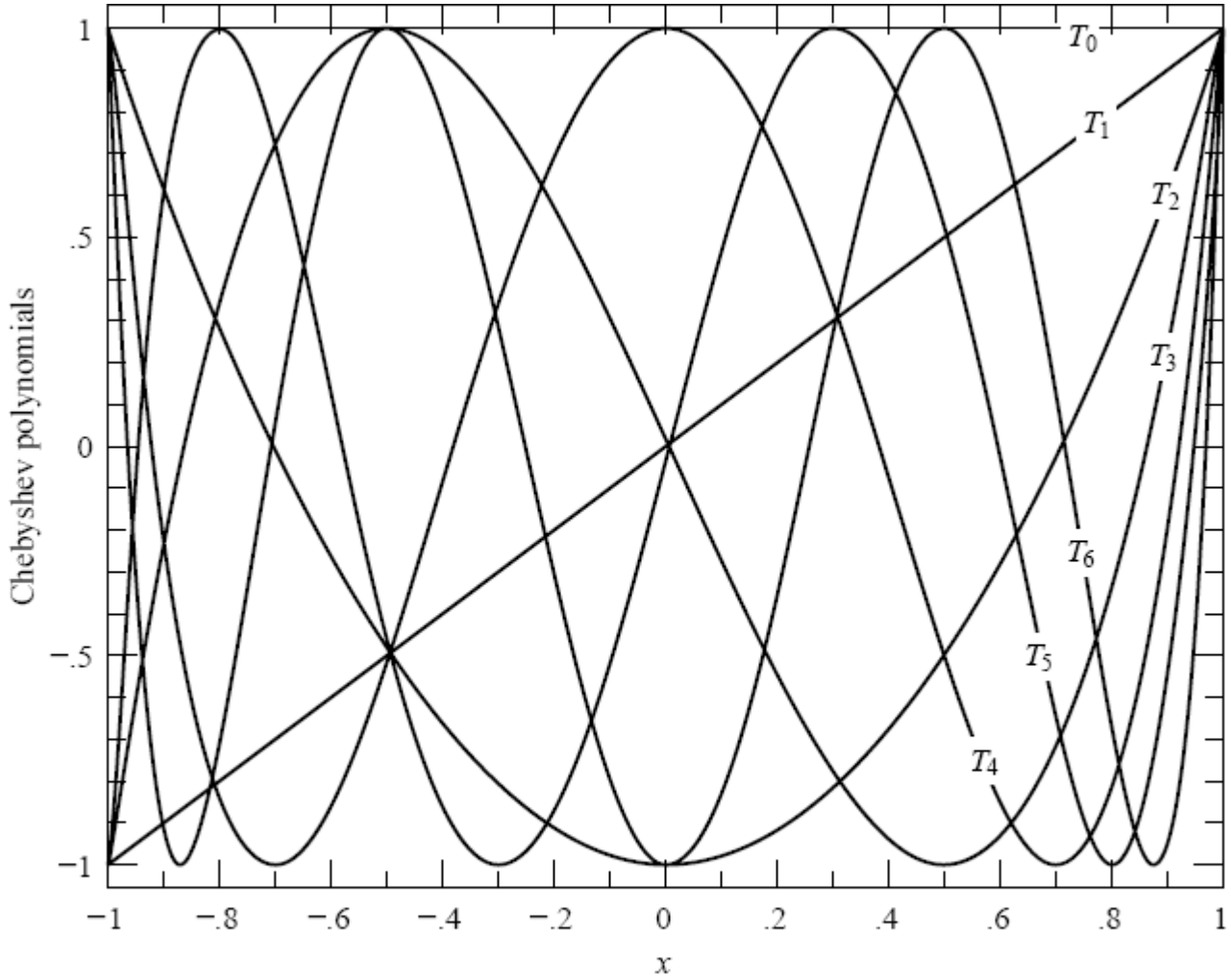


Figure 5.8.1. Chebyshev polynomials $T_0(x)$ through $T_6(x)$. Note that T_j has j roots in the interval $(-1, 1)$ and that all the polynomials are bounded between ± 1.

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

Chebyshev expansion

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

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

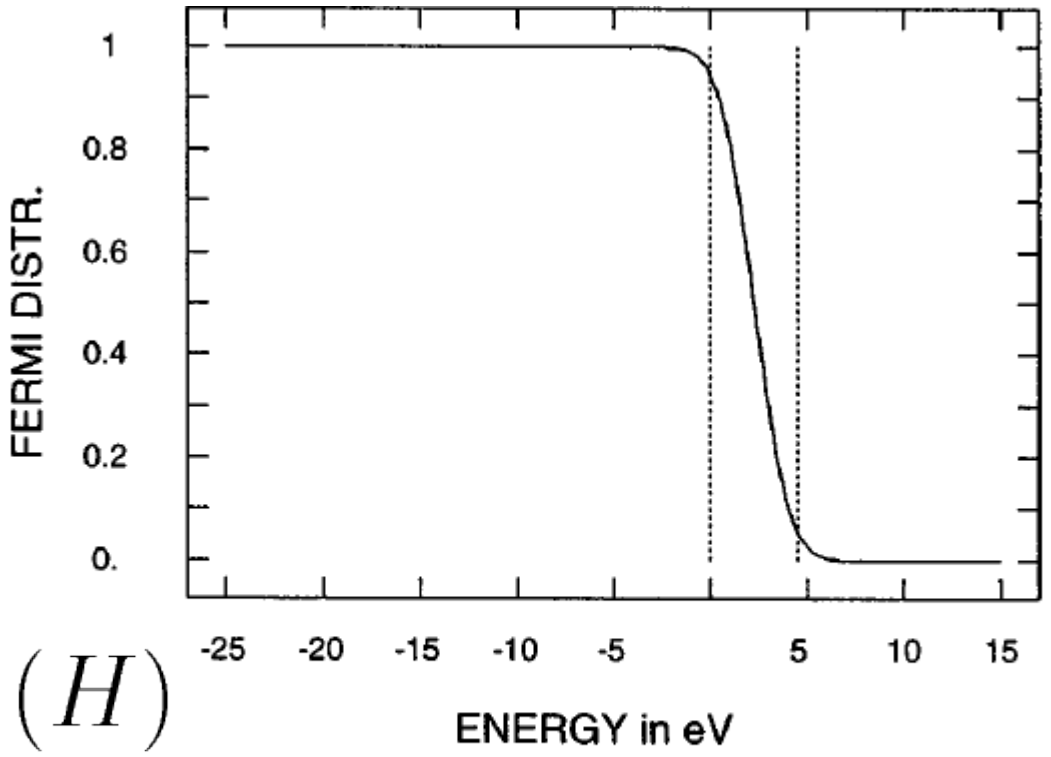


FIG. 7. The Fermi distribution as obtained by a Chebyshev fit of degree 40 in the case of a diamond structure. The band gap is in between the two vertical lines.

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

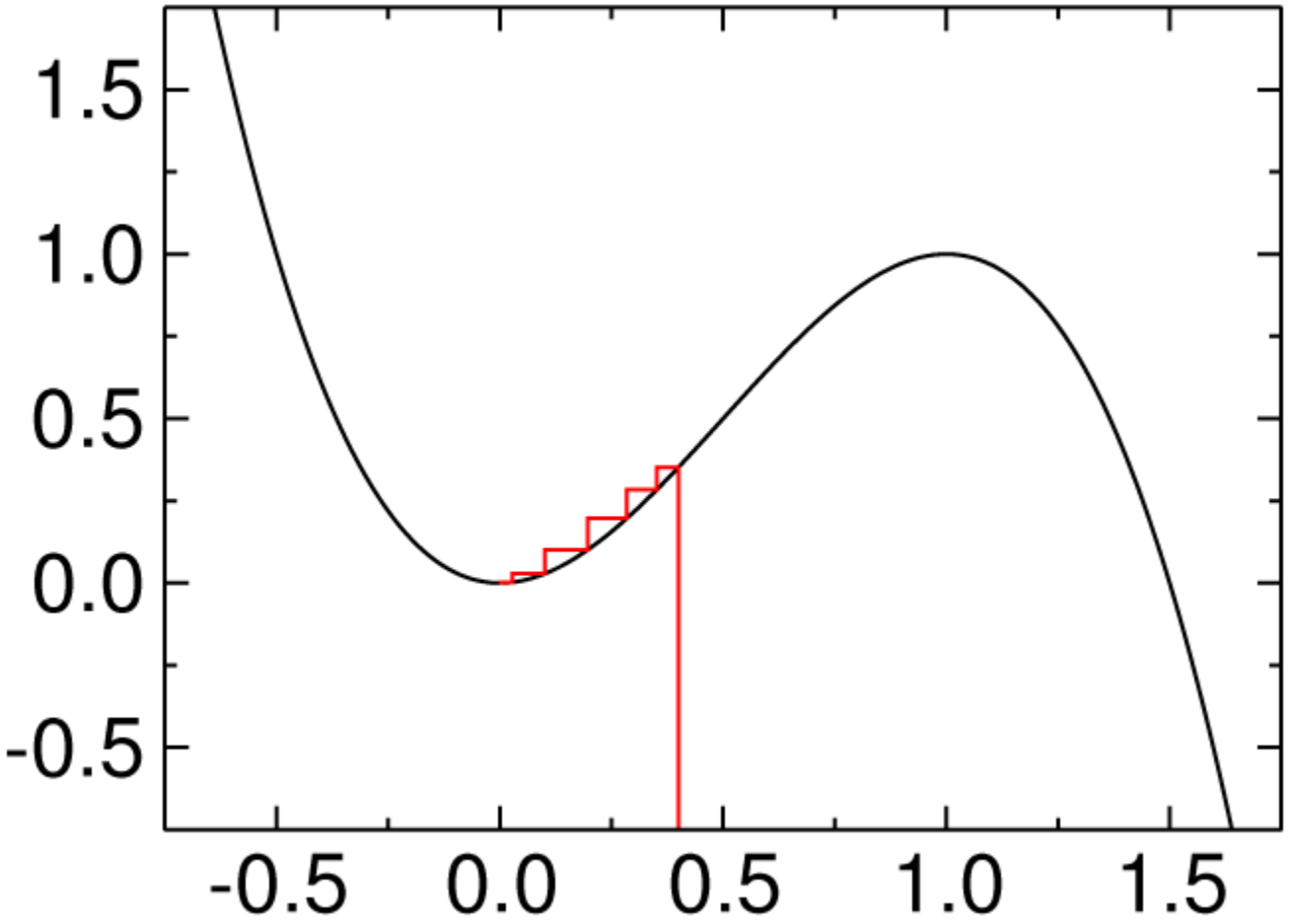
McWeeny, *Rev. Mod. Phys.* **32**, 335 (1960)

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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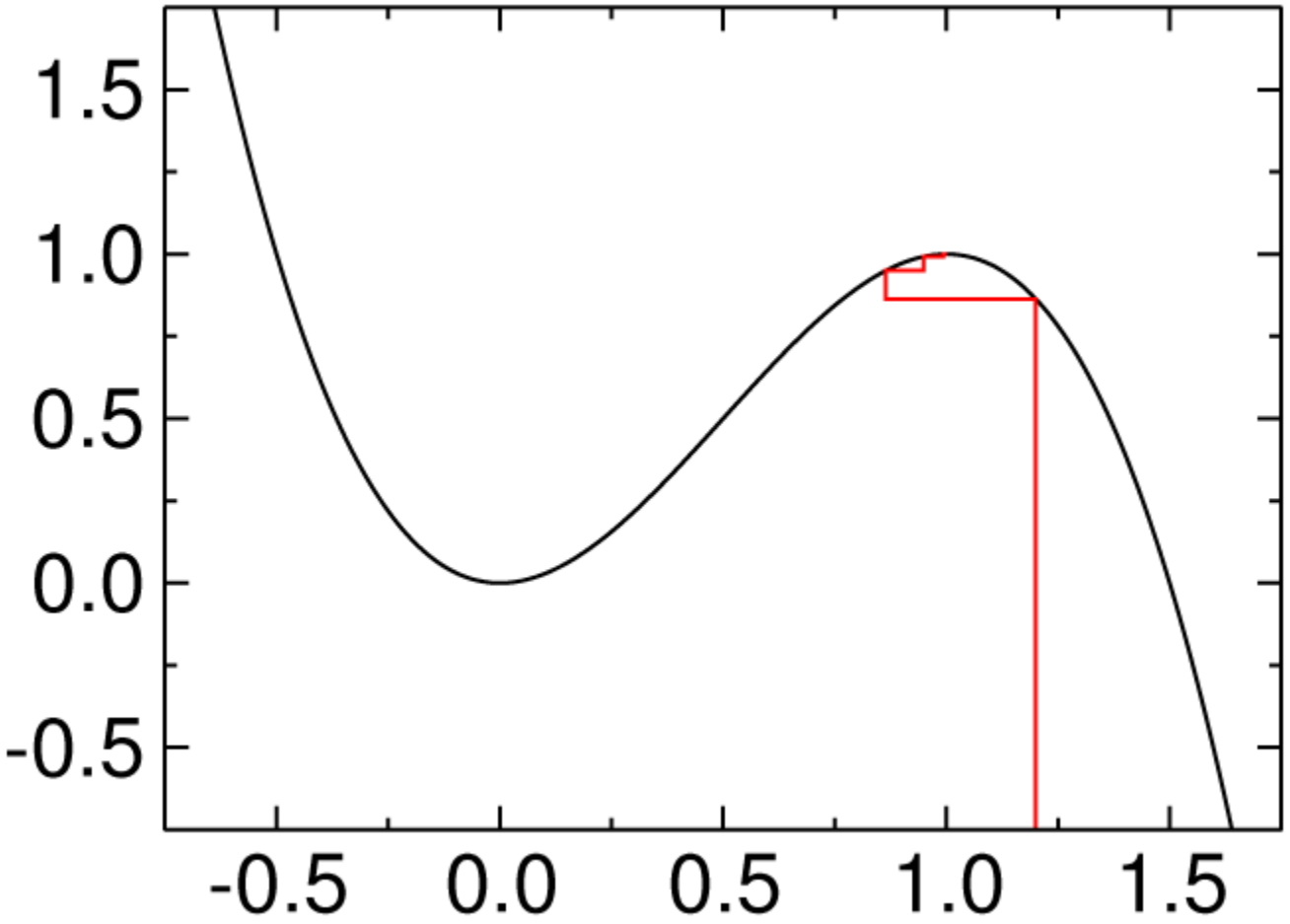

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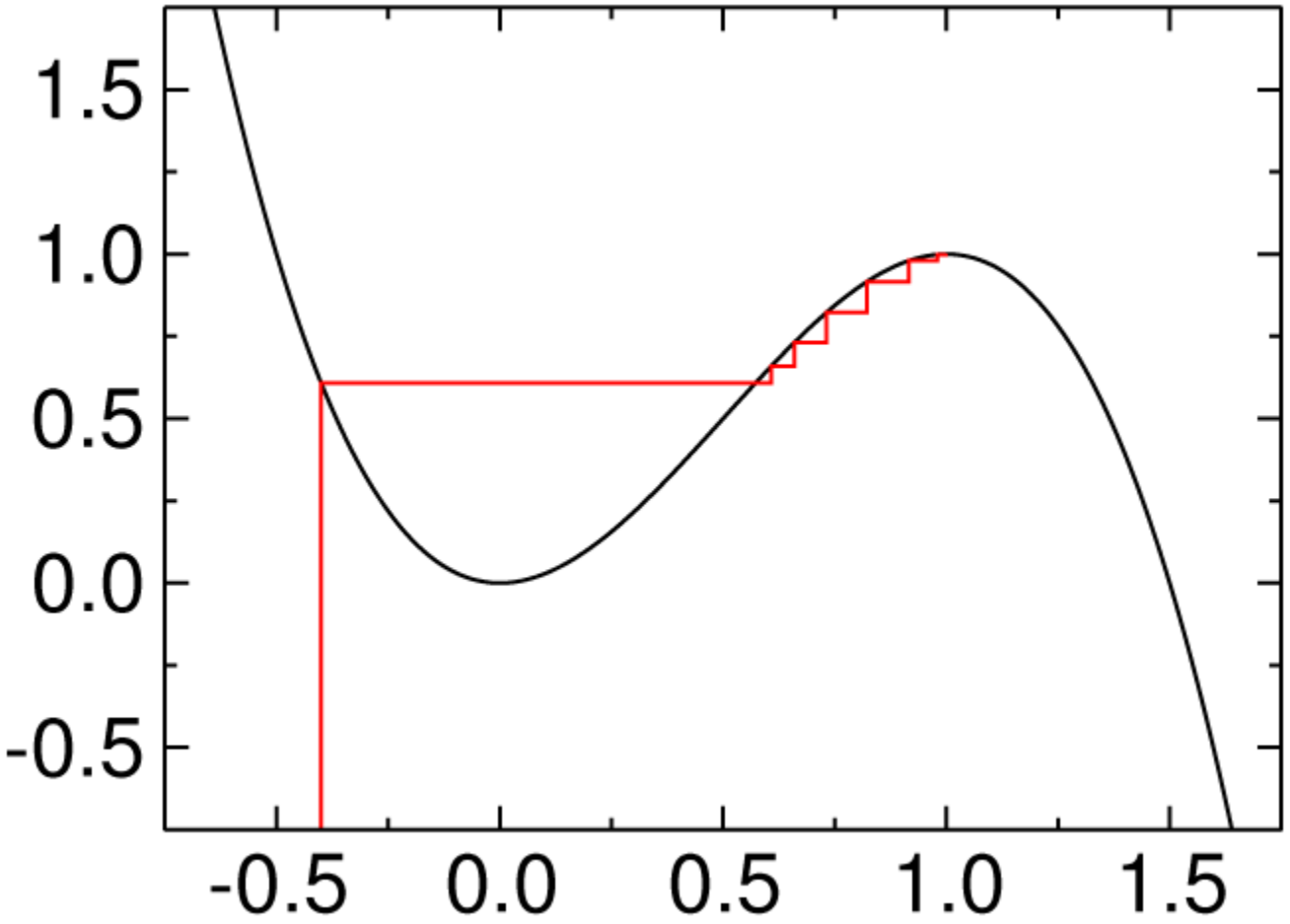


