

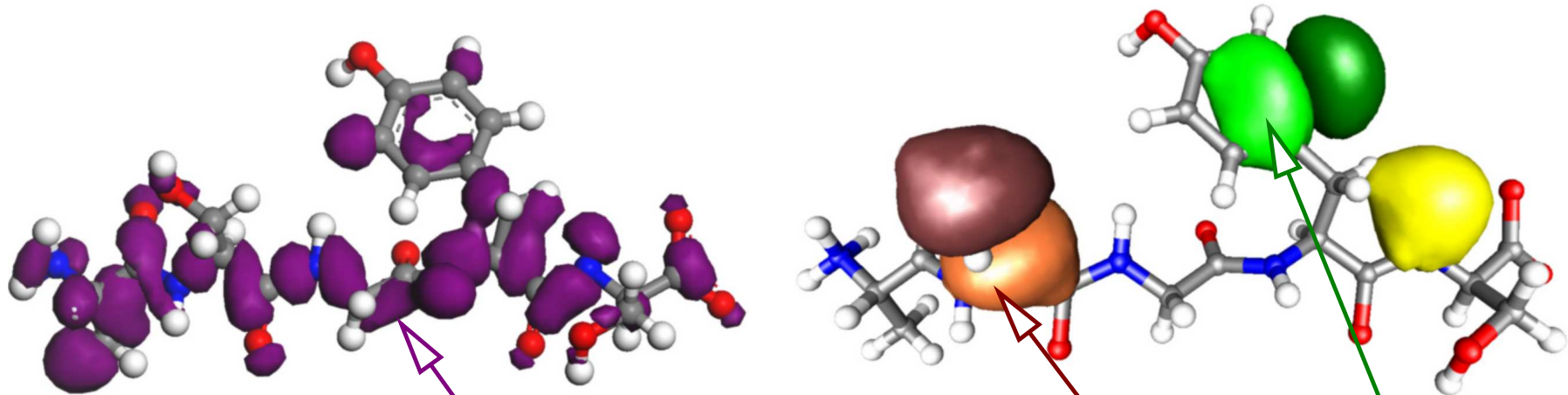
# Linear-scaling density-functional theory with plane-waves

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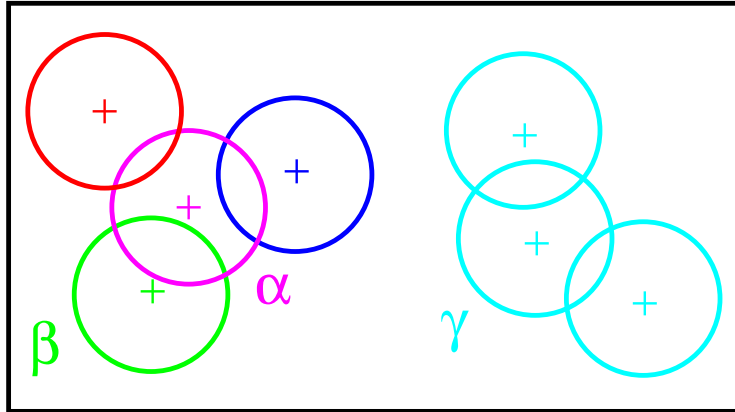
# Density–matrix linear–scaling methods



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

- Optimise non–orthogonal localised functions  $\{\phi_\alpha(\mathbf{r})\}$  instead of orthogonal extended wavefunctions  $\{\psi_n(\mathbf{r})\}$  } linear scaling
- Aim: to achieve the same accuracy as traditional plane–wave methods

# Density–matrix formulation



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

$$\text{Density } n(\mathbf{r}) = 2 \rho(\mathbf{r}, \mathbf{r})$$

$$\text{Energy } E = 2 \text{Tr}(KH)$$

Short–ranged:  $\rho(\mathbf{r}, \mathbf{r}') \longrightarrow 0$  as  $|\mathbf{r} - \mathbf{r}'| \longrightarrow \infty$

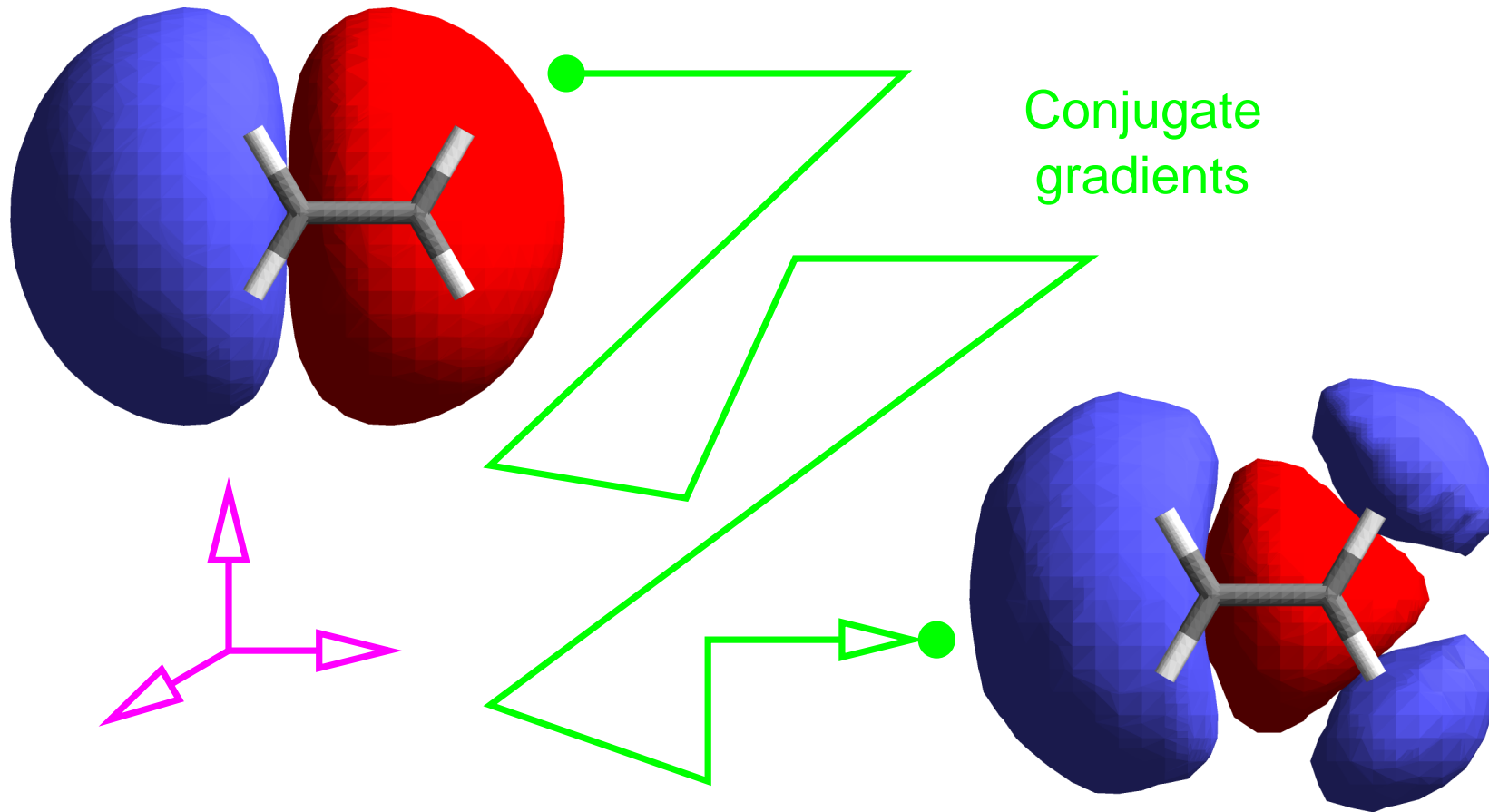
$\Rightarrow$  impose cutoffs:  $\phi_{\alpha}(\mathbf{r}) = 0$  when  $|\mathbf{r} - \mathbf{R}_{\alpha}| > R_{\text{reg}}$

