Linear−scaling density−functional theory with plane−waves

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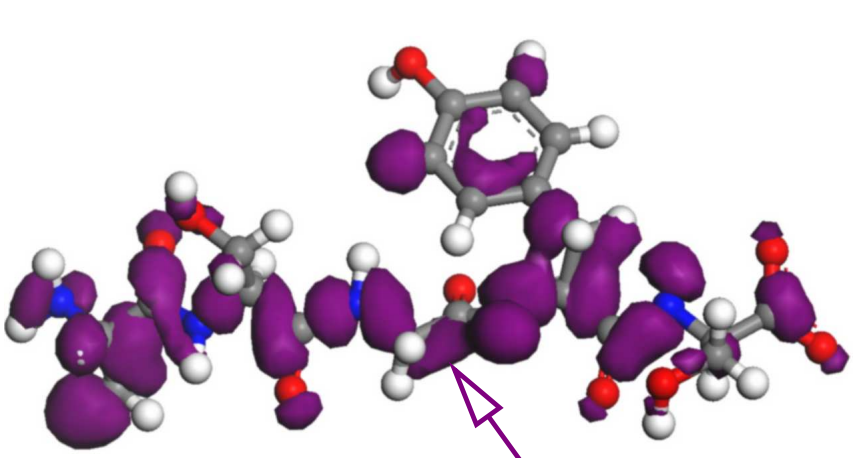
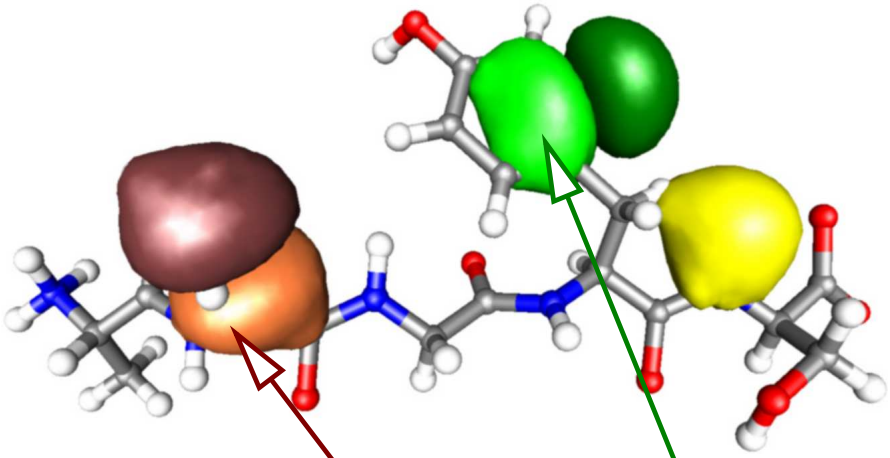
Density−matrix linear−scaling methods

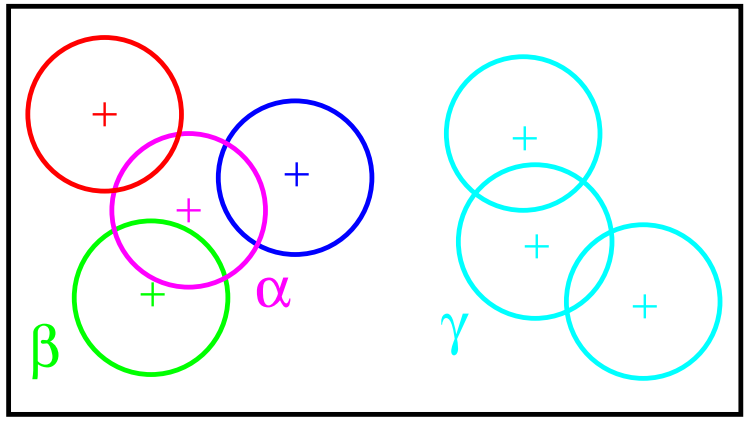




$$\rho(\mathbf{r},\mathbf{r}') \quad = \quad \sum_n f_n \, \psi_n(\mathbf{r}) \, \psi_n^*(\mathbf{r}') \quad = \quad \sum_{\alpha\beta} \phi_\alpha(\mathbf{r}) \, K^{\alpha\beta} \, \phi_\beta^*(\mathbf{r}')$$