Purifying transformation

- Apply it to the density matrix:

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

- Iteration converges to 0 or 1 as long as:

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

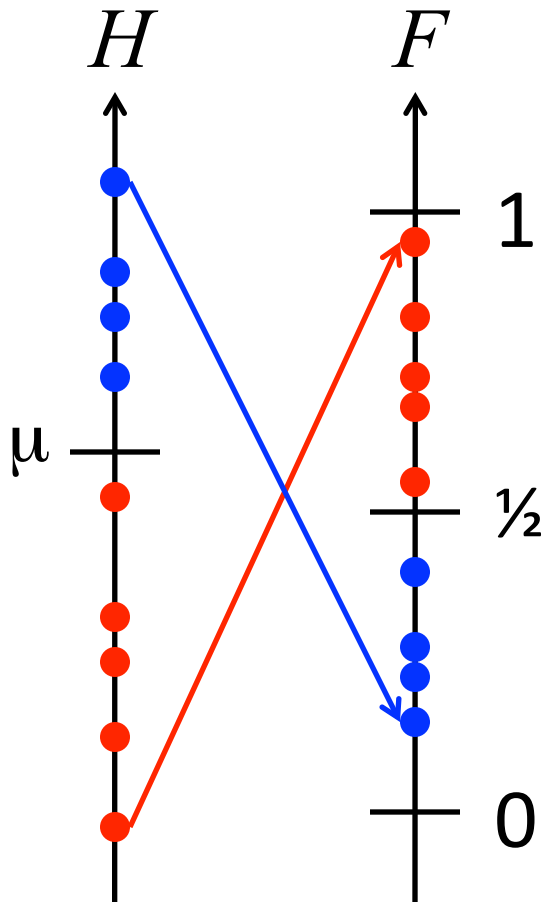
- Converges without "flipping" if:

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

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

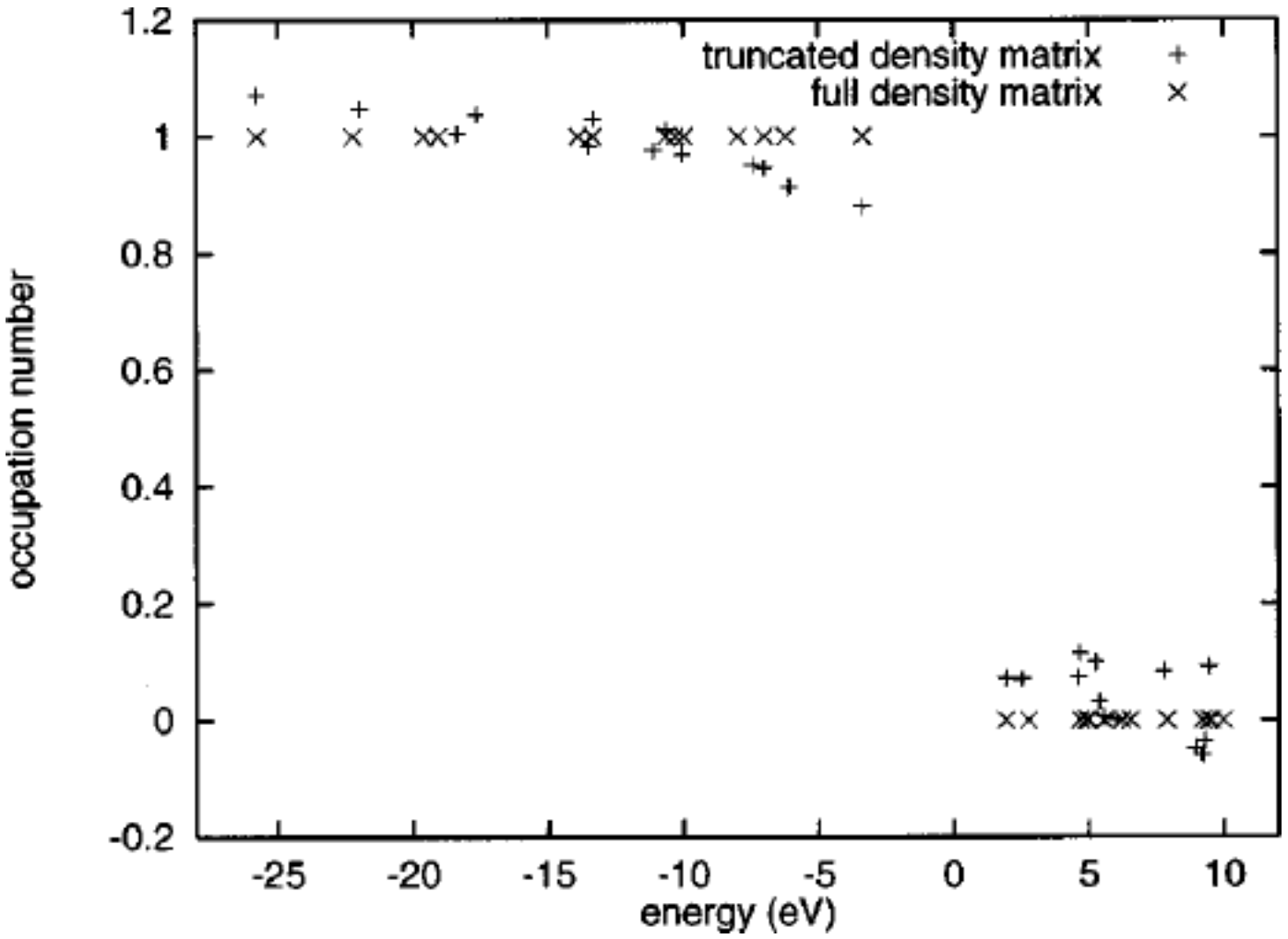
$$P = 3F^2 - 2F^3$$

- Minimize $E = \mathrm{tr}(PH)$ 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:

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

Orbital minimization

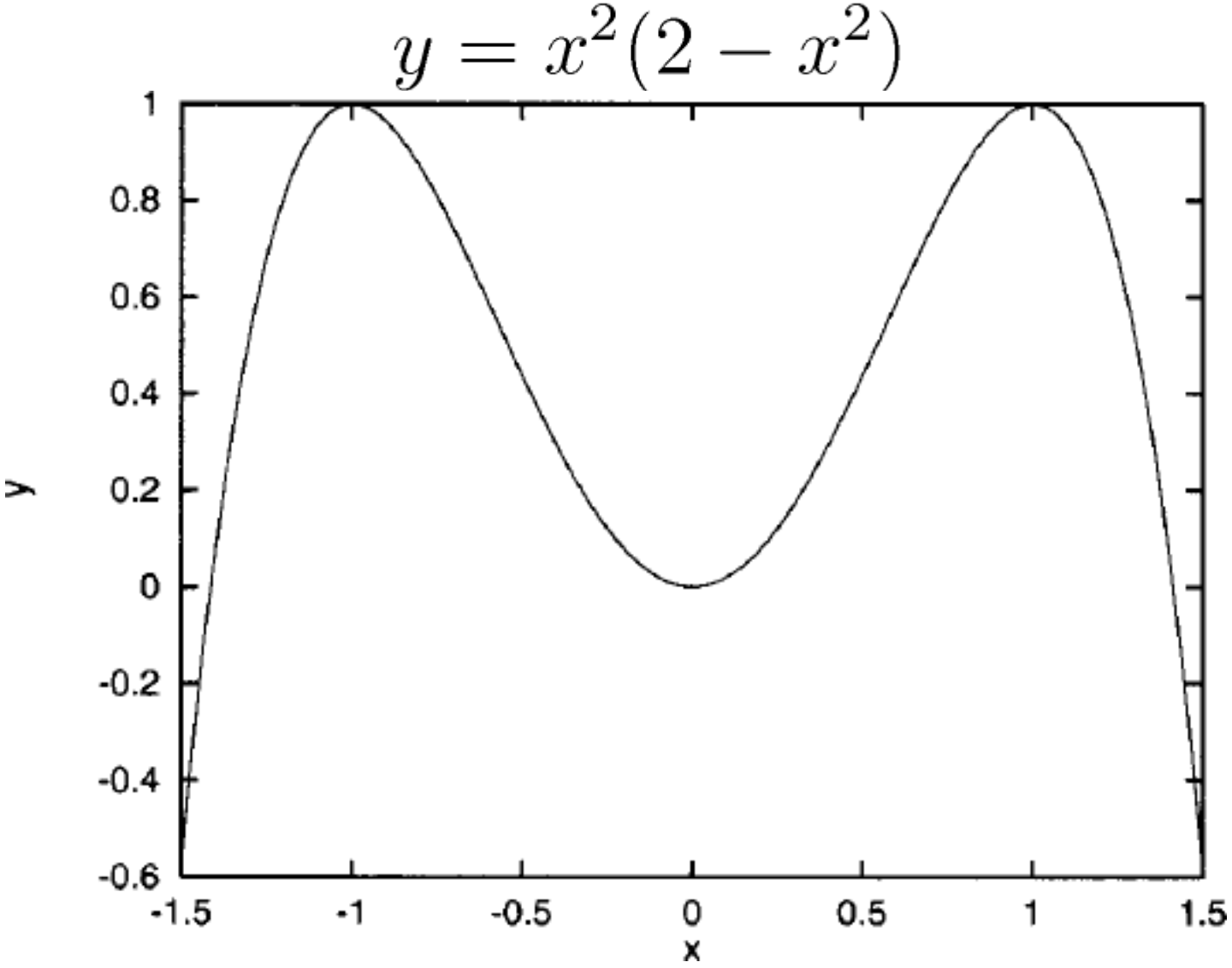
- Leads to a generalized functional:

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

  – 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:

$$T_{\mathrm{s}}[n] = \frac{3}{10}\left(3\pi^2\right)^{2/3} \int n(\mathbf{r})^{5/3}\,\mathrm{d}^3r$$

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

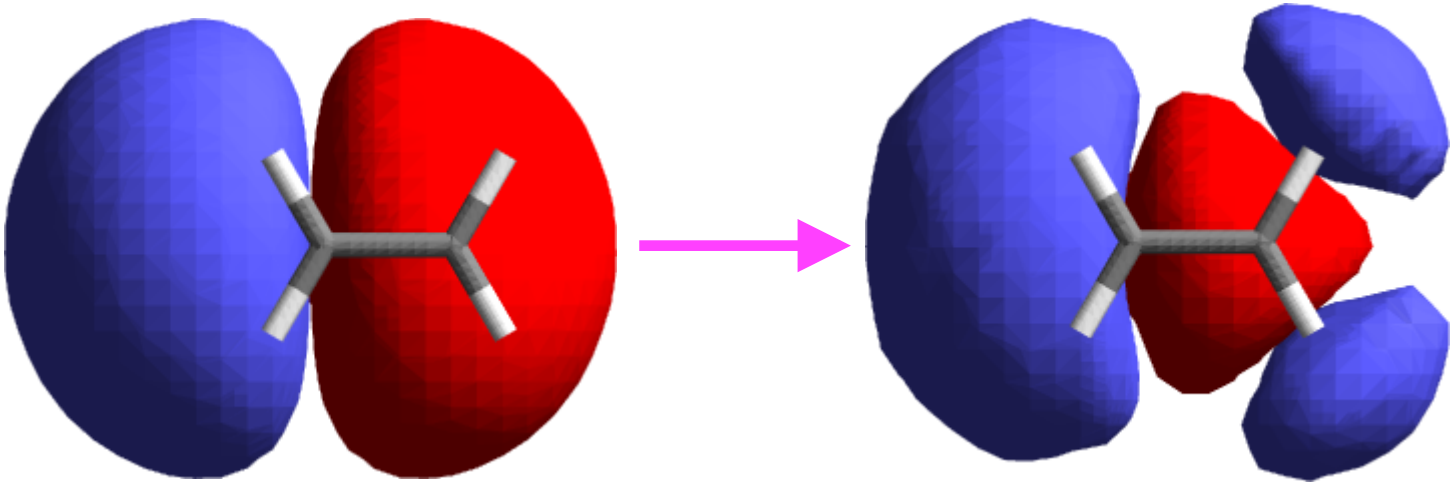
$$+\frac{\lambda}{8}\int \frac{\left|\nabla n(\mathbf{r})\right|^2}{n(\mathbf{r})}\,\mathrm{d}^3r$$

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

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

Brief overview of ONETEP

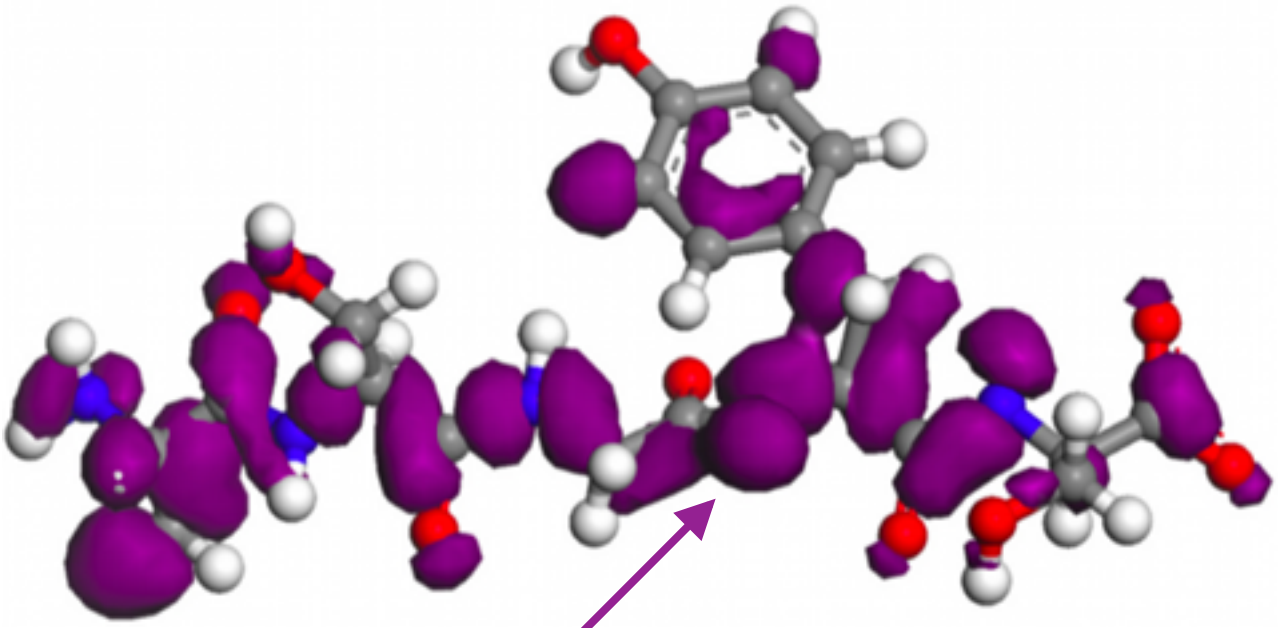
PDH, Nicholas Hine, Arash Mostofi, Mike Payne, Chris Skylaris