$K^{\alpha\beta} = 0$  when  $|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}| > R_{\text{cut}}$

Idempotent:

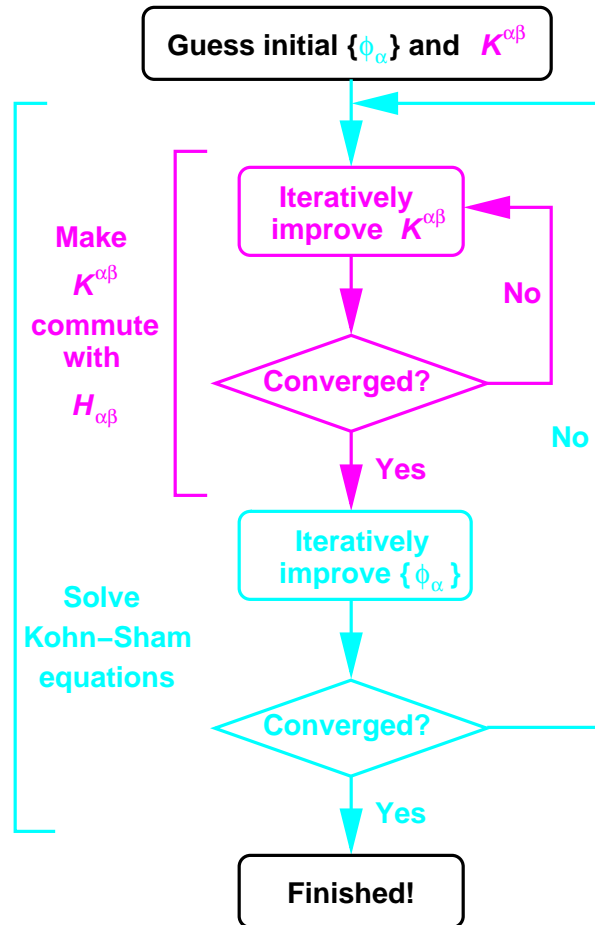
$$\rho^2(\mathbf{r}, \mathbf{r}') = \int \rho(\mathbf{r}, \mathbf{r}'') \rho(\mathbf{r}'', \mathbf{r}') d^3 r'' = \rho(\mathbf{r}, \mathbf{r}')$$

# Advantages of orthogonal basis sets



$$\hat{P} = 1 - |v\rangle\langle v| = 1 - \sum_{\alpha\beta} v_{\alpha} |\chi_{\alpha}\rangle S_{\alpha\beta}^{-1} \langle\chi_{\beta}| v_{\beta}$$

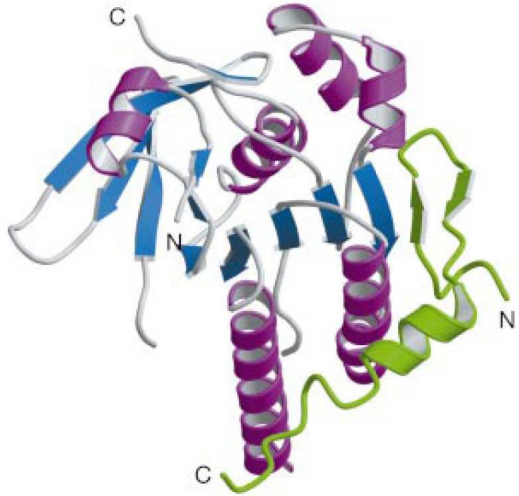
# Overview of method



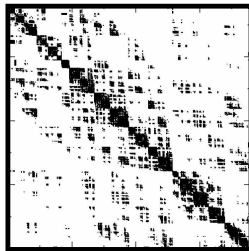
Use combination of methods:

- Li–Nunes–Vanderbilt (purification)  
*Phys. Rev. B* **47**, 10891 (1993)  
*Phys. Rev. B* **50**, 17611 (1994)  
[Millam–Scuseria variant:  
*J. Chem. Phys.* **106**, 5569 (1997)]
- Penalty functional  
*Phys. Rev. B* **59**, 12173 (1999)