- 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



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

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

Energy $\quad E \quad = \quad 2\,\mathrm{Tr}(KH)$

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

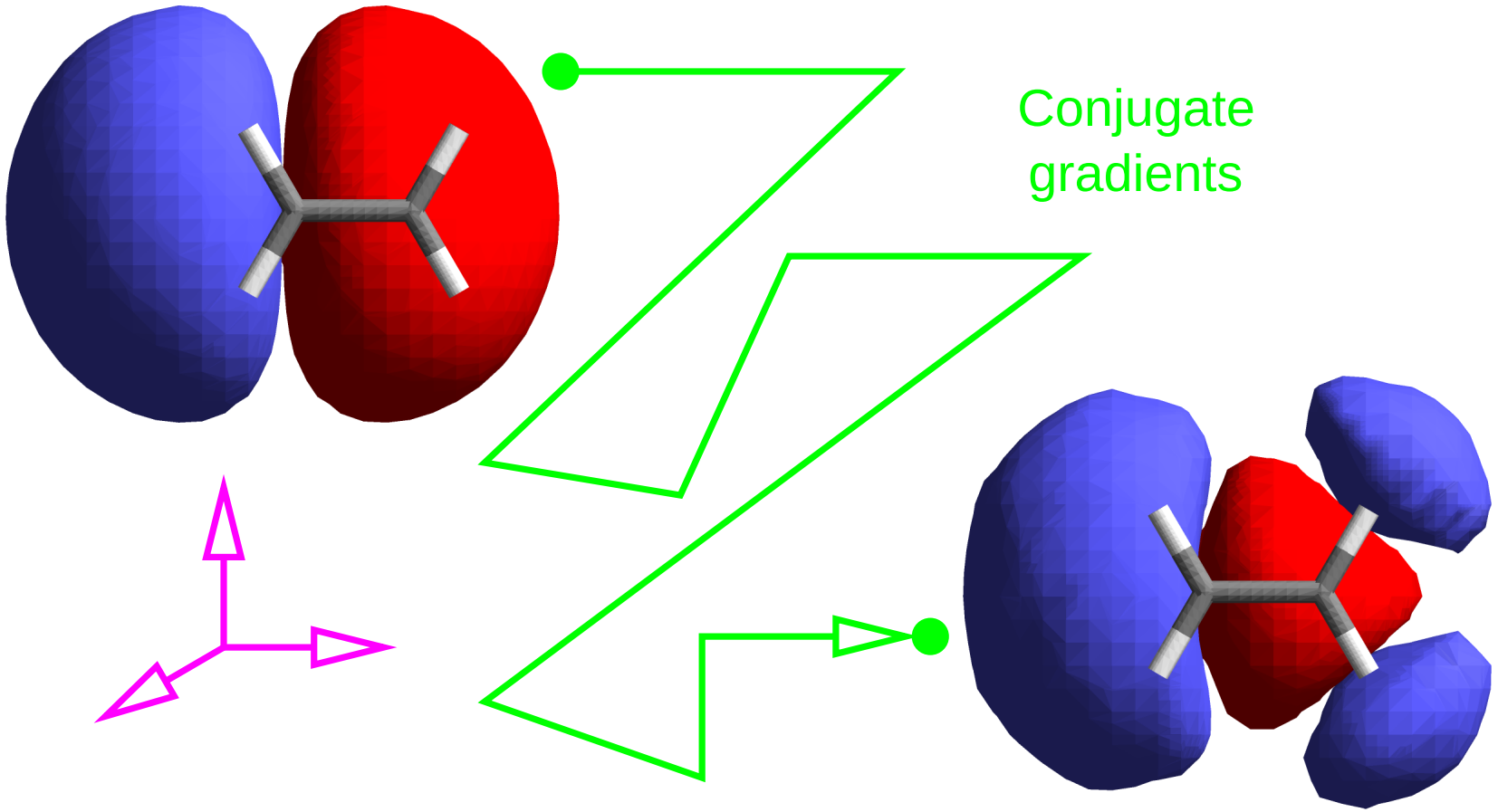
$\Rightarrow$ impose cutoffs: $\quad \phi_\alpha(\mathbf{r}) = 0 \quad$ when $\quad |\mathbf{r}-\mathbf{R}_\alpha| > R_{\mathrm{reg}}$