J. Chem. Phys. **122**, 084119 (2005)

www.onetep.org

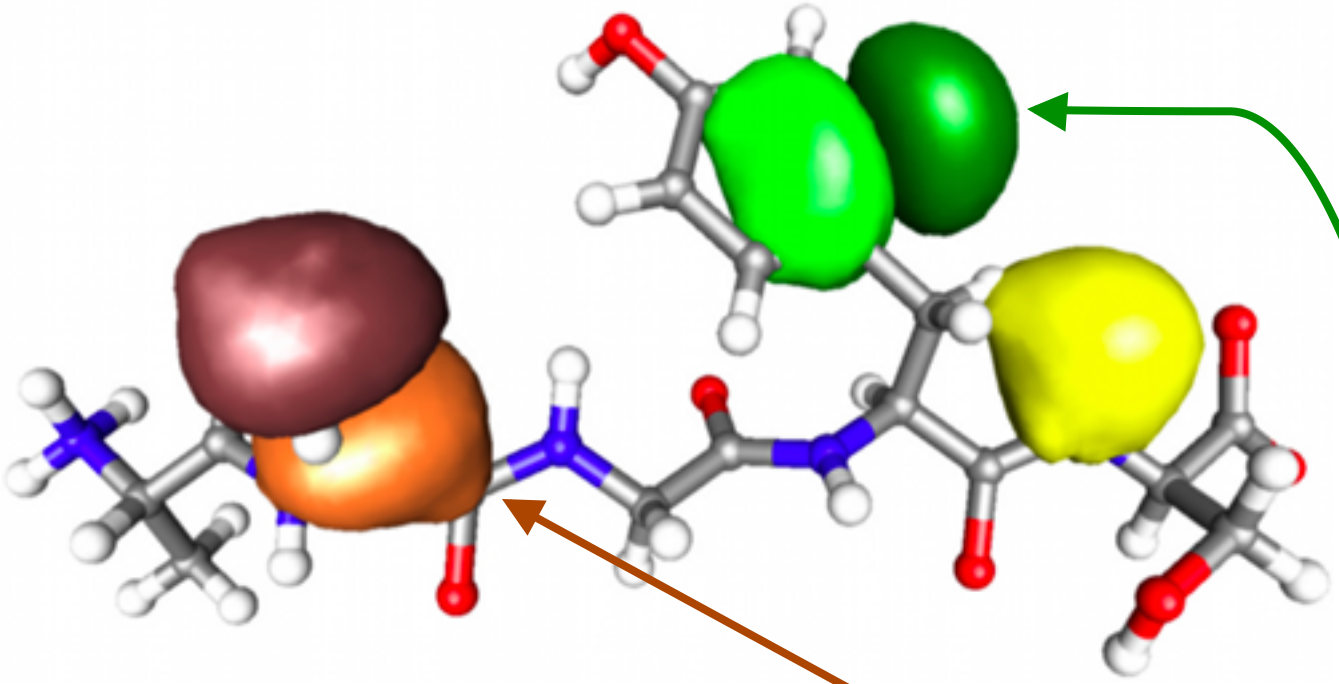
Density-matrix formulation



$$\rho(\mathbf{r},\mathbf{r}') = \sum_n f_n \, \psi_n(\mathbf{r}) \, \psi_n^*(\mathbf{r}')$$

Density-matrix formulation

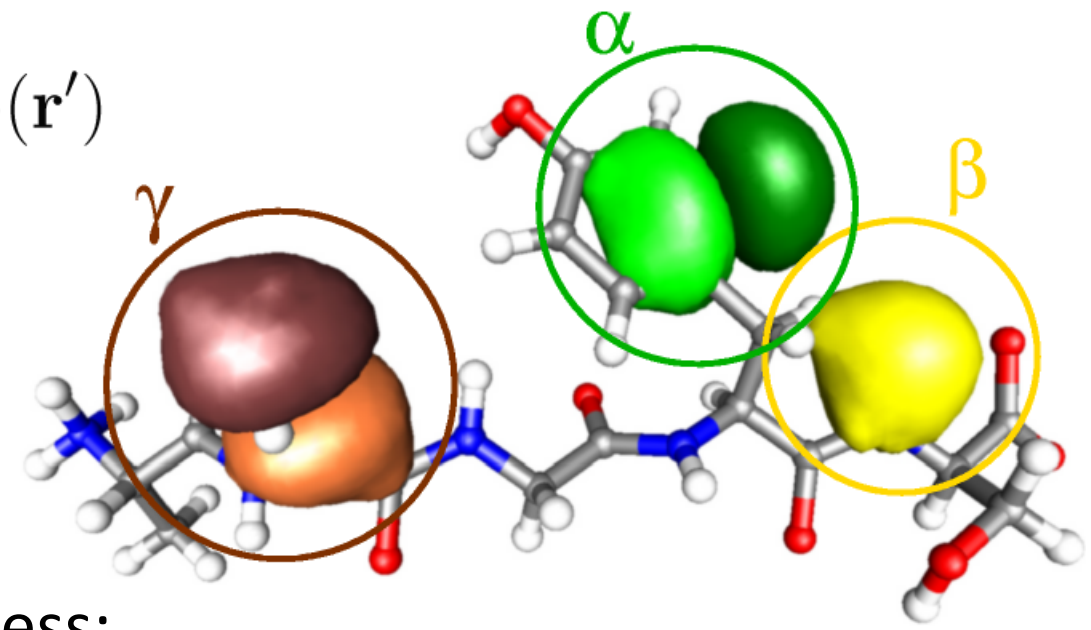
Galli & Parrinello, *Phys. Rev. Lett.* **69**, 3547 (1992)
Hernández & Gillan, *Phys. Rev. B* **51**, 10157 (1995)



$$\rho(\mathbf{r},\mathbf{r}') = \sum_n f_n\, \psi_n(\mathbf{r})\, \psi_n^*(\mathbf{r}') = \sum_{\alpha\beta} \phi_\alpha(\mathbf{r})\, K^{\alpha\beta}\, \phi_\beta^*(\mathbf{r}')$$

Density-matrix formulation

$$\rho(\mathbf{r},\mathbf{r}') = \sum_{\alpha\beta} \phi_\alpha(\mathbf{r}) K^{\alpha\beta} \phi_\beta(\mathbf{r}')$$



- Exploit near-sightedness:

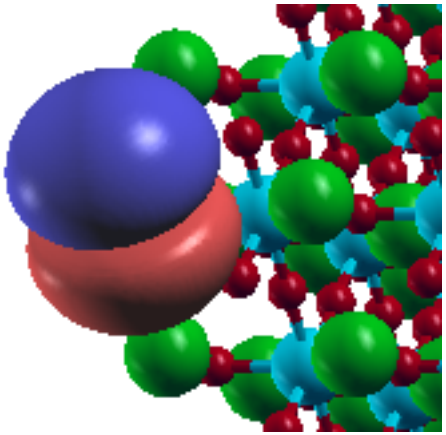
$$\rho(\mathbf{r},\mathbf{r}') \longrightarrow 0 \quad \text{as} \quad |\mathbf{r}-\mathbf{r}'| \longrightarrow \infty$$

  by imposing spatial cut-offs:
  - non-orthogonal generalised Wannier functions
  - sparse density kernel K

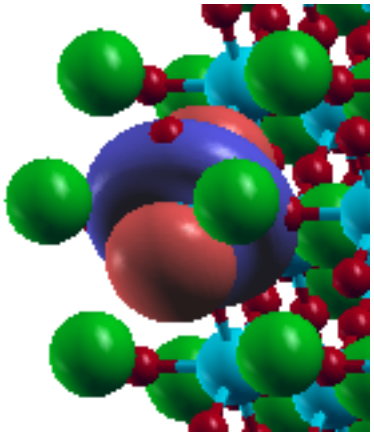
Local orbital optimization

Initial

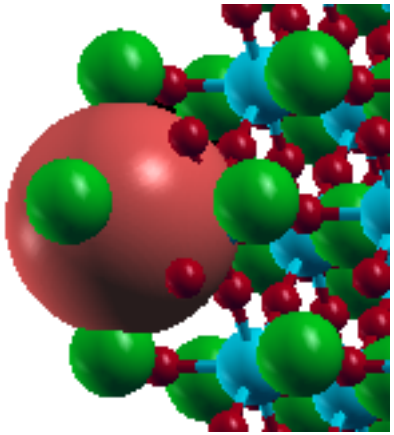
Ba *p*



Ti *d*



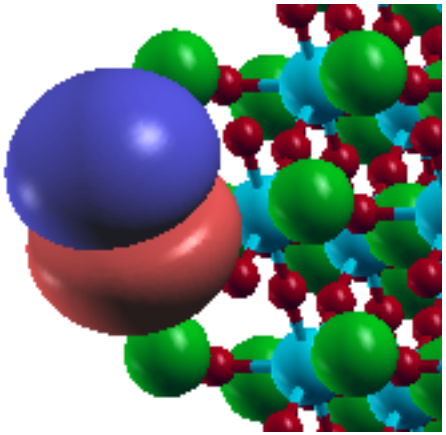
O *s*



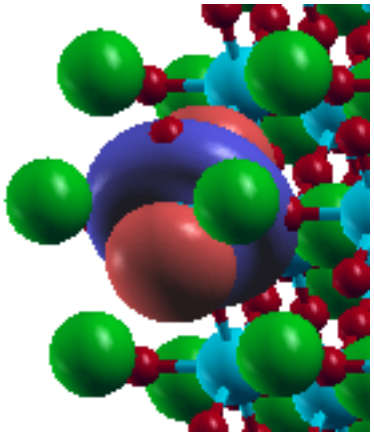
Local orbital optimization

Initial

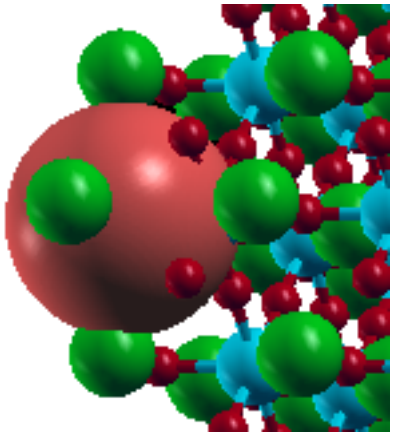
Ba *p*



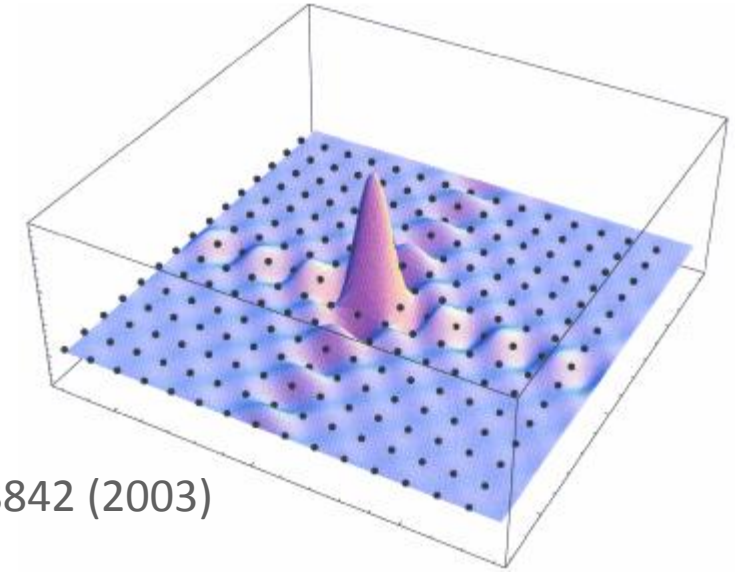
Ti *d*



O *s*

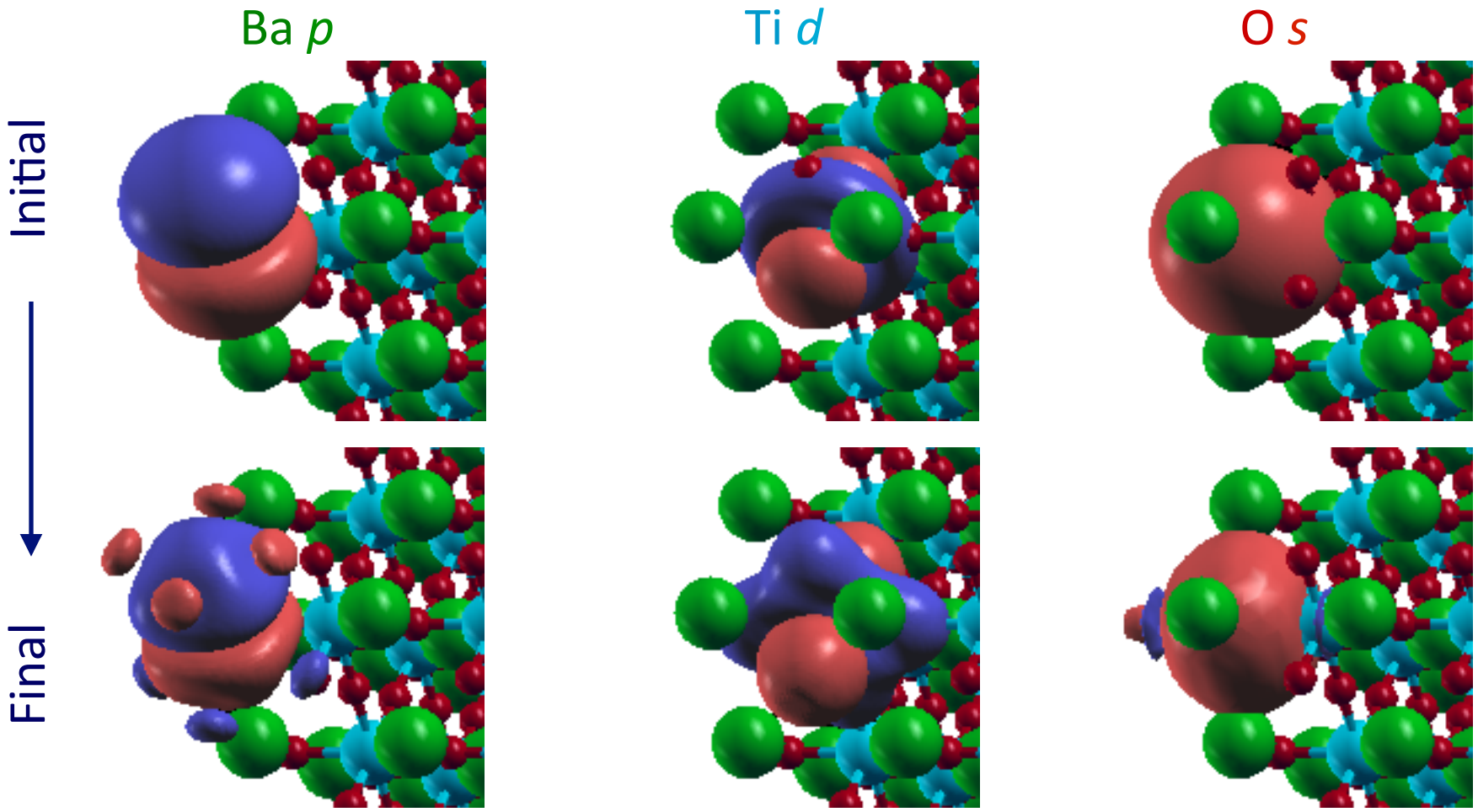


- Expand in terms of a “psinc” basis set (equivalent to plane-waves)