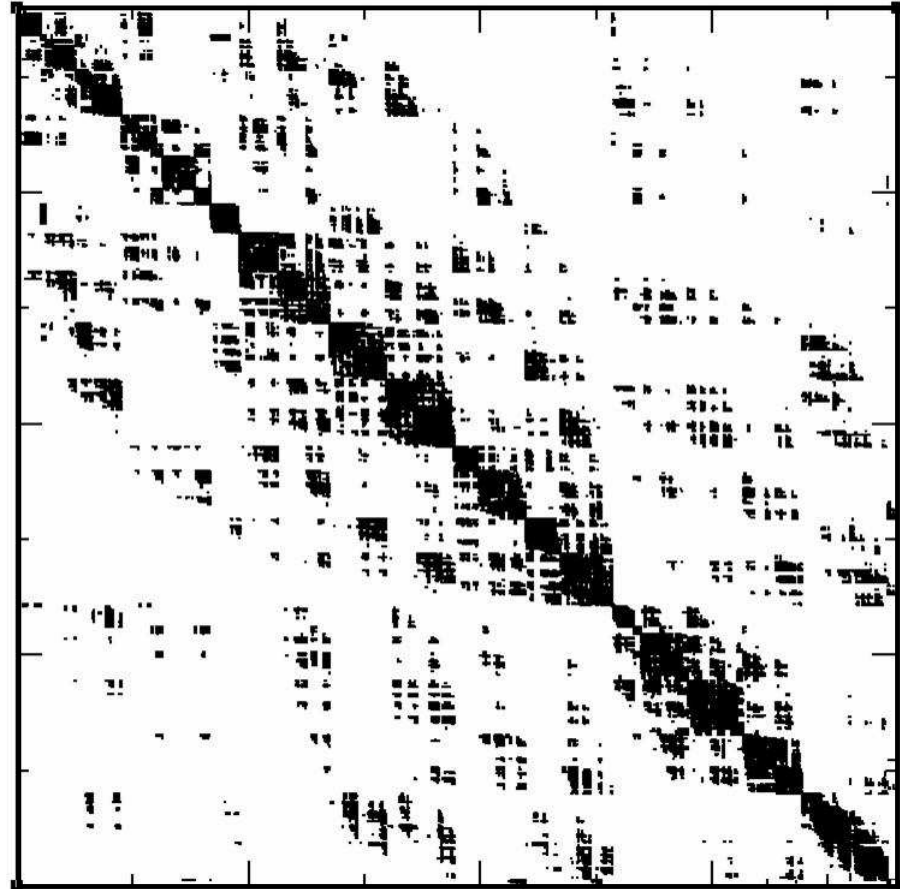
# Sparse matrix sizes



BRC4-RAD51  
complex (3000 atoms)

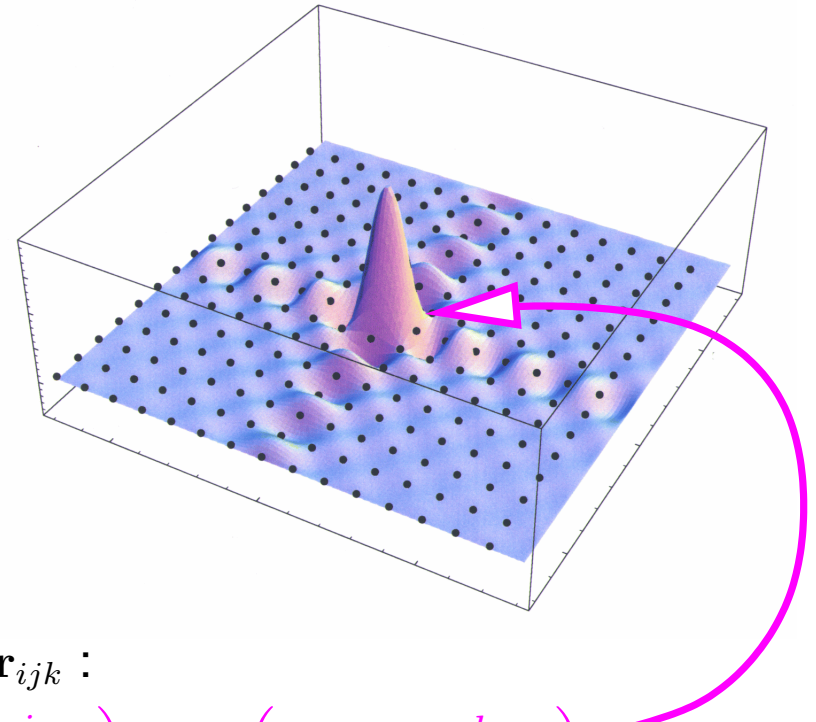
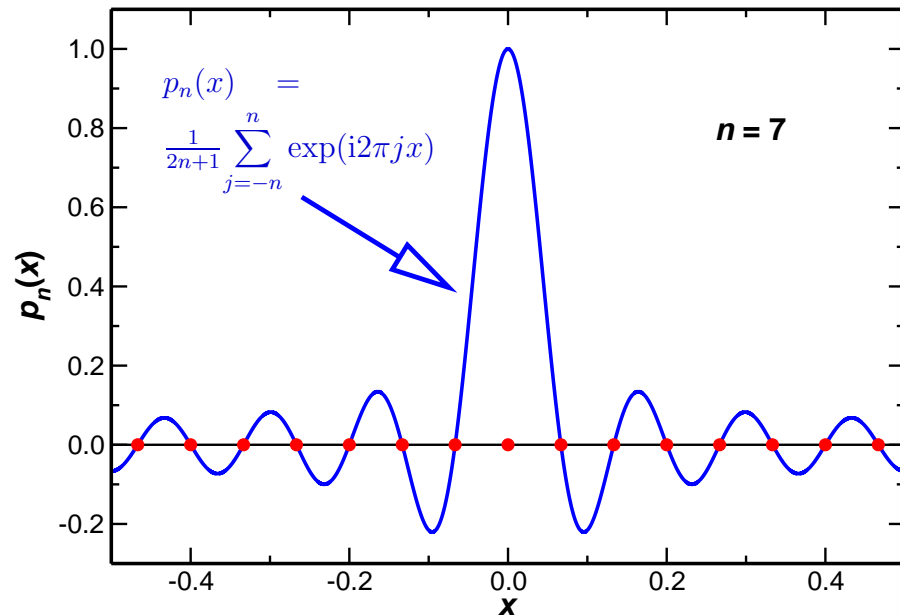


Optimized NGWFs:  
(7,600 x 7,600 : 4.4 MB)



DZP atomic orbital basis:  
(27,500 x 27,500 : 58 MB)