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

Idempotent:

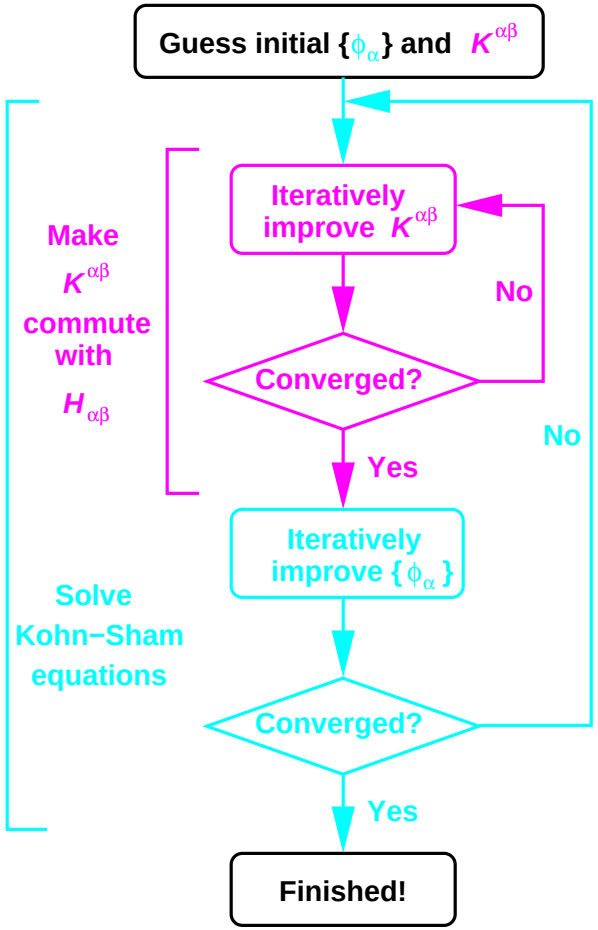
$$\rho^2(\mathbf{r},\mathbf{r}') \quad = \quad \int \rho(\mathbf{r},\mathbf{r}'')\,\rho(\mathbf{r}'',\mathbf{r}')\,d^3r'' \quad = \quad \rho(\mathbf{r},\mathbf{r}')$$

Advantages of orthogonal basis sets



$$\hat{P} \quad = \quad 1 - |v\rangle\langle v| \quad = \quad 1 - \sum_{\alpha\beta} v_\alpha \left|\chi_\alpha\right\rangle S^{-1}_{\alpha\beta} \left\langle\chi_\beta\right| v_\beta$$

Overview of method



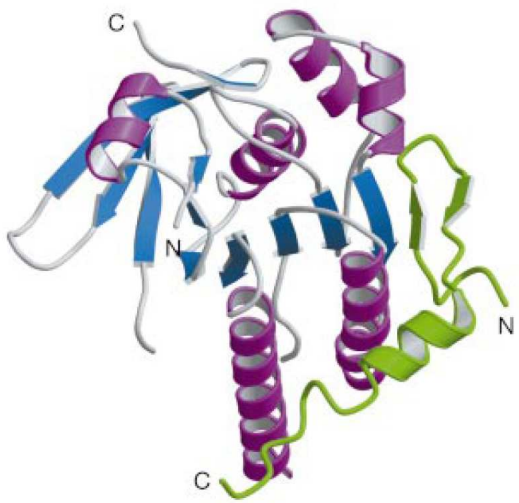
Use combination of methods:

- Li−Nunes−Vanderbilt (purification)
  Phys. Rev. B **47**, 10891 (1993)
  Phys. Rev. B **50**, 17611 (1994)

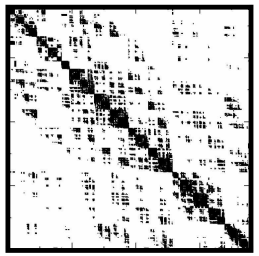
  [Millam−Scuseria variant:
  J. Chem. Phys. **106**, 5569 (1997)]

- Penalty functional
  Phys. Rev. B **59**, 12173 (1999)