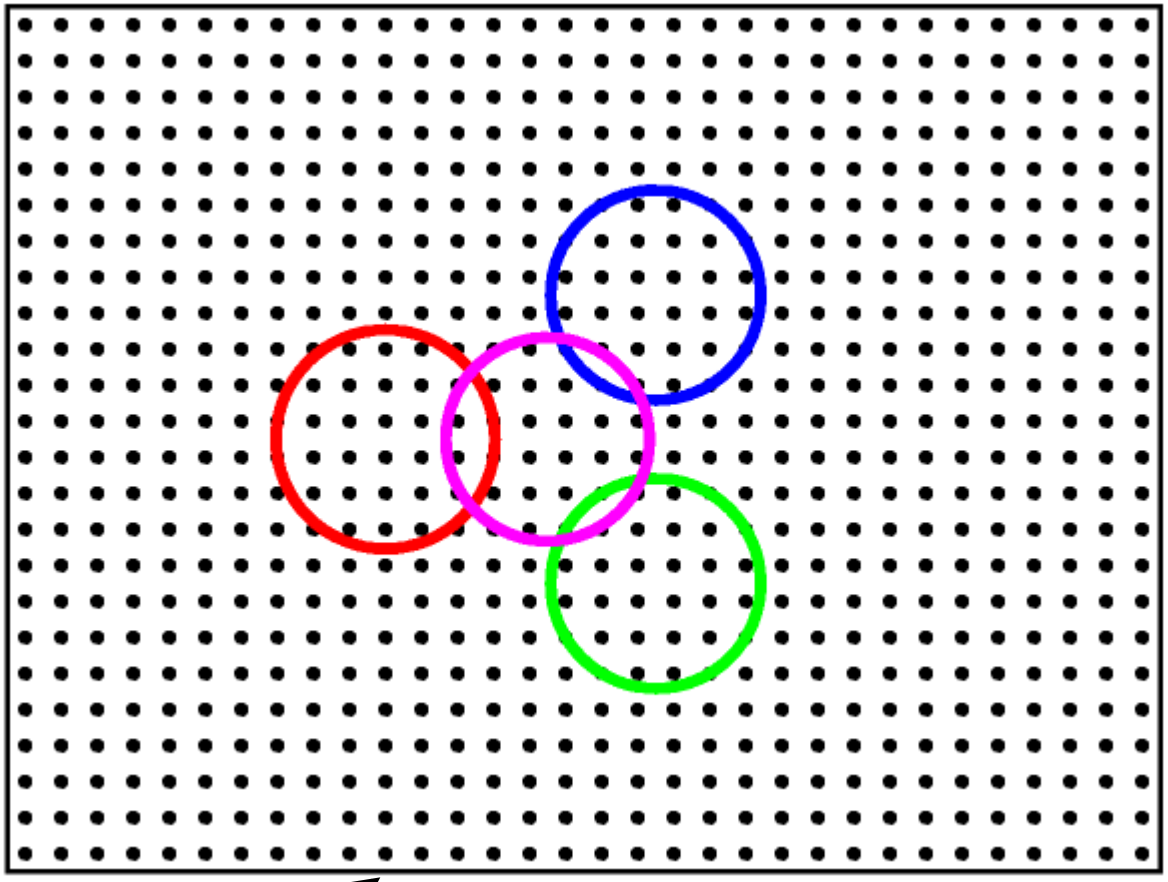
Mostofi, Haynes, Skylaris & Payne, *J. Chem. Phys.* **119**, 8842 (2003)
Baye & Heenen, *J. Phys. A: Math. Gen.* **19**, 2041 (1986)

Local orbital optimization



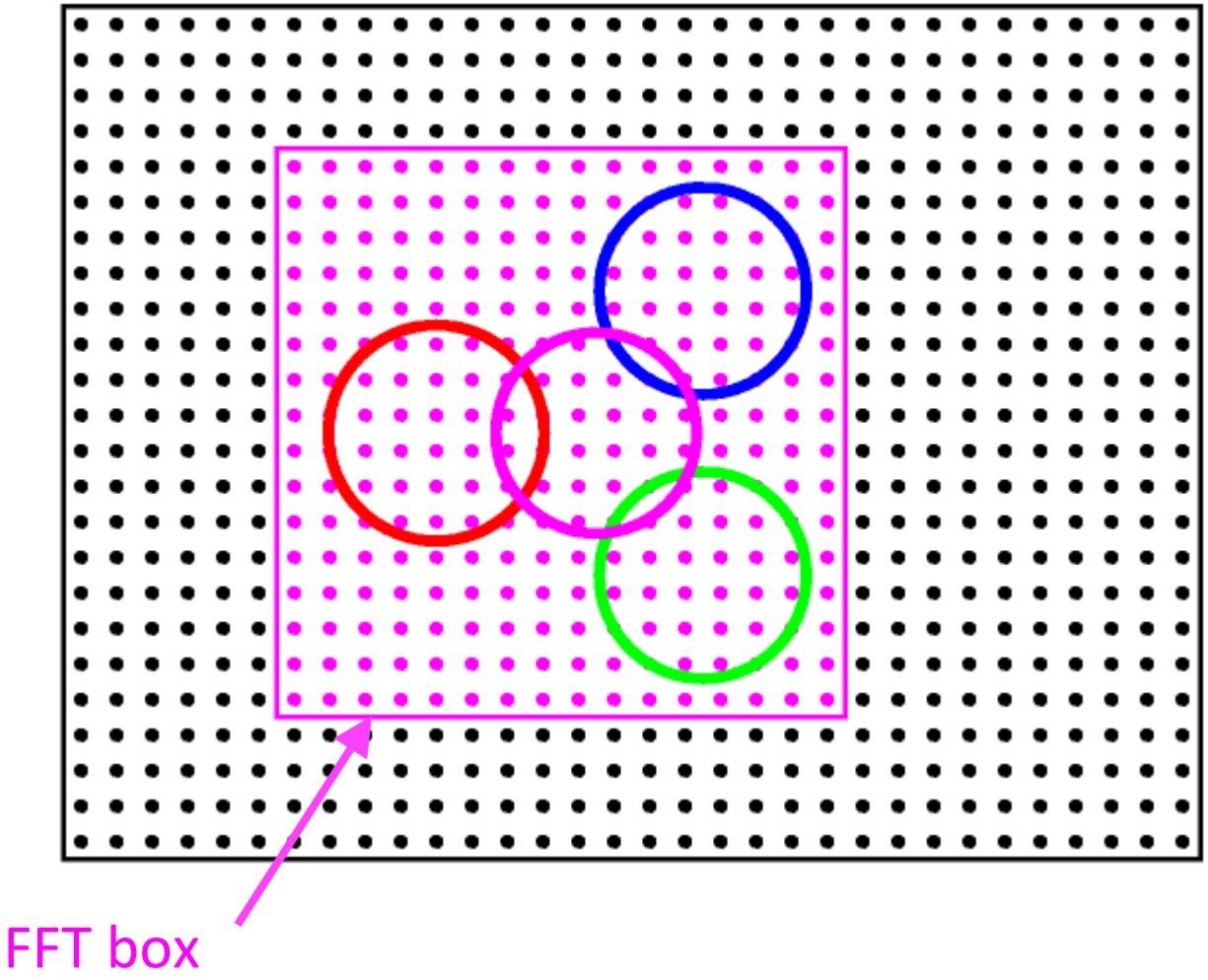
Skylaris, Mostofi, Haynes, Diéguez & Payne, *Phys. Rev. B* **66**, 035119 (2002)
On-site rotation from Foster & Weinhold, *J. Am. Chem. Soc.* **102**, 7211 (1980)

FFT box technique

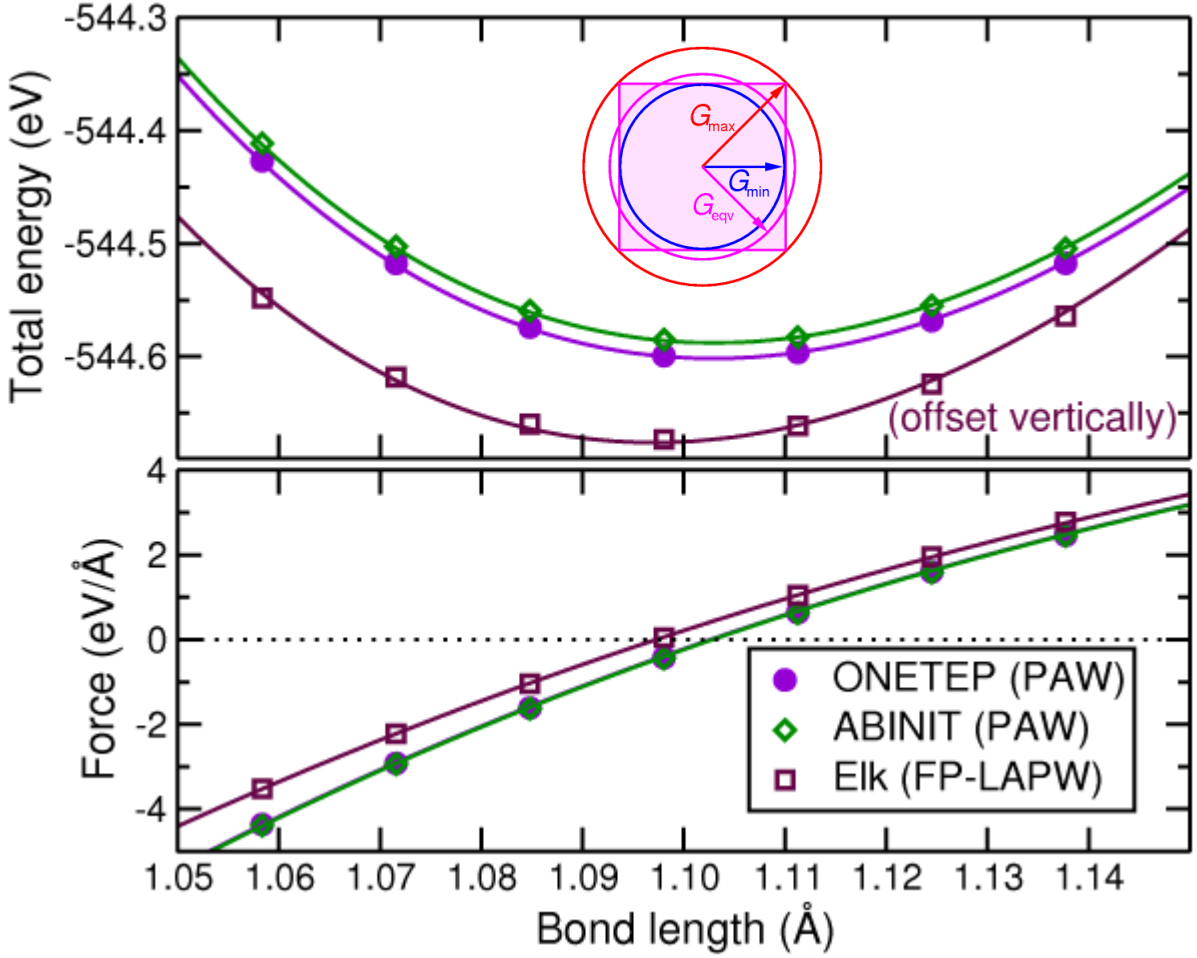


simulation cell

FFT box technique



Accuracy: N_2 dimer



	Bond length (Å)
ONETEP	1.1032
ABINIT	1.1035
Elk	1.0974

	Vibrational frequency (cm^{-1})
ONETEP	2522
ABINIT	2521
Elk	2481

Data from Nicholas Hine (unpublished)

http://elk.sourceforge.net/

Structural properties

- Crystalline silicon (1000 atoms):

Method	r_{NGWF}	r_{kernel}	a (Å)	B (GPa)
CASTEP	N/A	N/A	5.384	96.3
ONETEP	3.70	∞	5.382	96.5
ONETEP	3.44	∞	5.380	96.2
ONETEP	3.18	∞	5.365	96.8
ONETEP (fireballs)	3.70	∞	5.482	84.4
ONETEP (STO-3G*)	3.70	∞	5.290	134.2
ONETEP	3.70	10.58	5.385	97.8
ONETEP	3.70	7.94	5.378	99.5
ONETEP	3.70	5.29	5.412	122.7

Error in *a* < 0.1% Error in *B* c. 0.1%

Skylaris & Haynes, *J. Chem. Phys.* **127**, 164712 (2007)

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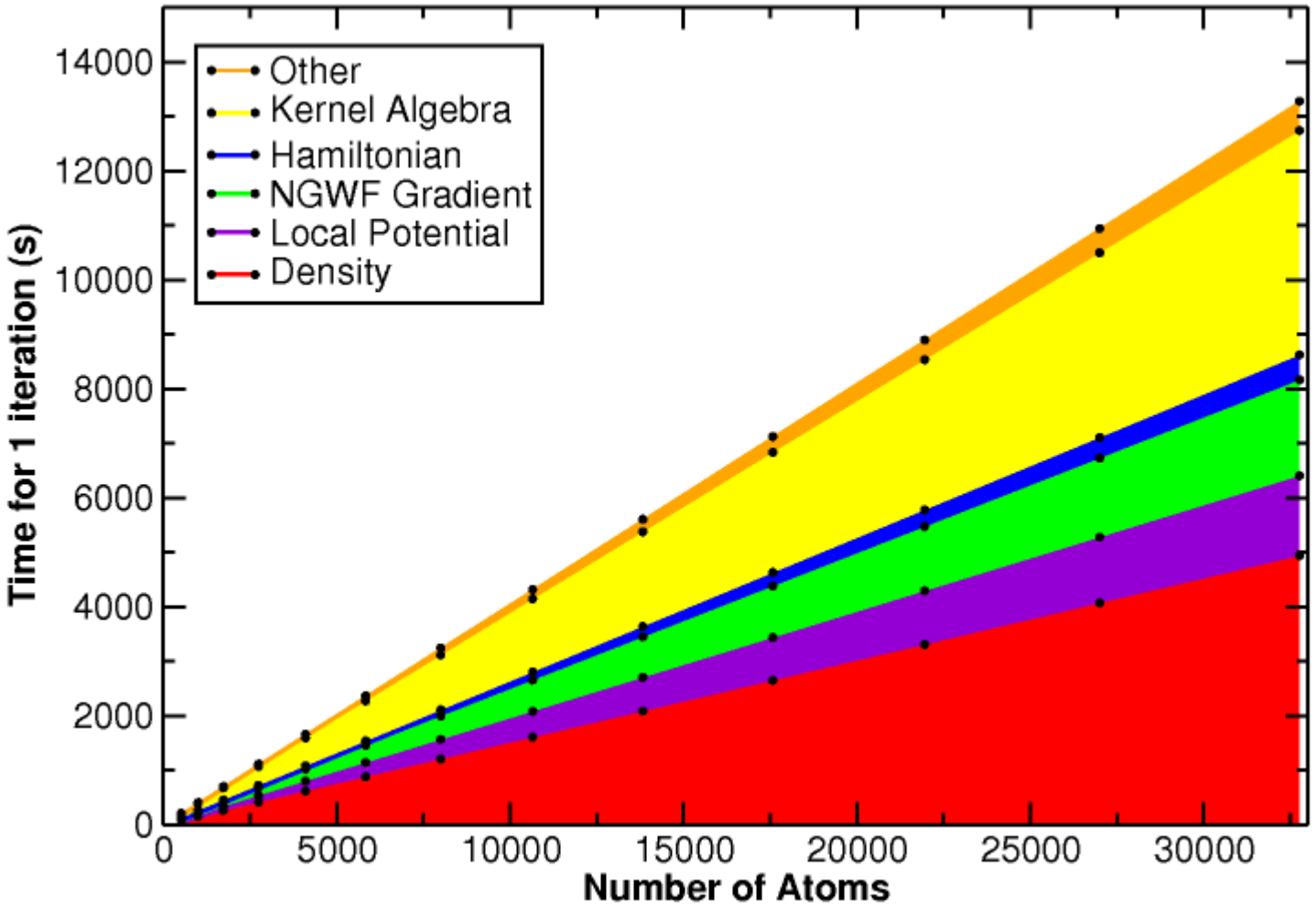
ONETEP	3.70	7.94	5.378	99.5
ONETEP	3.70	5.29	5.412	122.7

Error in *a* < 0.1% Error in *B* c. 1%

Skylaris & Haynes, *J. Chem. Phys.* **127**, 164712 (2007)

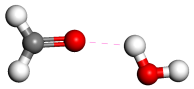
Linear scaling: bulk Si



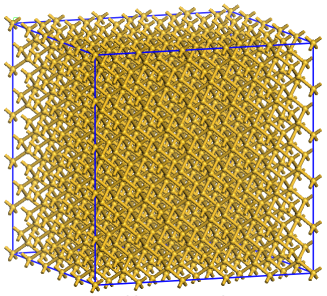
Single NGWF iteration
128 cores of CX2

Hine *et al.*, *Comput. Phys. Commun.* **180**, 1041 (2009)
Hine *et al.*, *J. Chem. Phys.* **133**, 114111 (2010)