# PSINC Orthogonal Basis Set (Periodic Cardinal Sine)

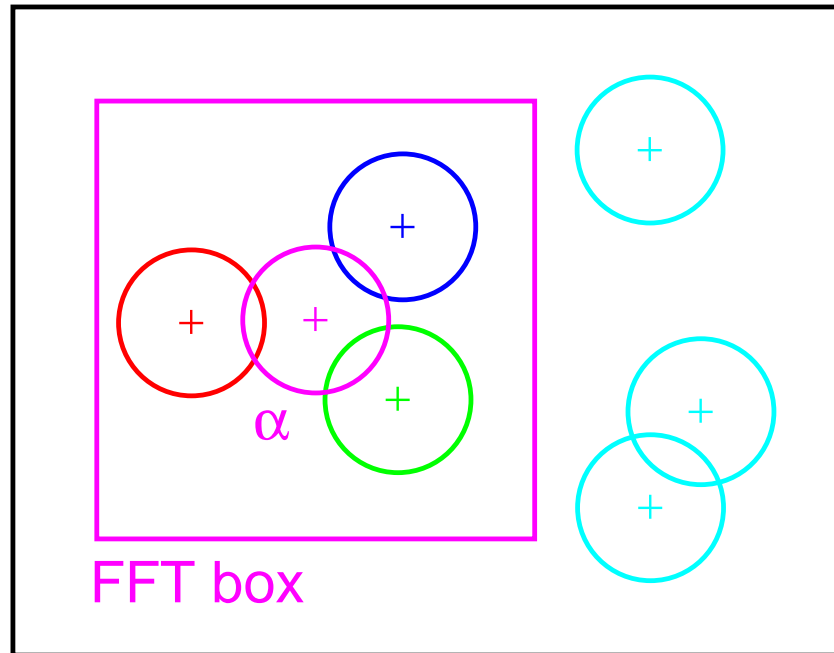


Define a basis set of 3D PSINC's on a regular grid  $\mathbf{r}_{ijk}$  :

$$D_{ijk}(\mathbf{r}) = p_{n_1} \left( \frac{x}{a_1} - \frac{i}{2n_1+1} \right) p_{n_2} \left( \frac{y}{a_2} - \frac{j}{2n_2+1} \right) p_{n_3} \left( \frac{z}{a_3} - \frac{k}{2n_3+1} \right)$$

- Real linear combinations of plane-waves
- Localized:  $D_{ijk}(\mathbf{r}_{lmn}) = \delta_{il} \delta_{jm} \delta_{kn}$
- Orthogonal:  $\int D_{ijk}(\mathbf{r}) D_{lmn}(\mathbf{r}) d^3r = w \delta_{il} \delta_{jm} \delta_{kn}$

# FFT box technique – introduction



Simulation cell

- Define a box for each function  $\phi_{\alpha}(\mathbf{r})$ 
  - centred on that function
  - universal shape and size
- Apply fast Fourier transforms in this box
  - to generate the charge density
  - to apply all terms in the Hamiltonian
- This method guarantees
  - consistent action of the Hamiltonian
  - Hermitian Hamiltonian matrix
  - linear scaling cost per iteration

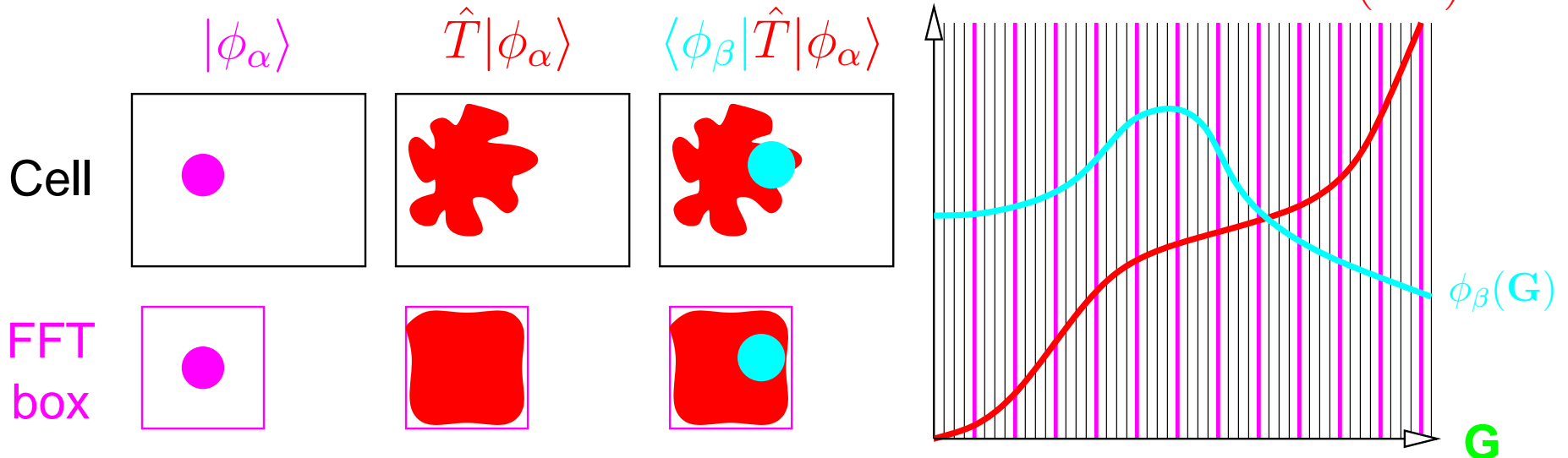
# FFT box technique – justification

- Define a set of PSINC's for the FFT box:  $d_{ijk}^\alpha(\mathbf{r})$
- Transfer functions from the cell to the FFT box using projection operators