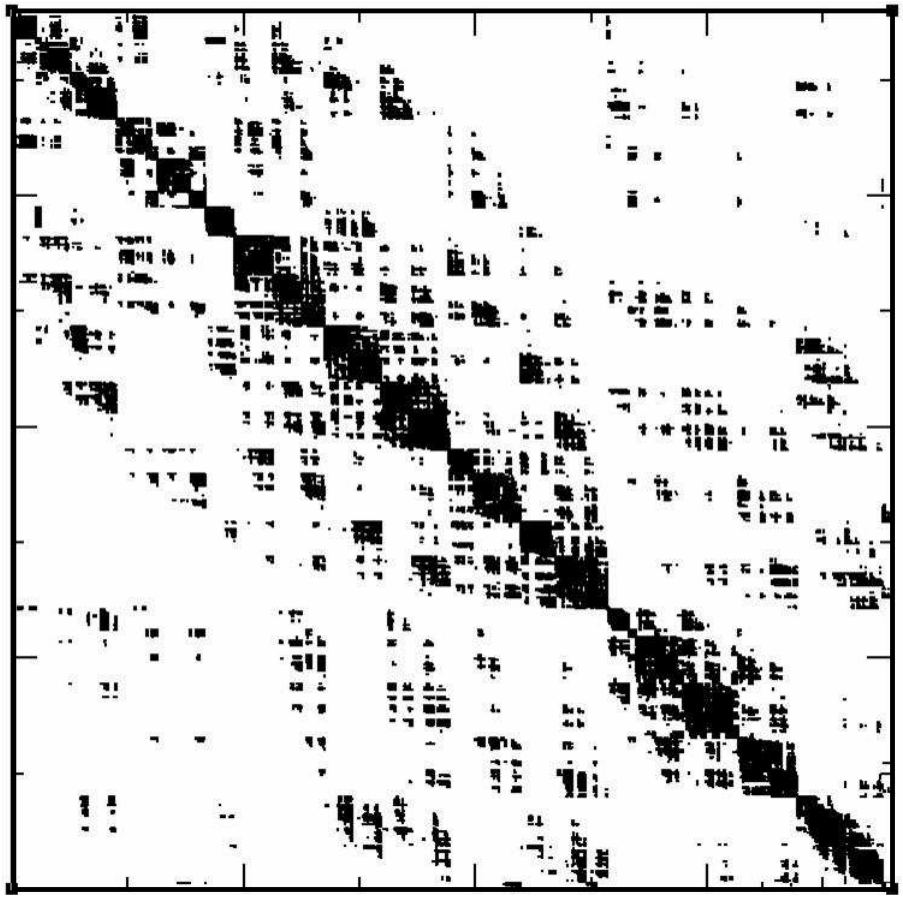
Sparse matrix sizes



BRC4−RAD51
complex (3000 atoms)



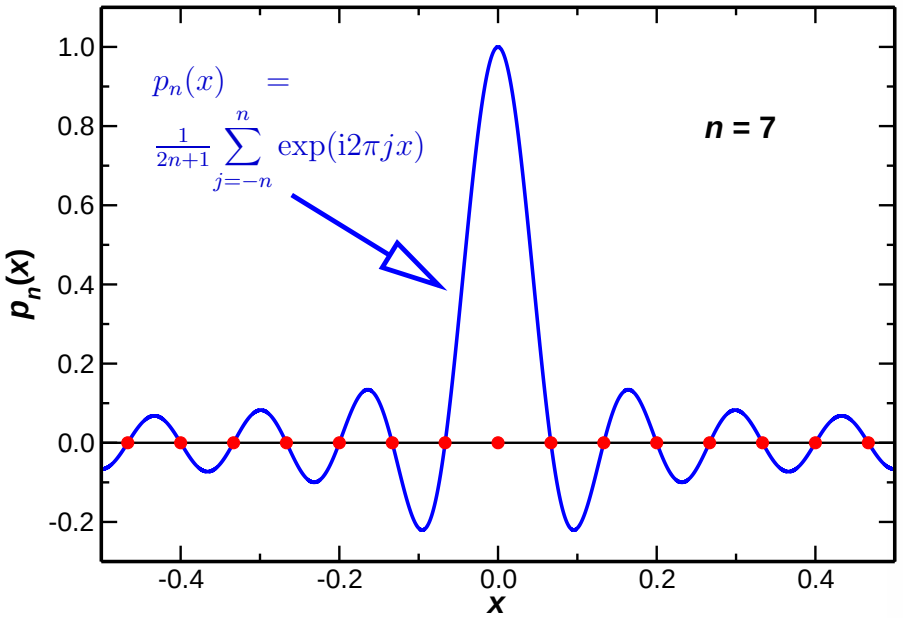
Optimized NGWFs:
(7,600 x 7,600 : 4.4 MB)