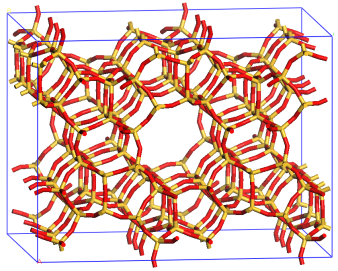
True linear scaling



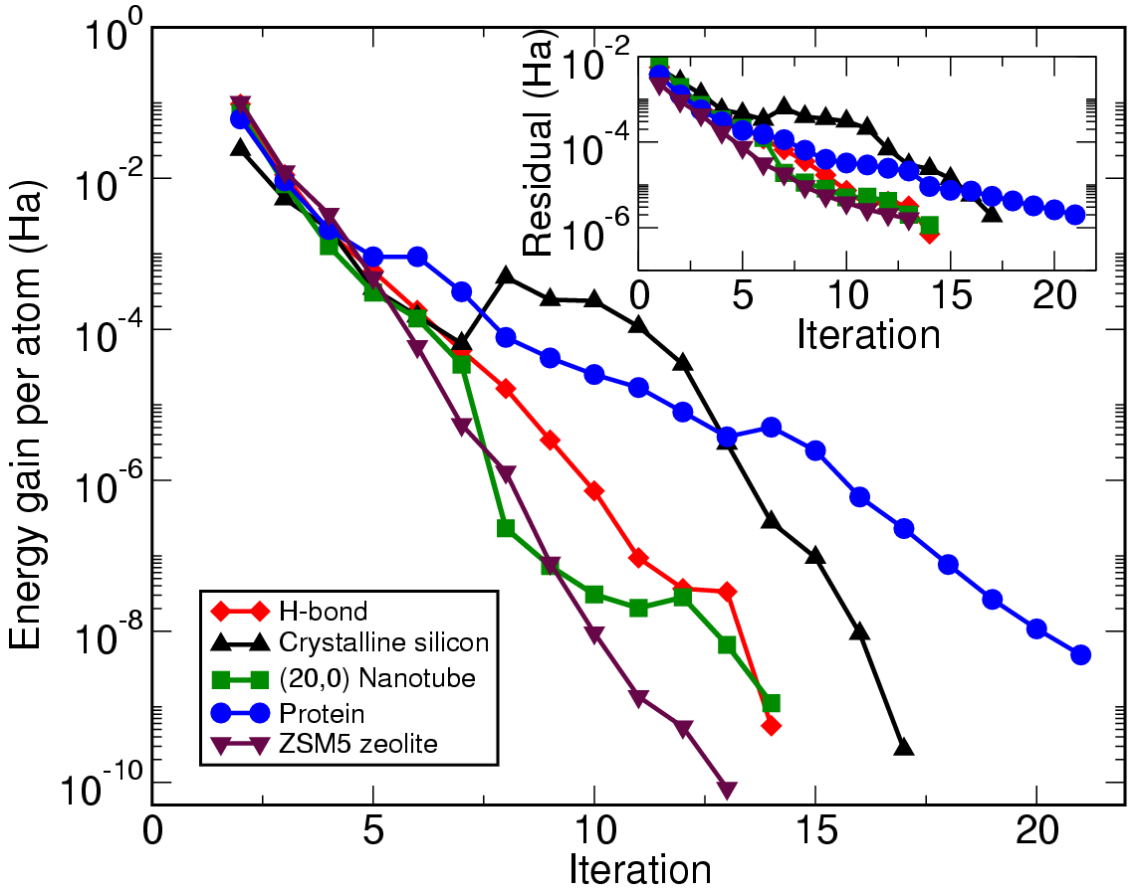
H-bond
(7 atoms)

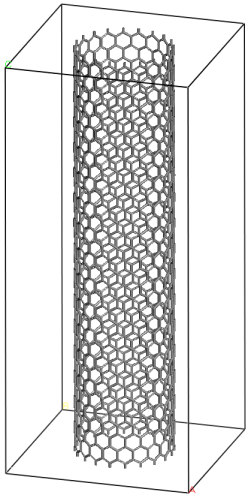


Crystalline silicon
(1000 atoms)

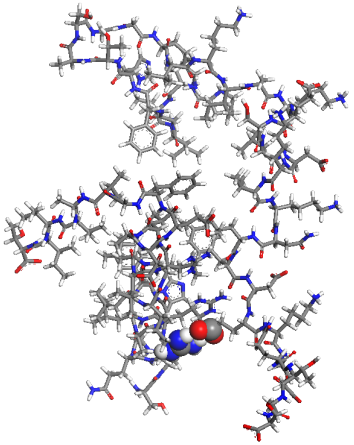


ZSM5 zeolite
(576 atoms)





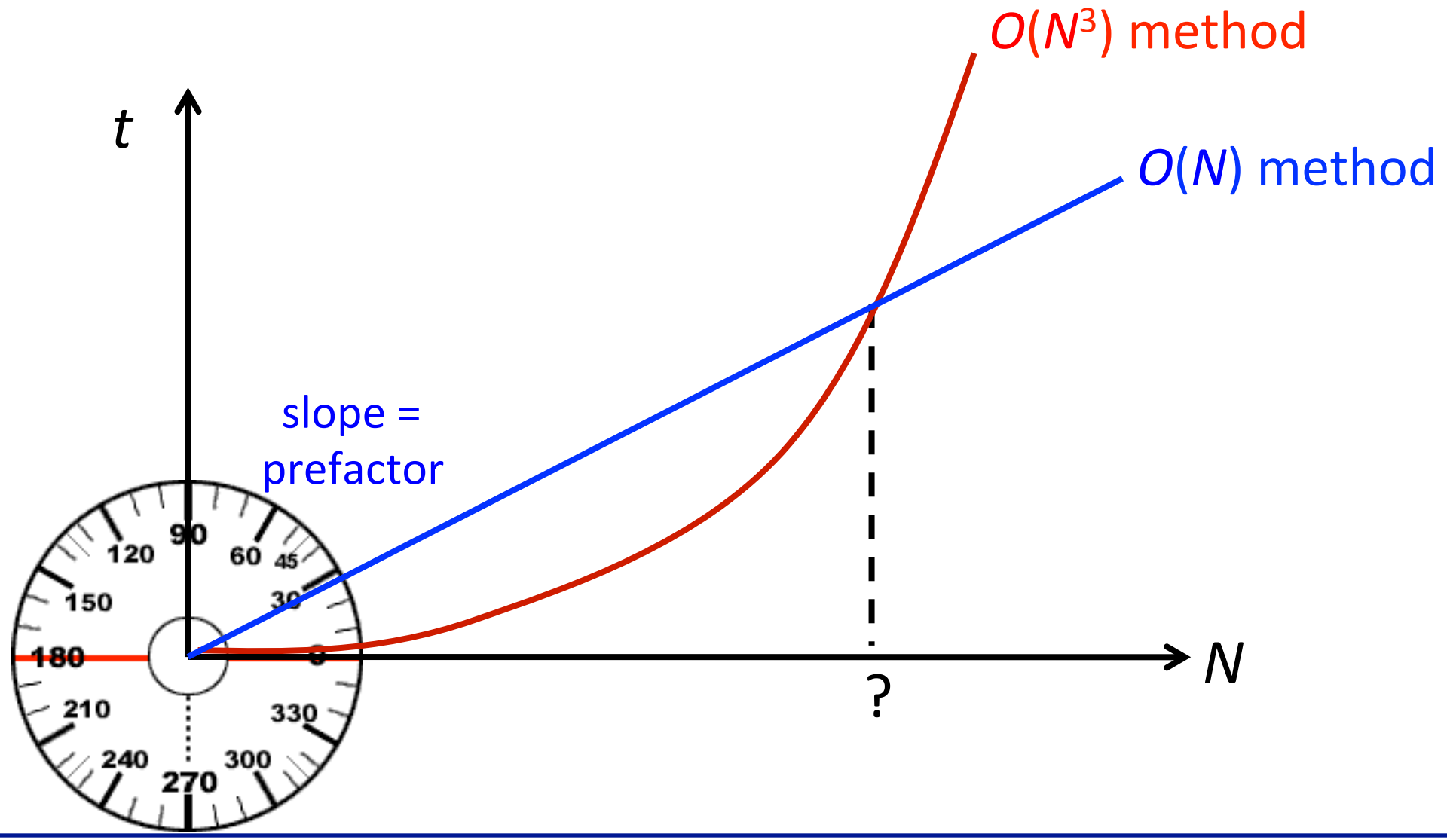
(20, 0) Nanotube
(1280 atoms)



Protein (988
atoms)

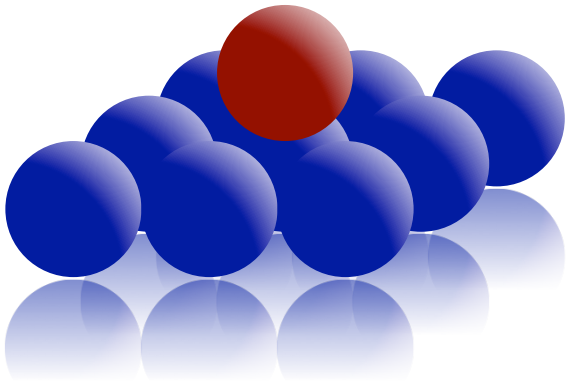
Skylaris, Haynes, Mostofi & Payne, *J. Phys.: Condens. Matter* **17**, 5757 (2005)

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



1. The possibilities are endless

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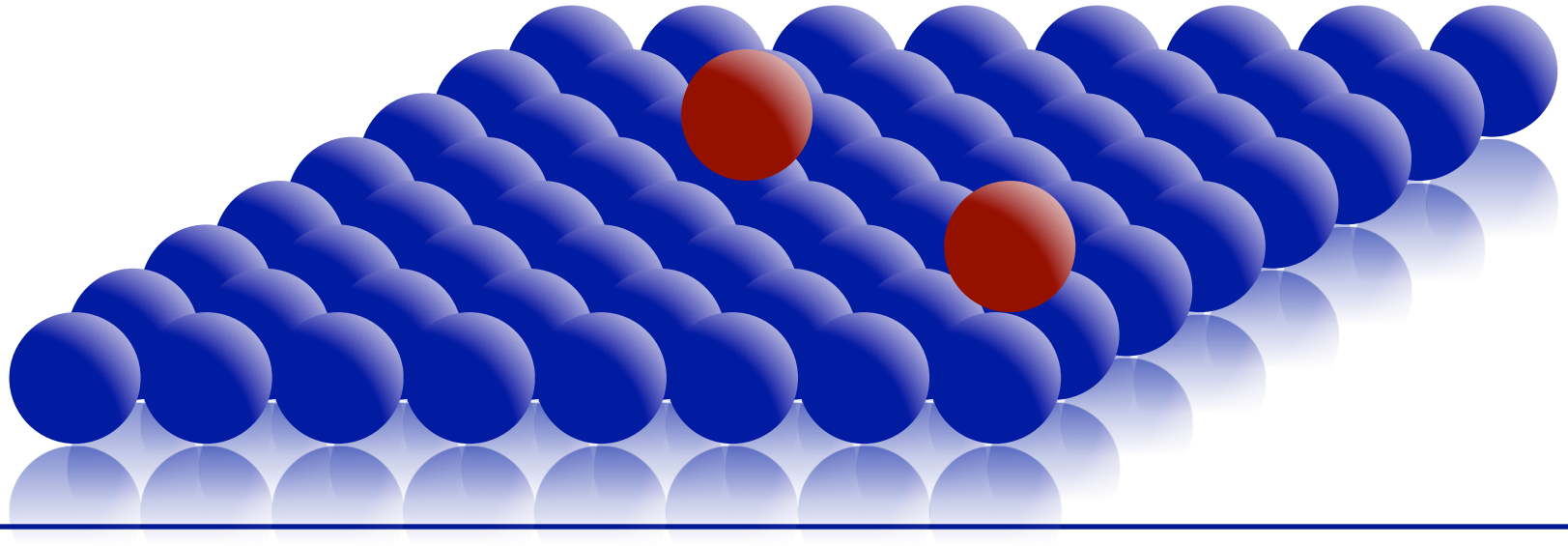


2. Energy and forces are not enough

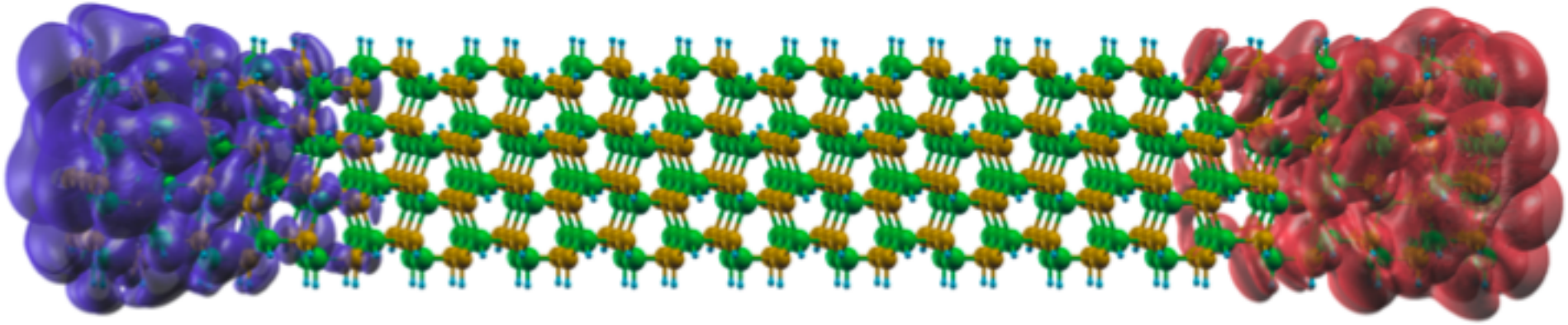
- That is all most $O(N)$ codes output
  - but vastly more information is generated
  - e.g. optimized local orbitals (Wannier functions)

- Importance of link to experiment

So what is linear-scaling DFT good for?