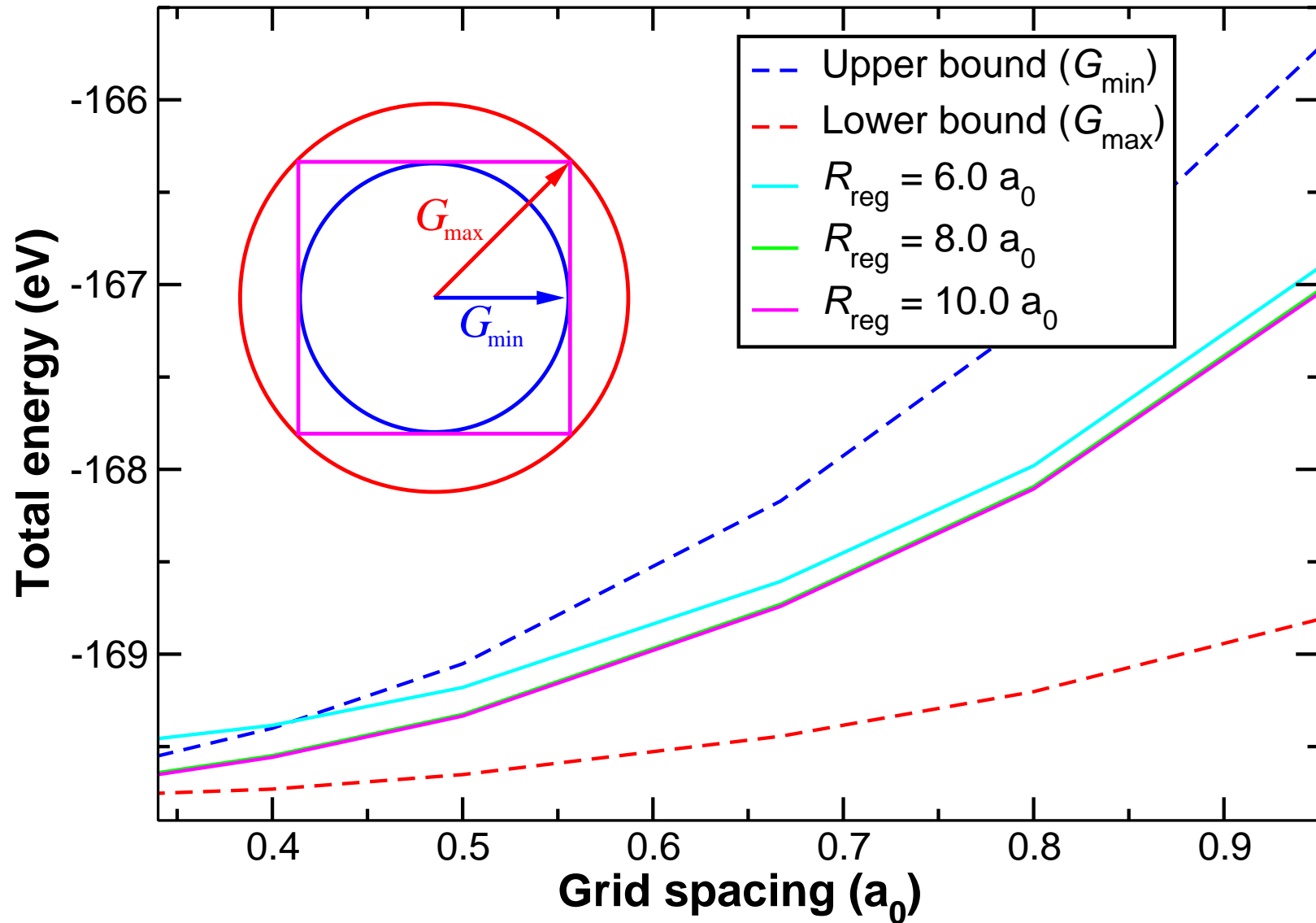
$$\hat{P}_\alpha = \sum_{\mathbf{r}_{ijk} \in \text{box } \alpha} |d_{ijk}^\alpha\rangle \langle D_{ijk}|$$

- Replaces  $\hat{H}|\phi_\alpha\rangle$  by  $\hat{P}_\alpha^\dagger \hat{H} \hat{P}_\alpha |\phi_\alpha\rangle$

Equivalent to a coarse sampling in momentum–space:



# Total energies



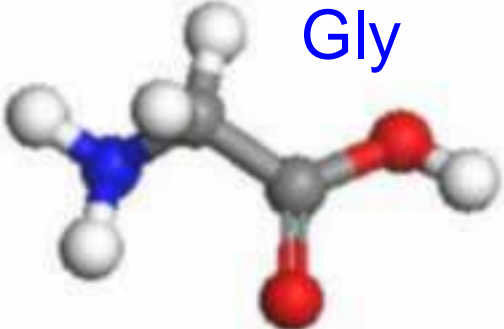
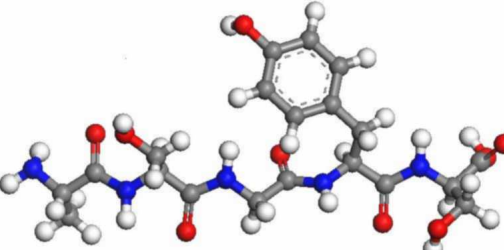
# Energy differences