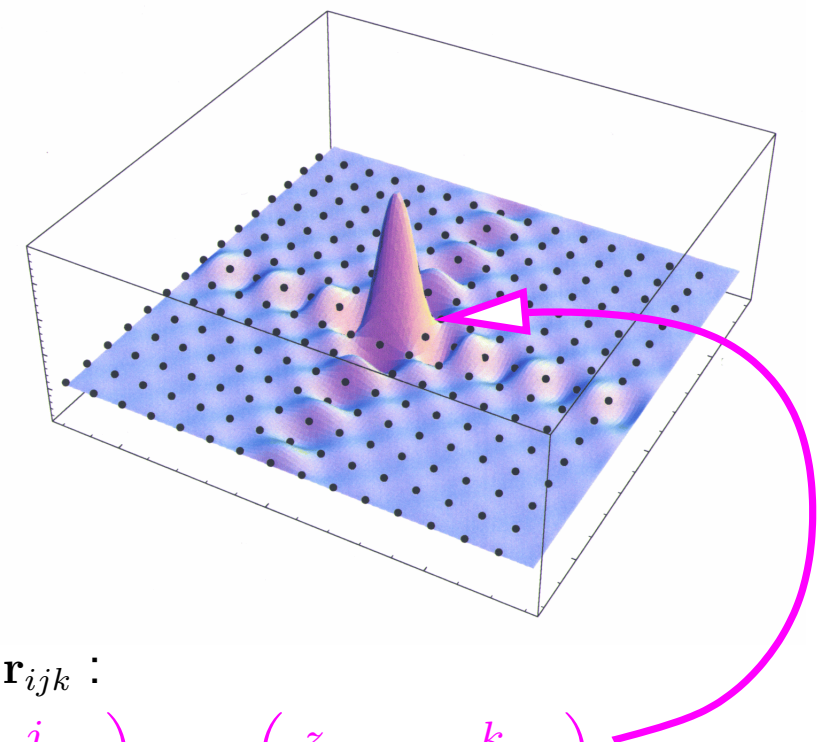


DZP atomic orbital basis:
(27,500 x 27,500 : 58 MB)

PSINC Orthogonal Basis Set

(Periodic Cardinal Sine)