1. Specific systems that exploit the advantages of the method

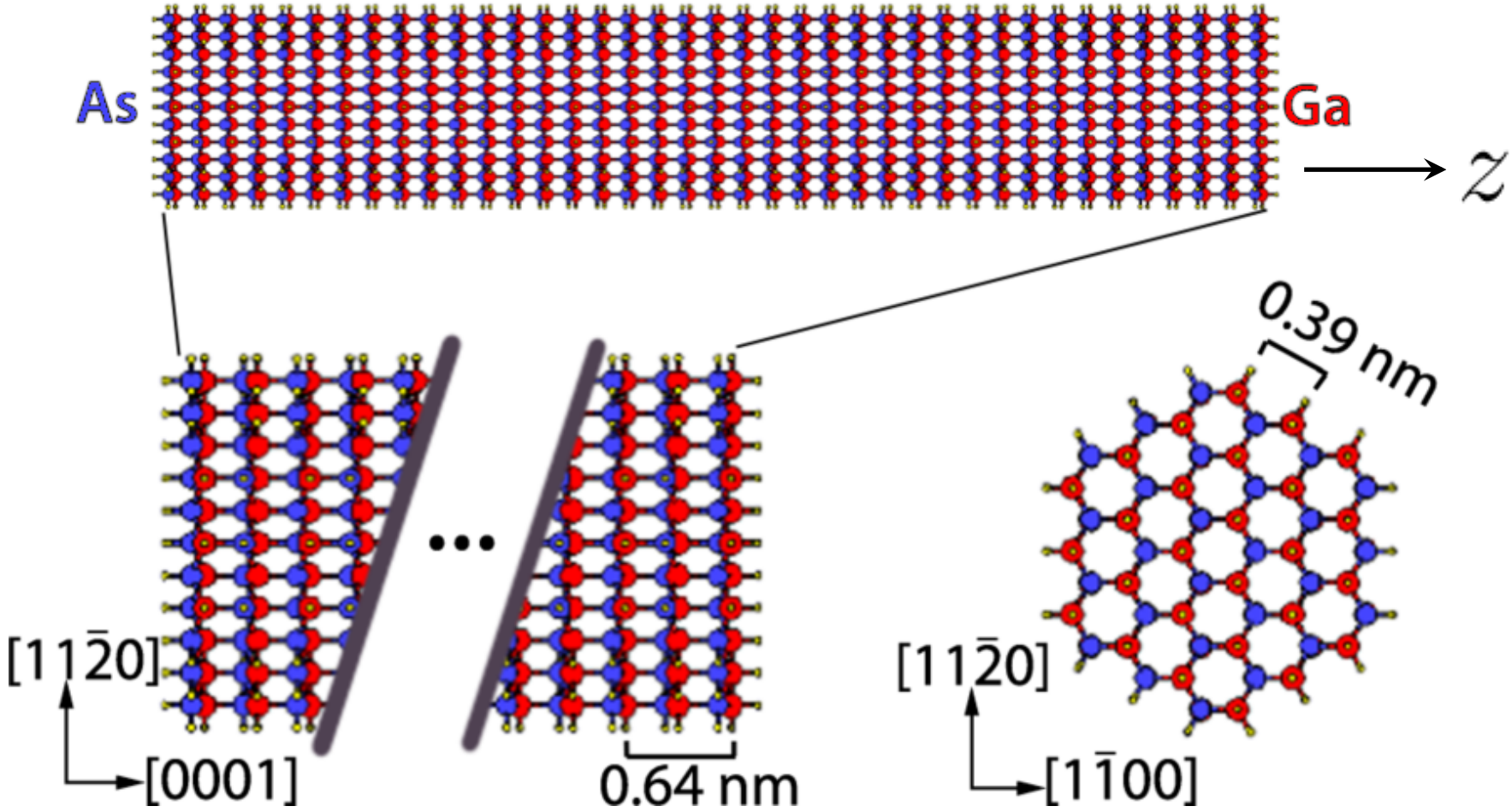
Phil Avraam, Nicholas Hine, Paul Tangney, PDH



Phys. Rev. B **83**, 241402(R) (2011)
Phys. Rev. B **85**, 115404 (2012)

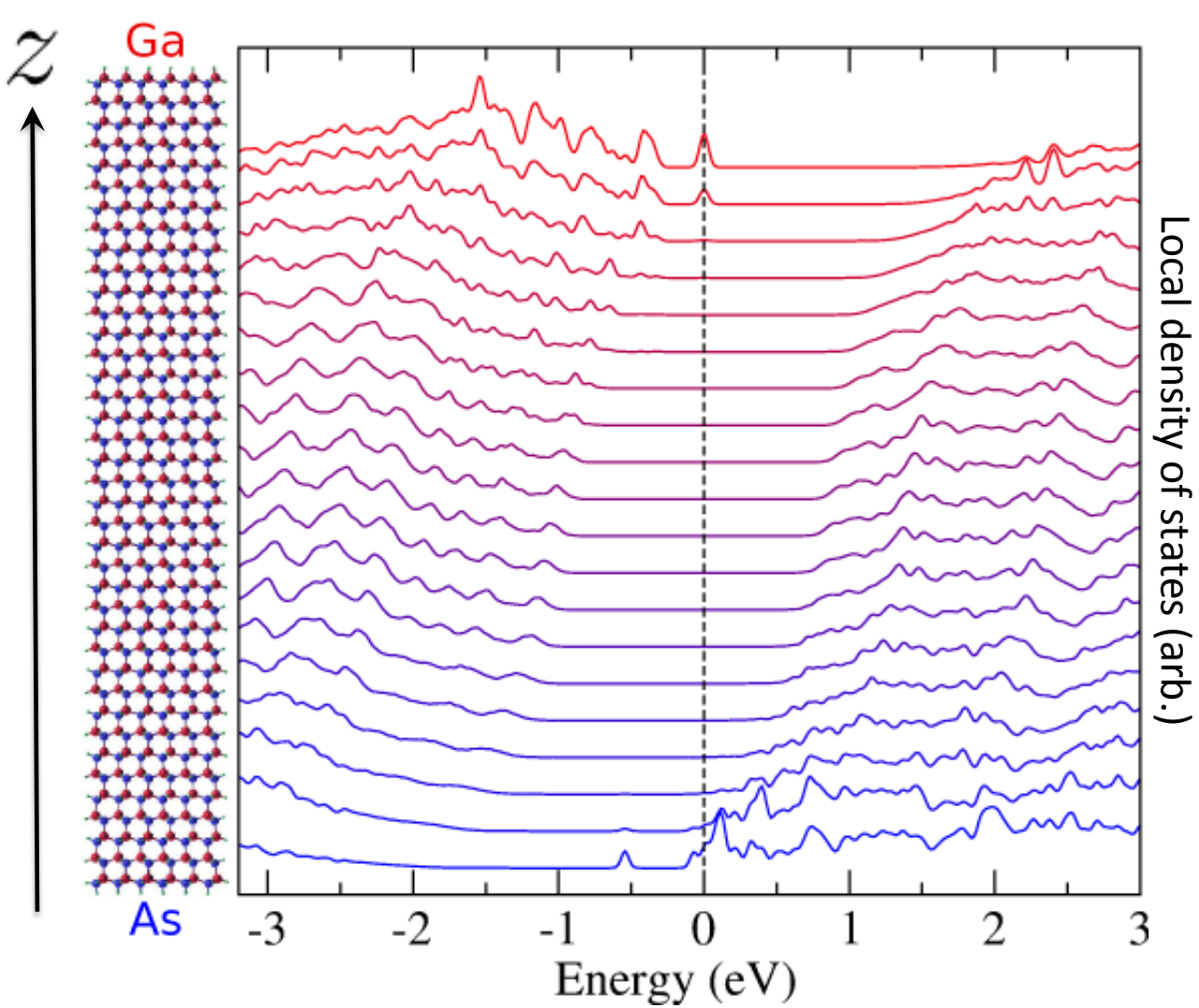
Model polar nanorod

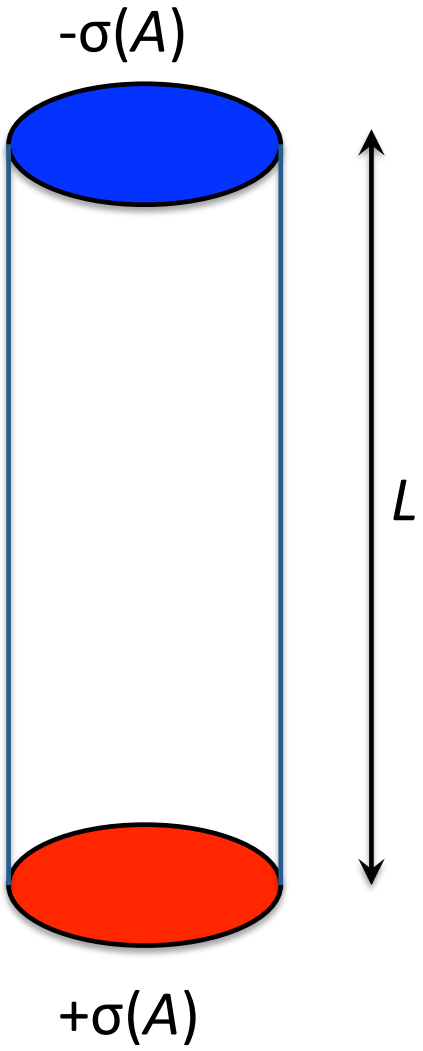
Variety of surface terminations: bare, H, “pseudo-atoms”



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

Fermi level pinning





Model predictions

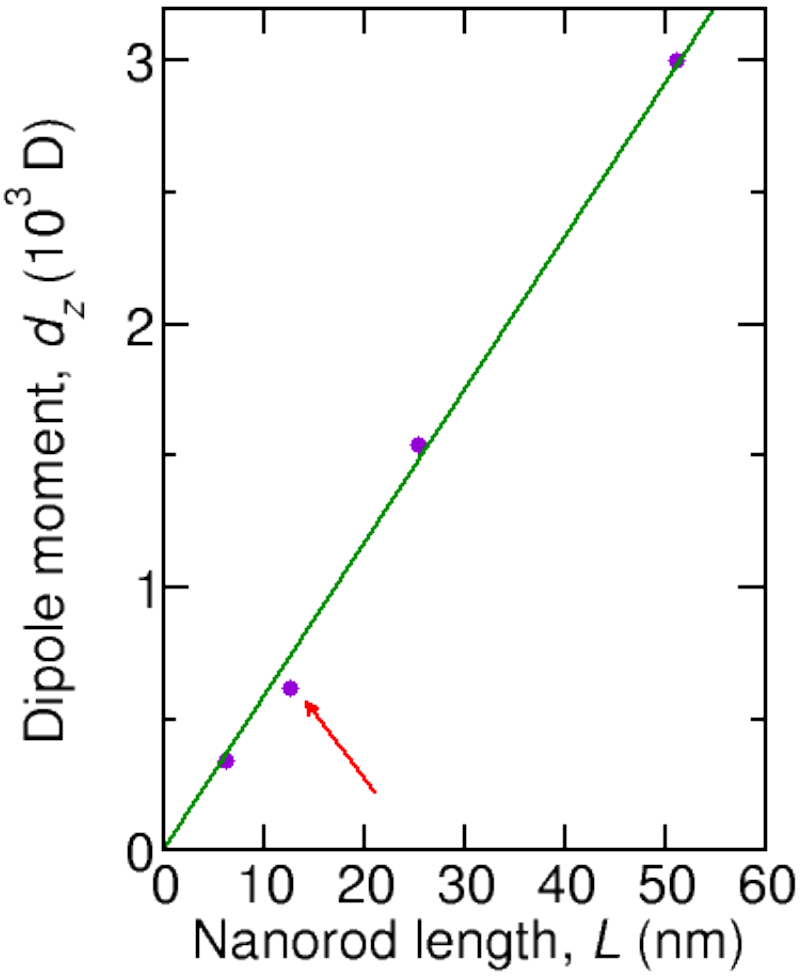
- Fermi level pinning requires (for rod radius a):

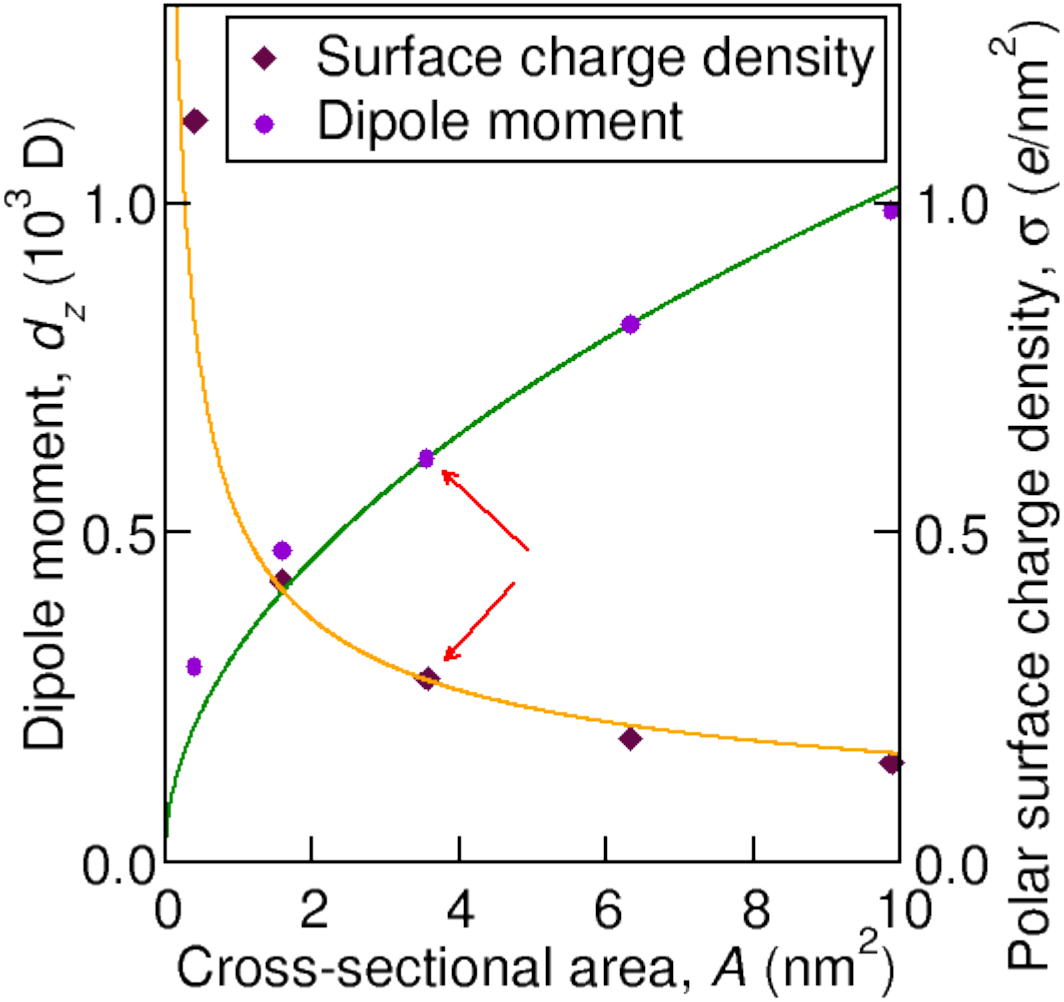
$$\sigma \approx \frac{E_{\mathrm{g}}}{4\pi\left(a + L - \sqrt{a^2 + L^2}\right)}$$

- Predicts dipole moment: $d_z = \sigma A L$
  - $d_z \propto E_{\mathrm{g}}\sqrt{A}L$ (thin rods)
  - $d_z \propto E_{\mathrm{g}}A$ (thick rods)

Avraam, Hine, Tangney & Haynes, arxiv:1110.6656

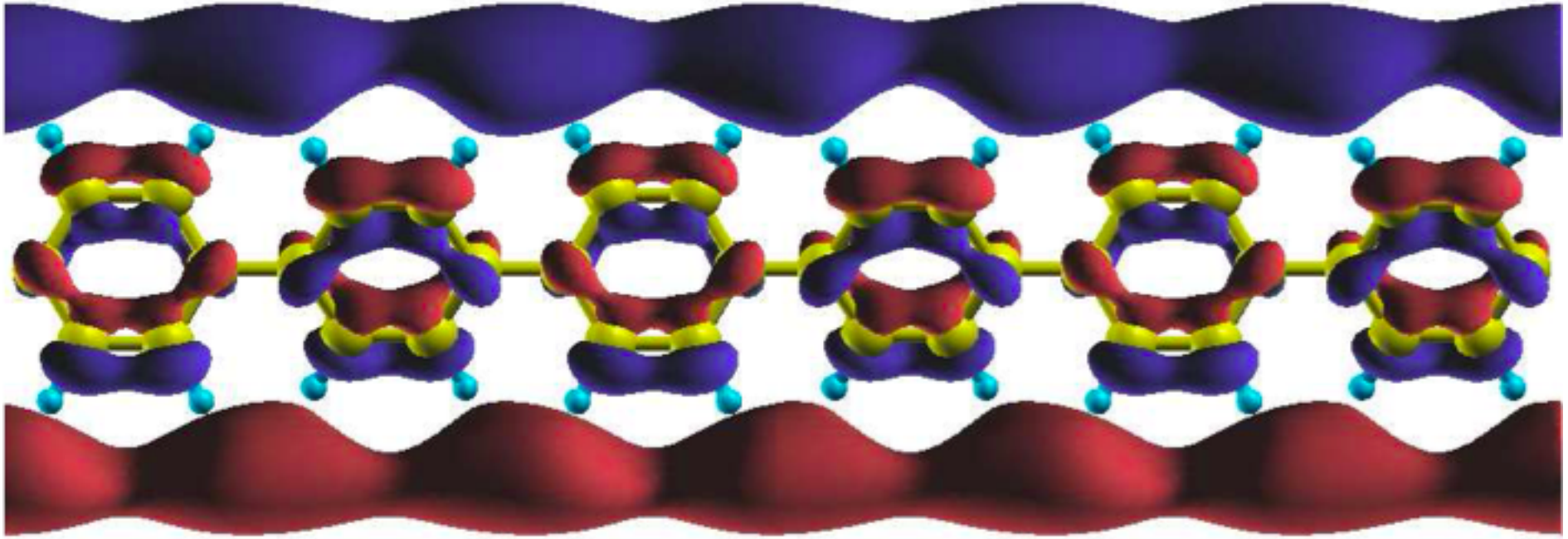
How good is the model?