## Comparison with a traditional plane-wave code

Energy differences between  
nonionic and zwitterionic forms

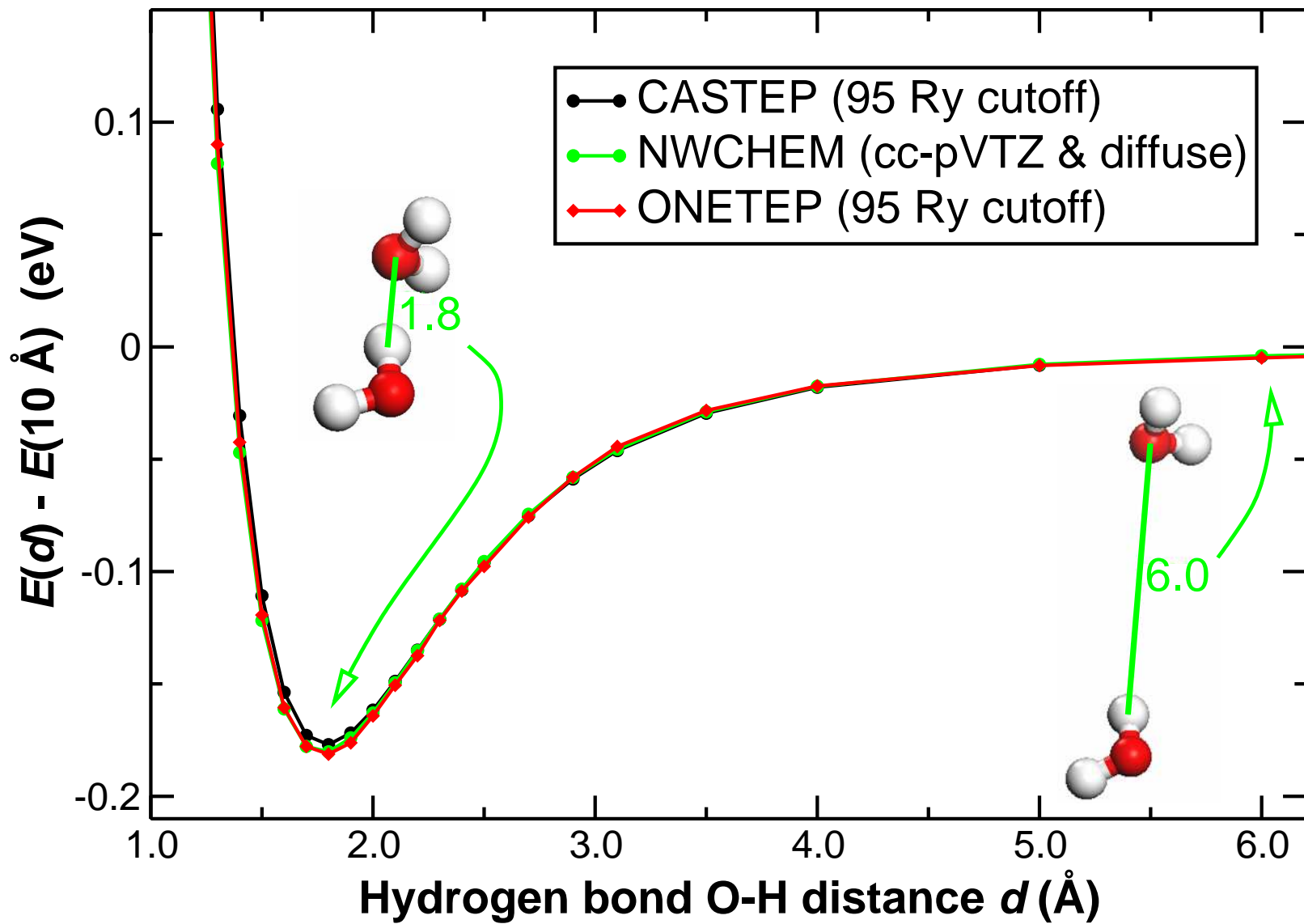
CASTEP

ONETEP

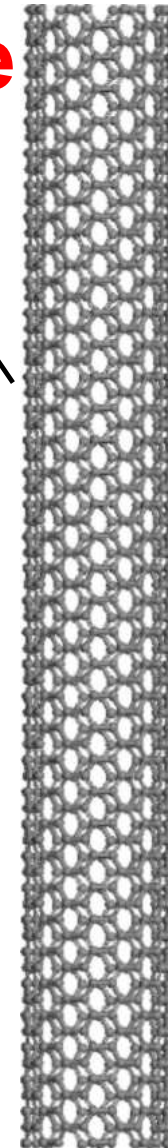
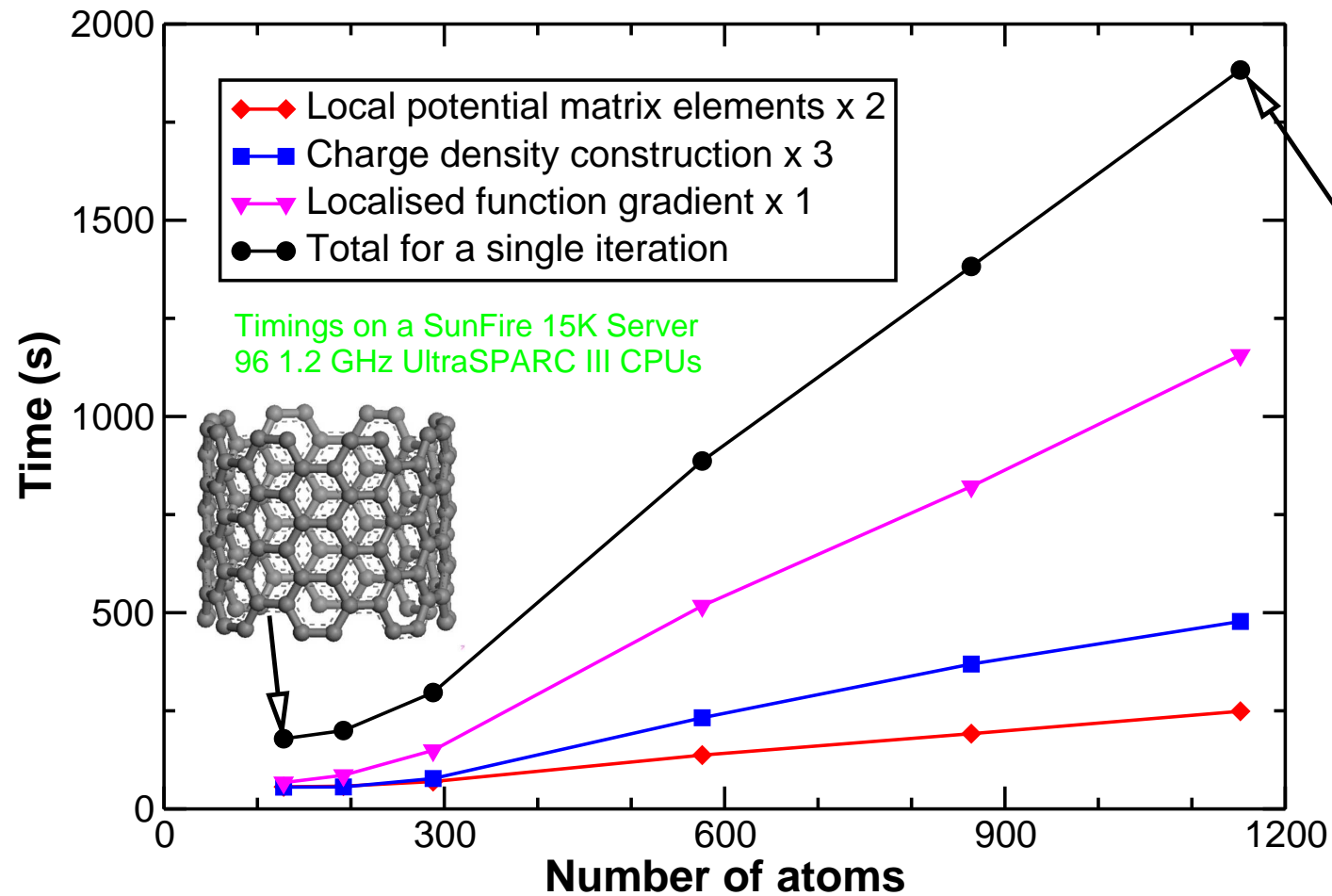
 <p>Gly</p>	1.21 eV (28.0 kcal mol <sup>-1</sup> )	1.20 eV (27.7 kcal mol <sup>-1</sup> )
 <p>AlaSerGlyTyrSer</p>	1.07 eV (24.7 kcal mol <sup>-1</sup> )	1.08 eV (24.9 kcal mol <sup>-1</sup> )

- Same simulation cell and energy cutoff: 40 Ry
- Same pseudopotentials: Troullier–Martins norm-conserving
- Same XC functional: LDA

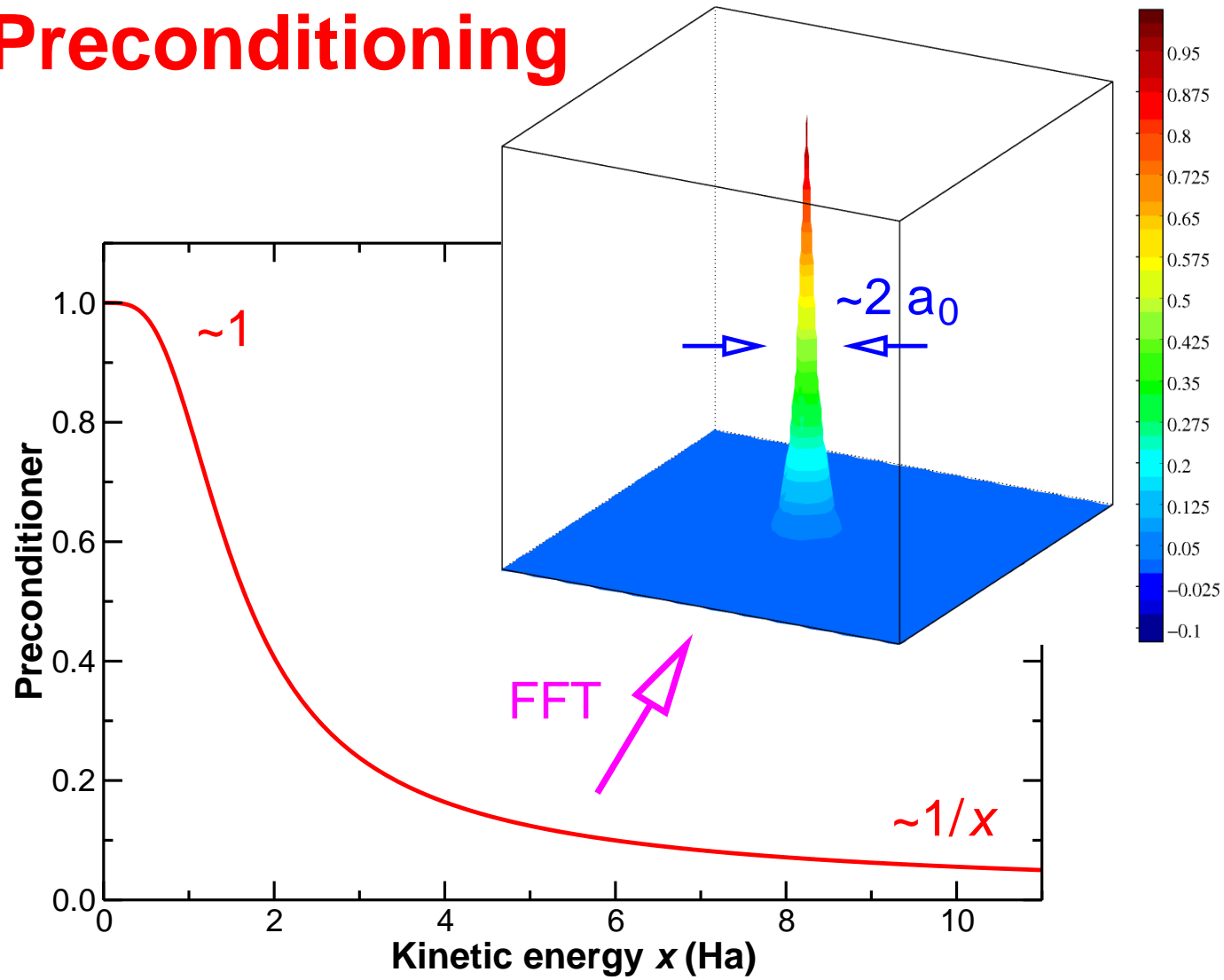
# Hydrogen bonds



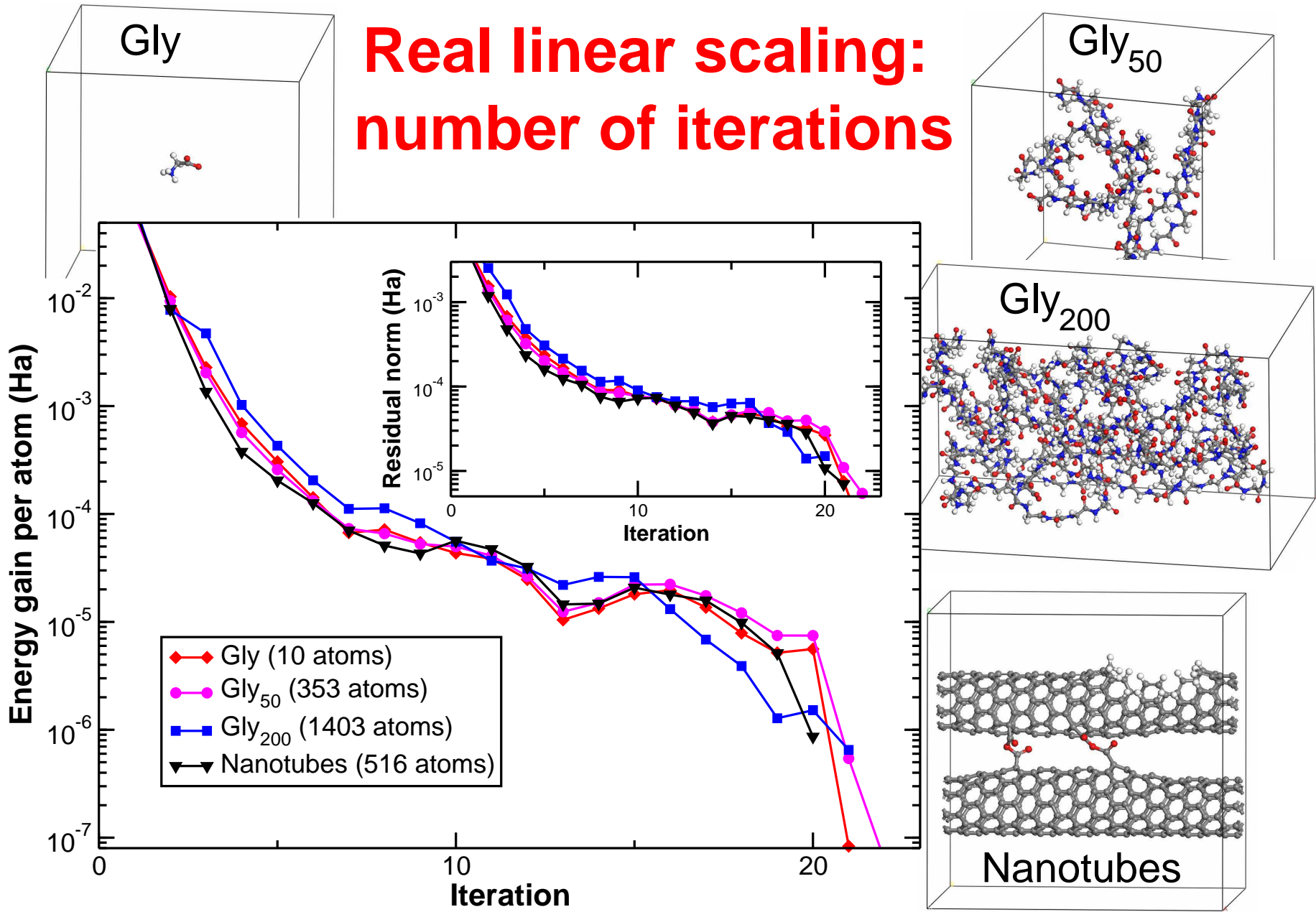
# Linear scaling with system-size



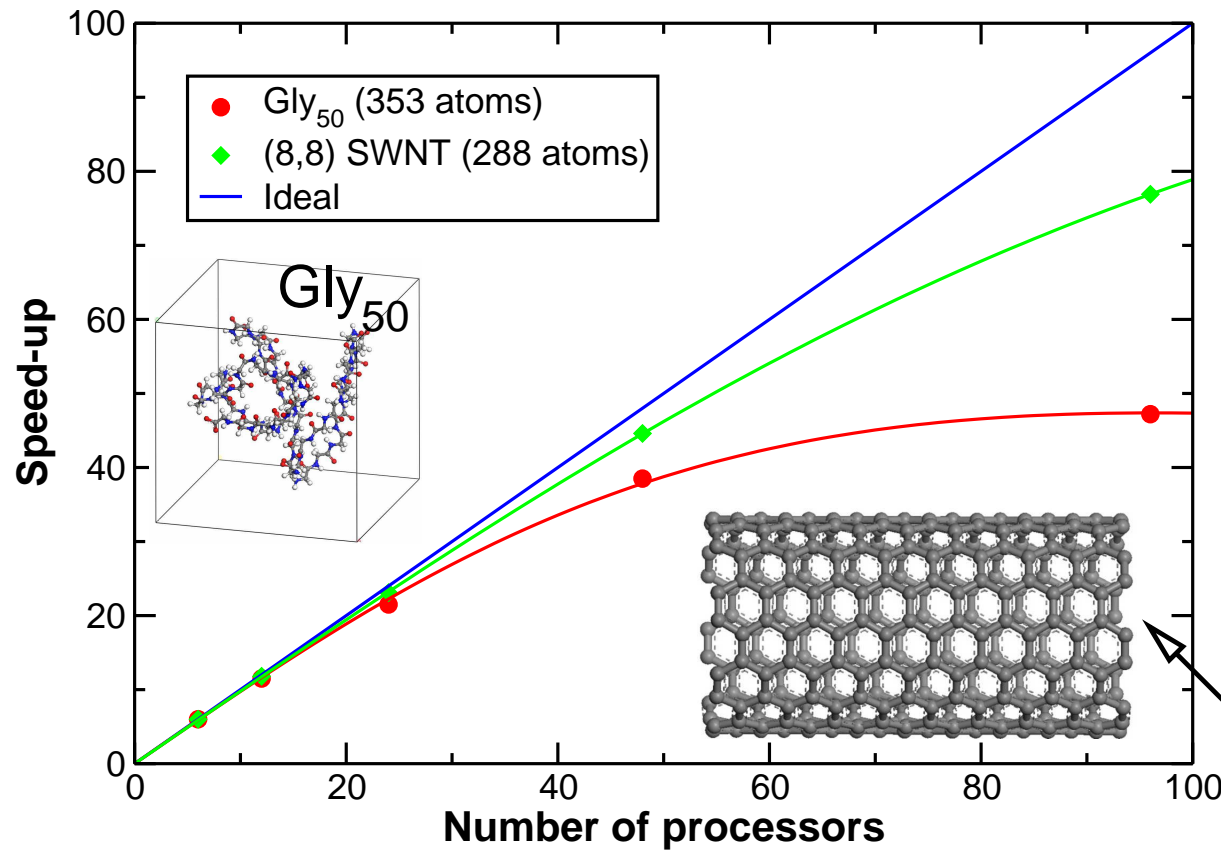
# Preconditioning



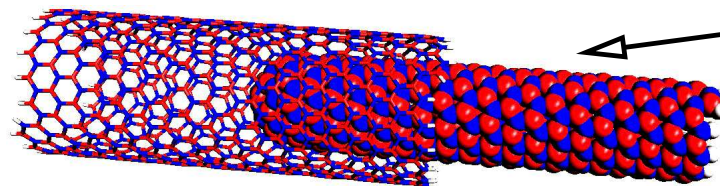
# Real linear scaling: number of iterations



# Parallel scalability



System	Number of atoms	Speed-up on 96 procs
Gly <sub>50</sub>	353	47.2
Gly <sub>100</sub>	703	88.8
Gly <sub>200</sub>	1403	80.0
(8,8) SWNT	288	76.9
BN DWNT	1192	71.5



# Conclusions

We have demonstrated a linear–scaling DFT method with:

- plane–wave accuracy
  - excellent convergence properties
  - good parallel scalability
- 
- Nonorthogonal generalized Wannier function pseudopotential plane–wave method  
*Phys. Rev. B* **66**, 035119 (2002)
  - Preconditioned iterative minimisation for linear–scaling electronic structure calculations  
*J. Chem. Phys.* **119**, 8842 (2003)
  - Total–energy calculations on a real space grid with localized functions and a plane–wave basis  
*Comput. Phys. Commun.* **147**, 788 (2002)
  - Comparison of variational real–space representations of the kinetic energy operator  
*Phys. Rev. B* **66**, 073103 (2002)
  - Accurate kinetic energy evaluation in electronic structure calculations with localized functions...  
*Comput. Phys. Commun.* **140**, 315 (2001)