2. Theoretical spectroscopy?

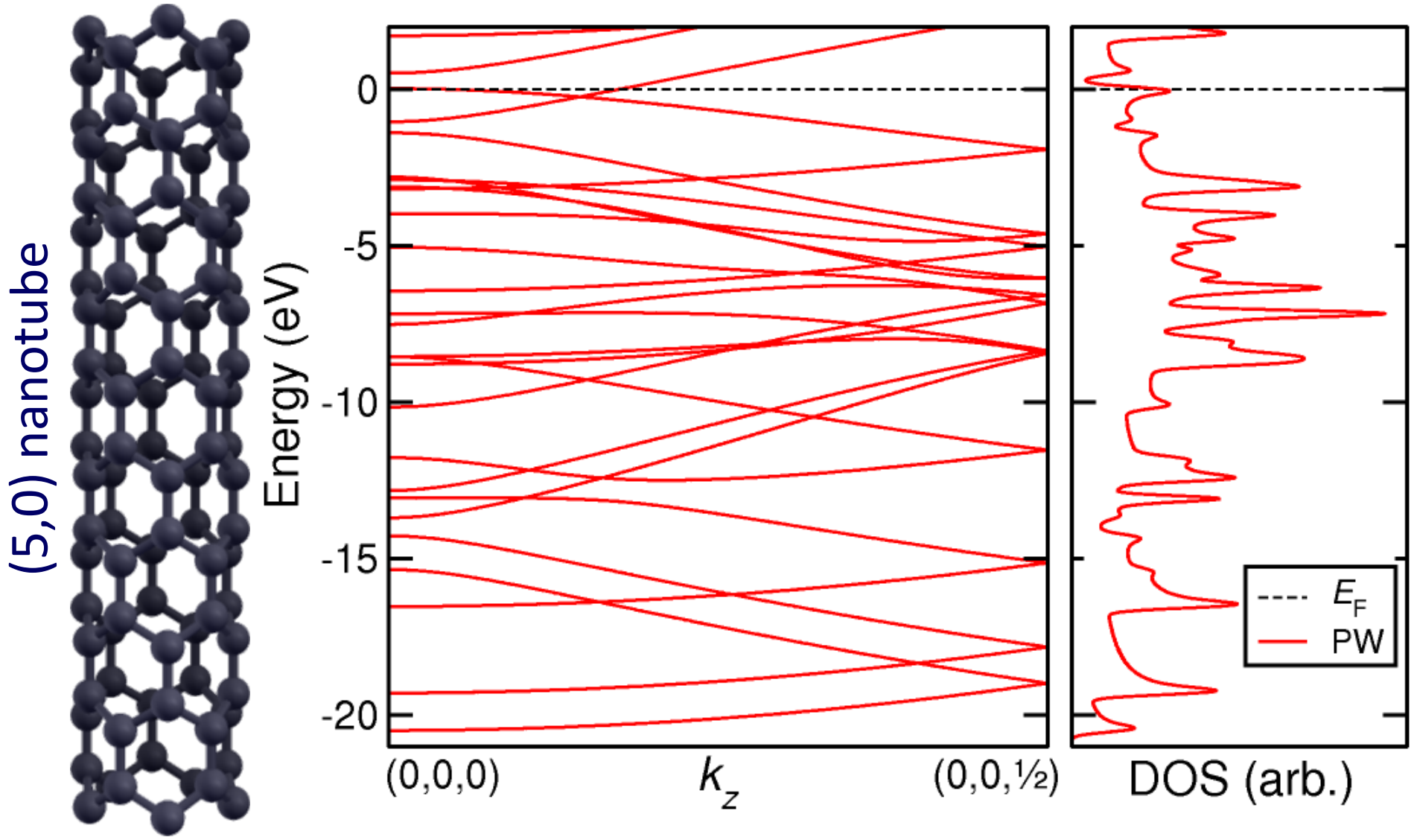
Laura Ratcliff, Nicholas Hine, Tim Zuehlsdorff, PDH



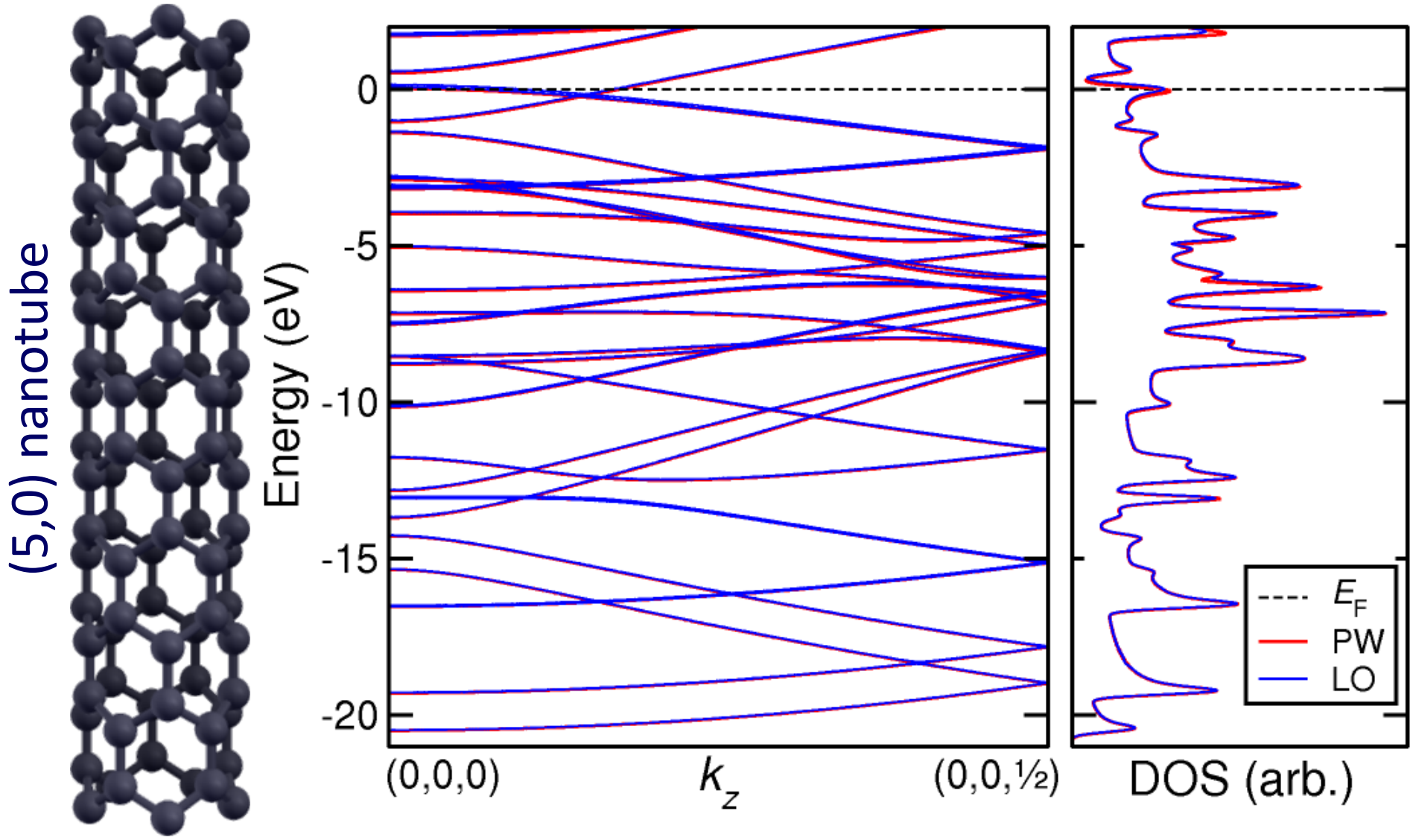
Phys. Rev. B **84**, 165131 (2011)

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

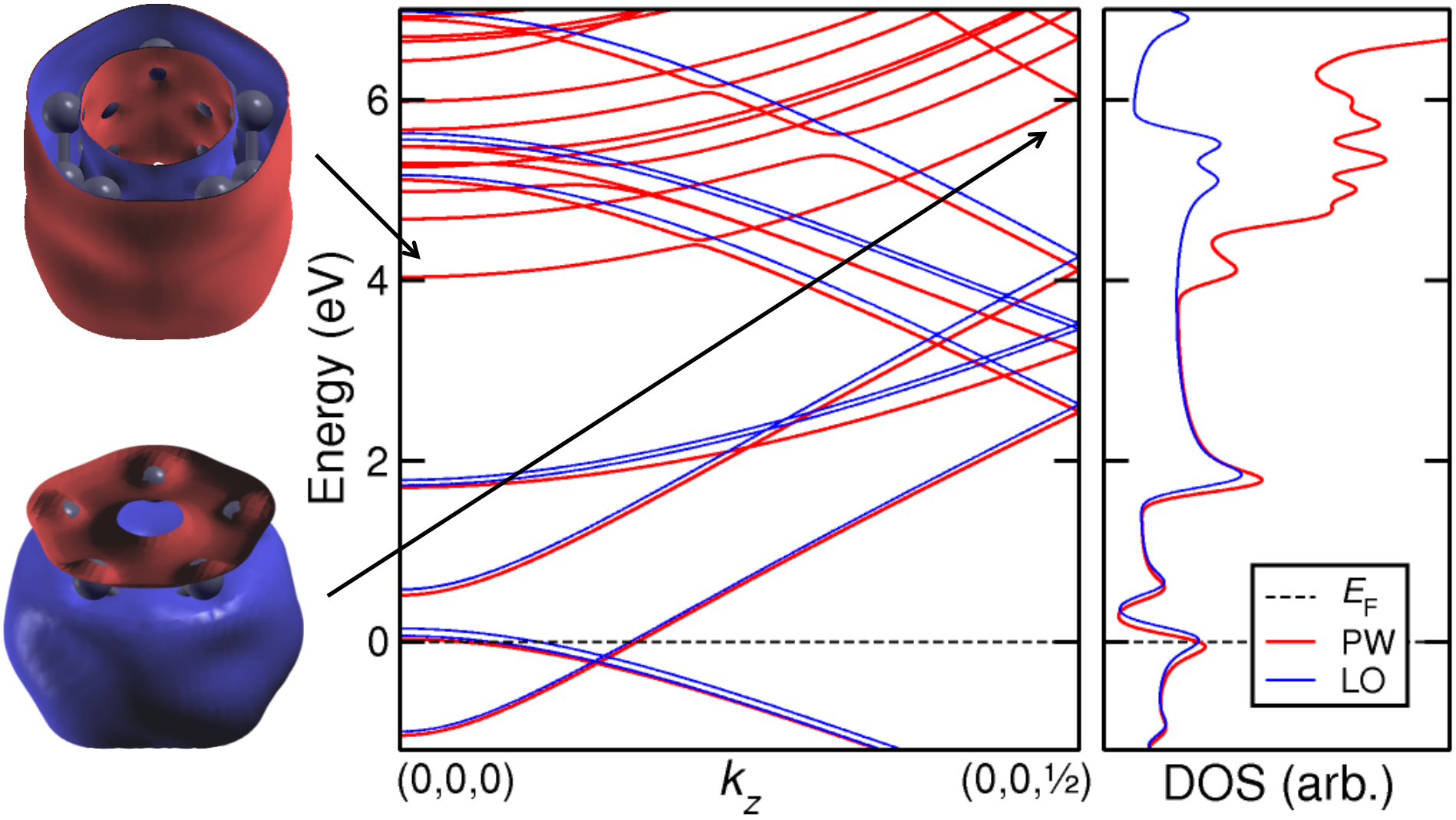
Plane-wave valence band structure



4x 3.7 Å NGWFs / C



Conduction band structure



Calculating unoccupied states

- Ground state DM defines a projection operator:

$$\hat{P} = \sum_{\alpha\beta} |\phi_\alpha\rangle K^{\alpha\beta} \langle\phi_\beta|$$

- Use this to define a projected Hamiltonian:

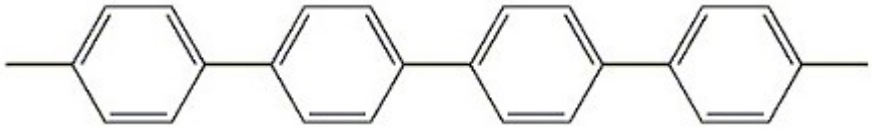
$$\hat{\mathcal{H}} = \left(\hat{H} - \epsilon\hat{1}\right) - \hat{P}\left(\hat{H} - \epsilon\hat{1}\right)\hat{P}$$

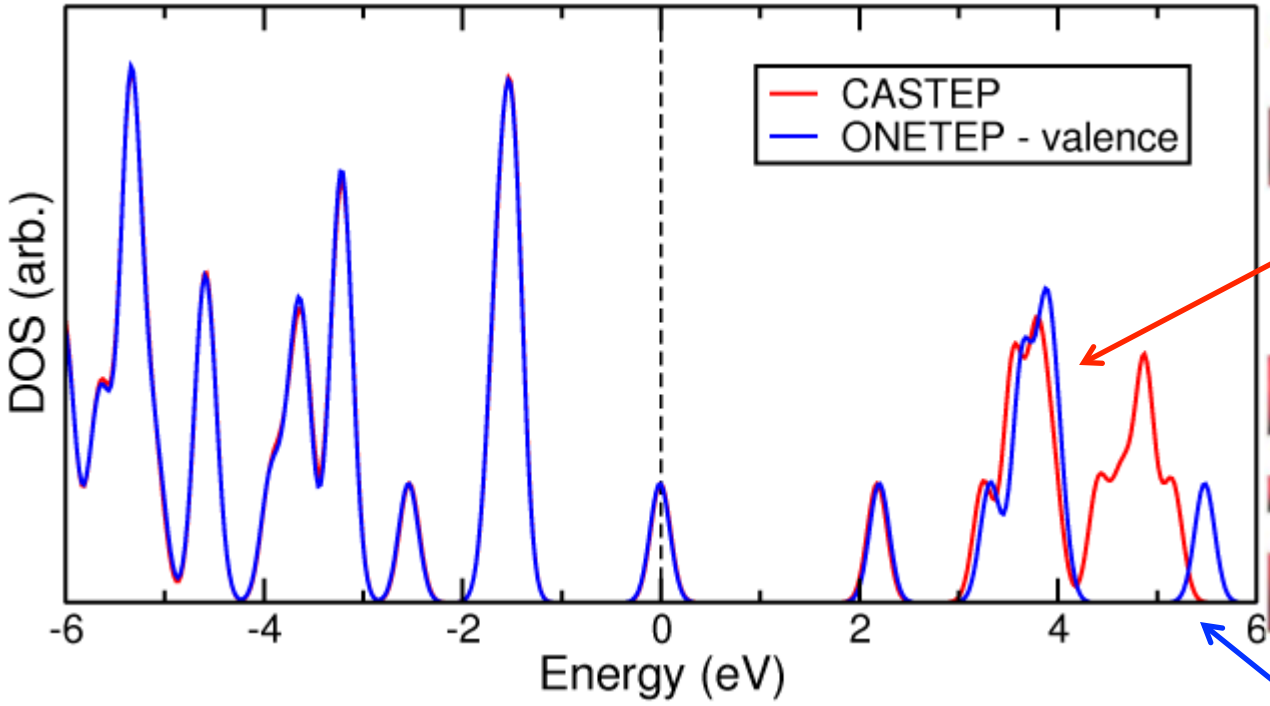
- Solve (non-self-consistently) for the new DM:

$$\hat{Q} = \sum_{\alpha\beta} |\chi_\alpha\rangle M^{\alpha\beta} \langle\chi_\beta|$$

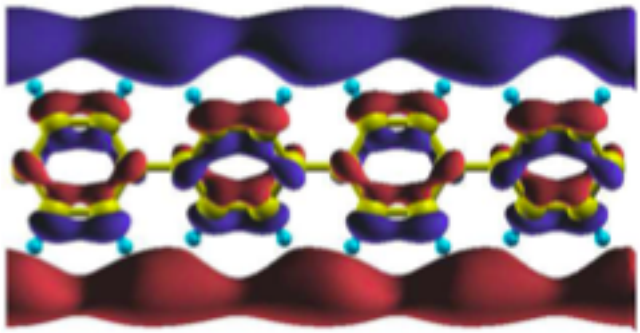
that minimises $\mathcal{E} = \mathrm{tr}\left(Q\mathcal{H}\right)$

poly(*para*-phenylene) chain

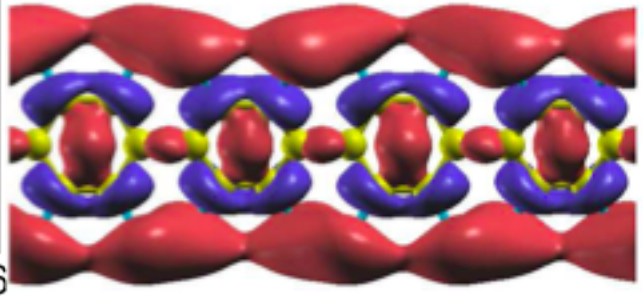




LUMO+8:



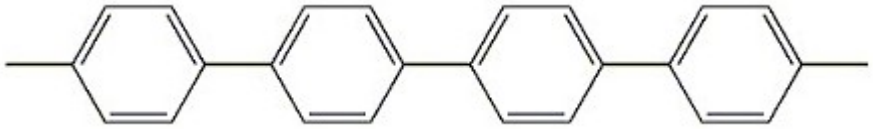
CASTEP

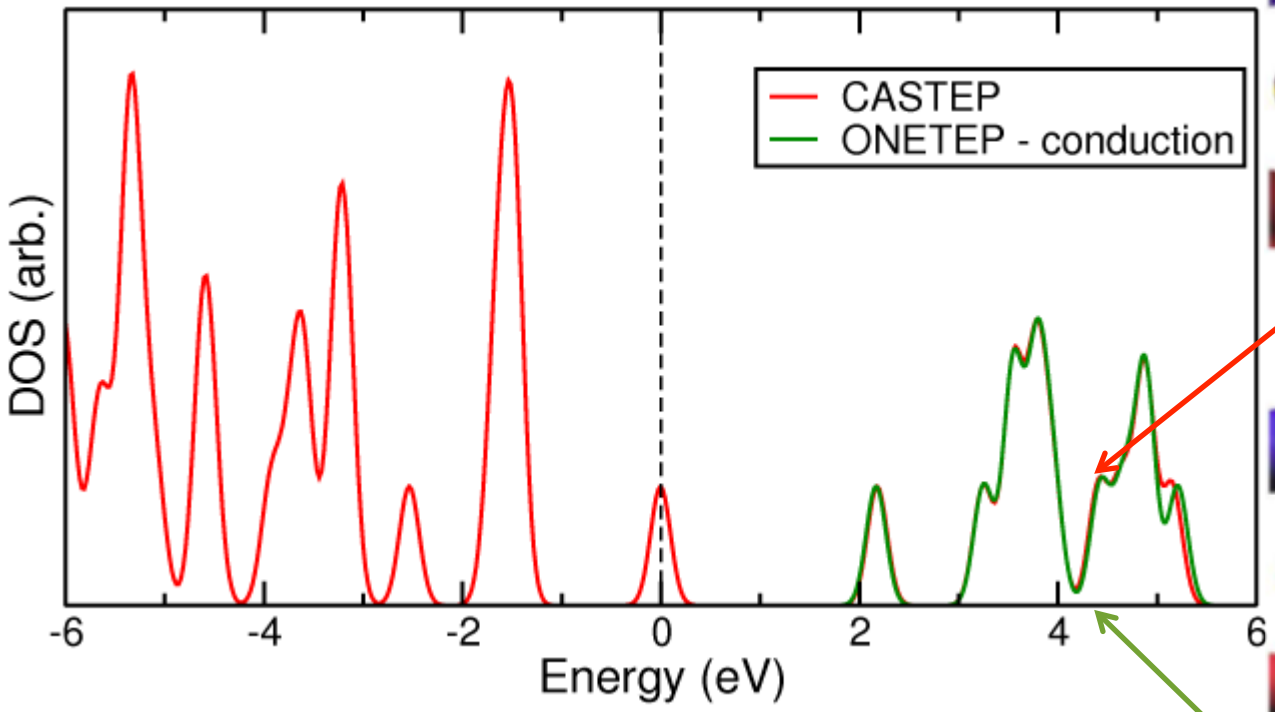


ONETEP

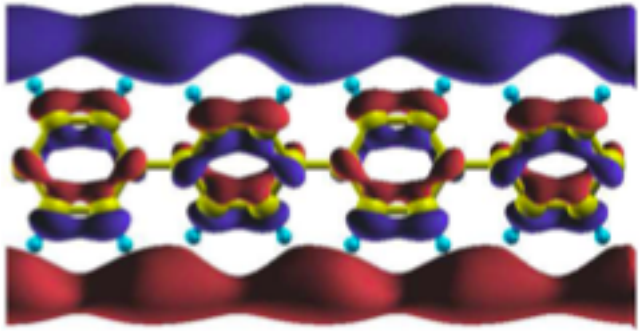
Valence only NGWFs ➔ wrong ordering of conduction states!

poly(*para*-phenylene) chain

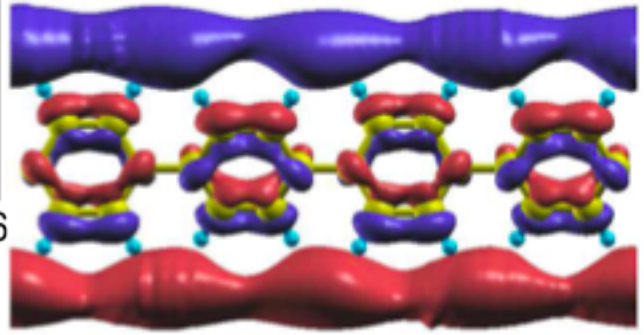




LUMO+8:

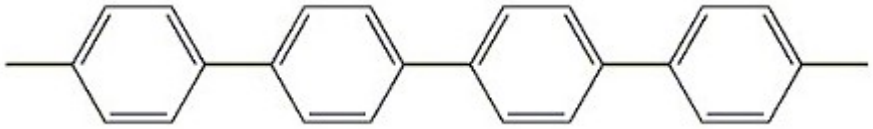


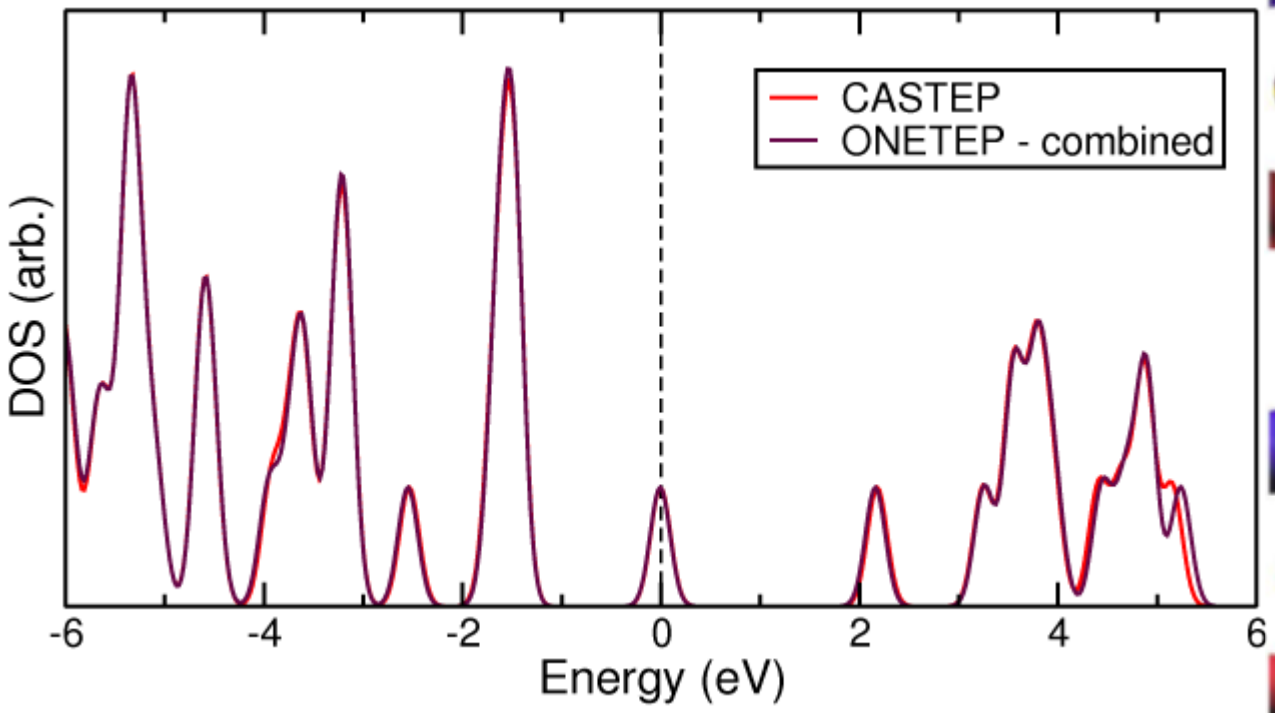
CASTEP



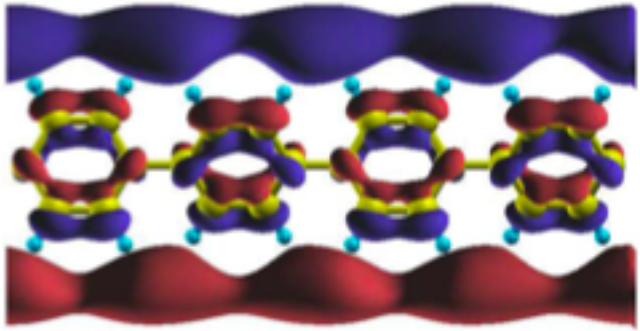
ONETEP

poly(*para*-phenylene) chain

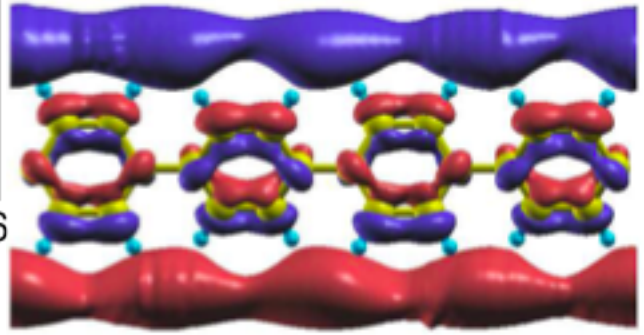




LUMO+8:



CASTEP



ONETEP

Time-dependent DFT

- TDDFT in the linear response formalism
- ALDA xc kernel
- Tamm-Dancoff approximation
- *O*(*N*) per excitation

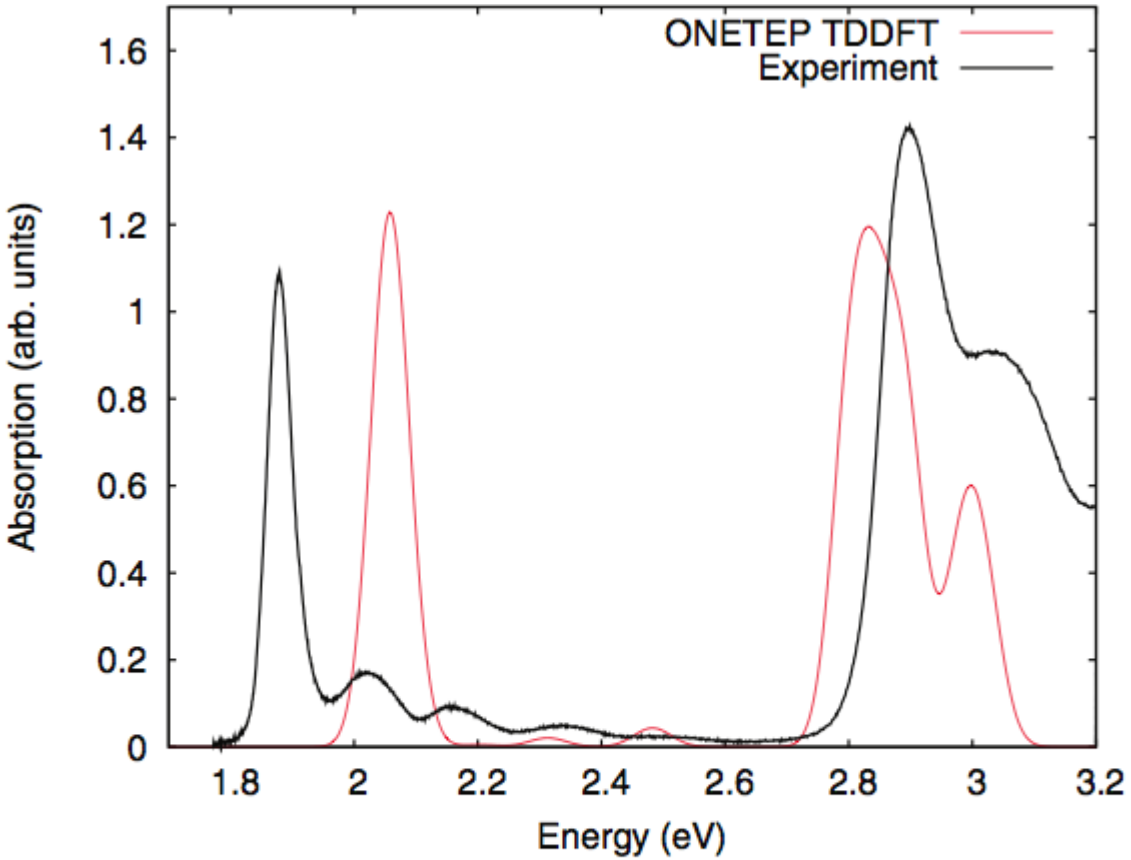
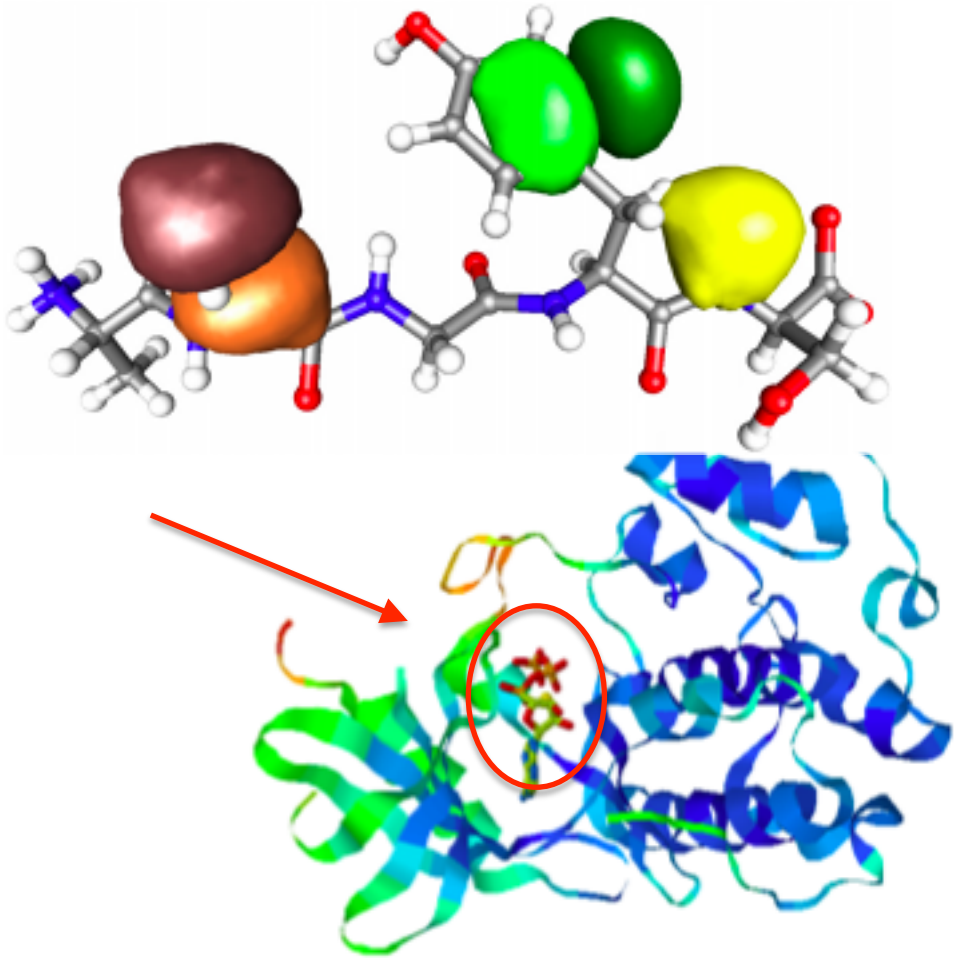


FIG. 4. Absorbtion spectrum of chlorophyll a generated from the 12 lowest excitation energies compared with the experimental spectrum of chlorophyll a in diethyl ether.[52] An artificial smearing width of 0.03 eV was used in producing the ONETEP TDDFT results.

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

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