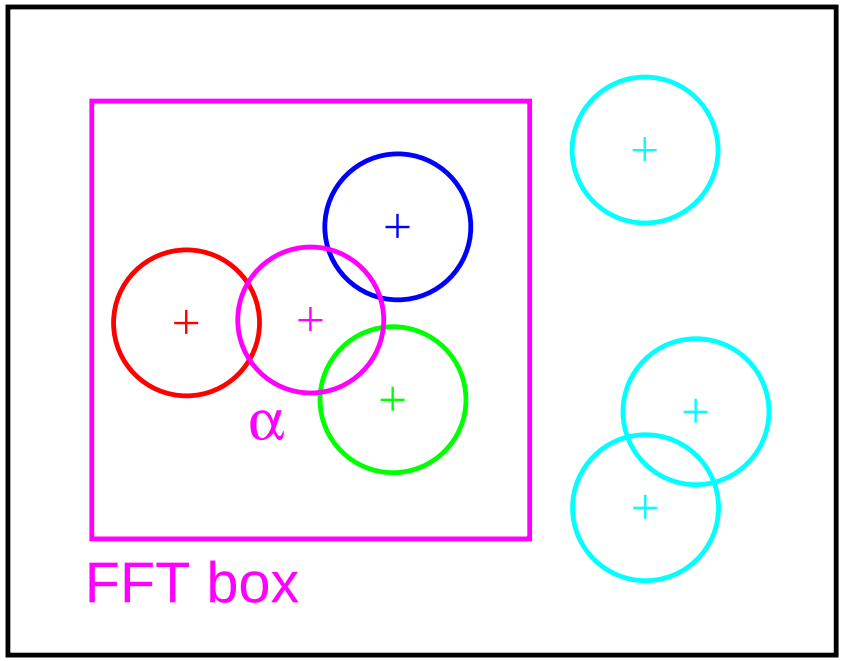


Define a basis set of 3D PSINC's on a regular grid $\mathbf{r}_{ijk}$:

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

- 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

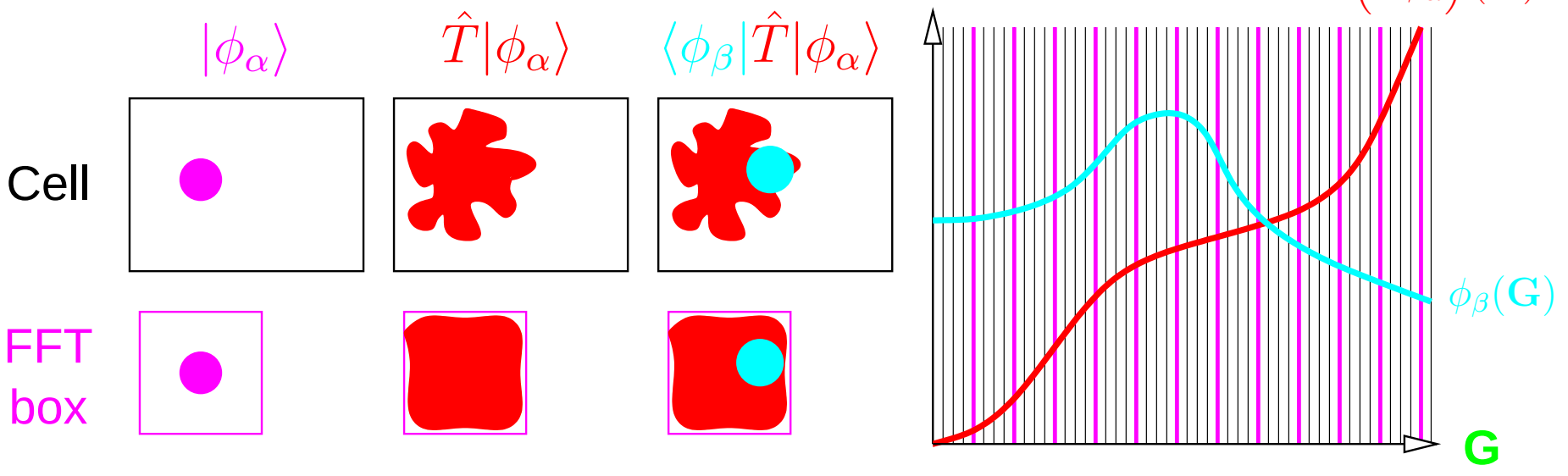
FFT box technique − justification

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

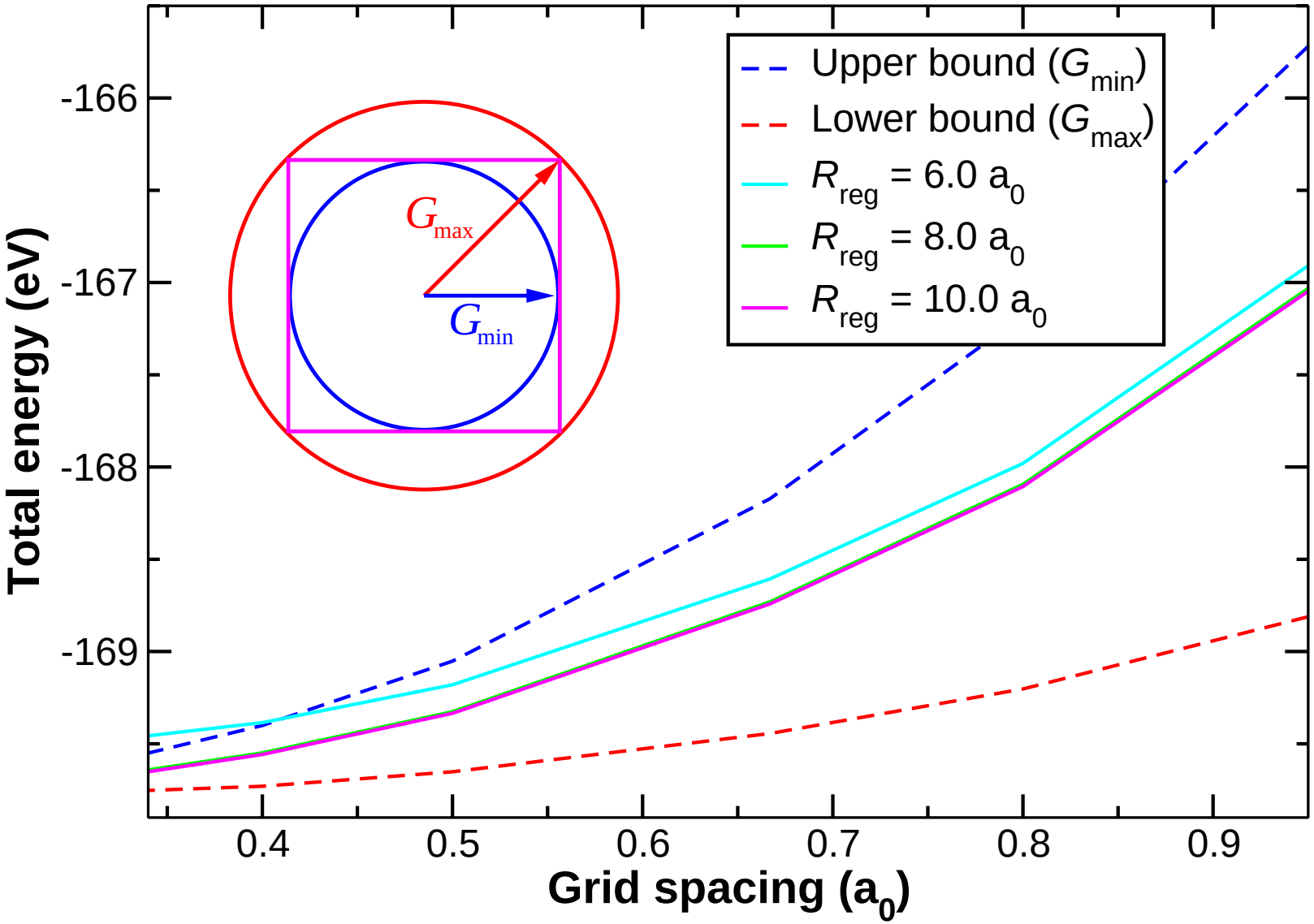
$$\hat{P}_{\alpha} = \sum_{\mathbf{r}_{ijk}\in \text{box}\ \alpha} \left| d^{\alpha}_{ijk} \right\rangle \left\langle D_{ijk} \right|$$

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

Equivalent to a coarse sampling in momentum−space:

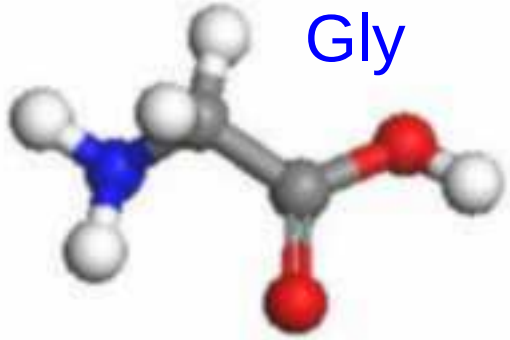
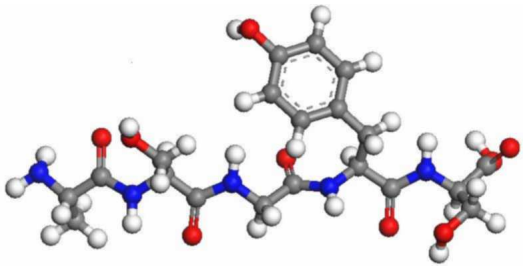


Total energies



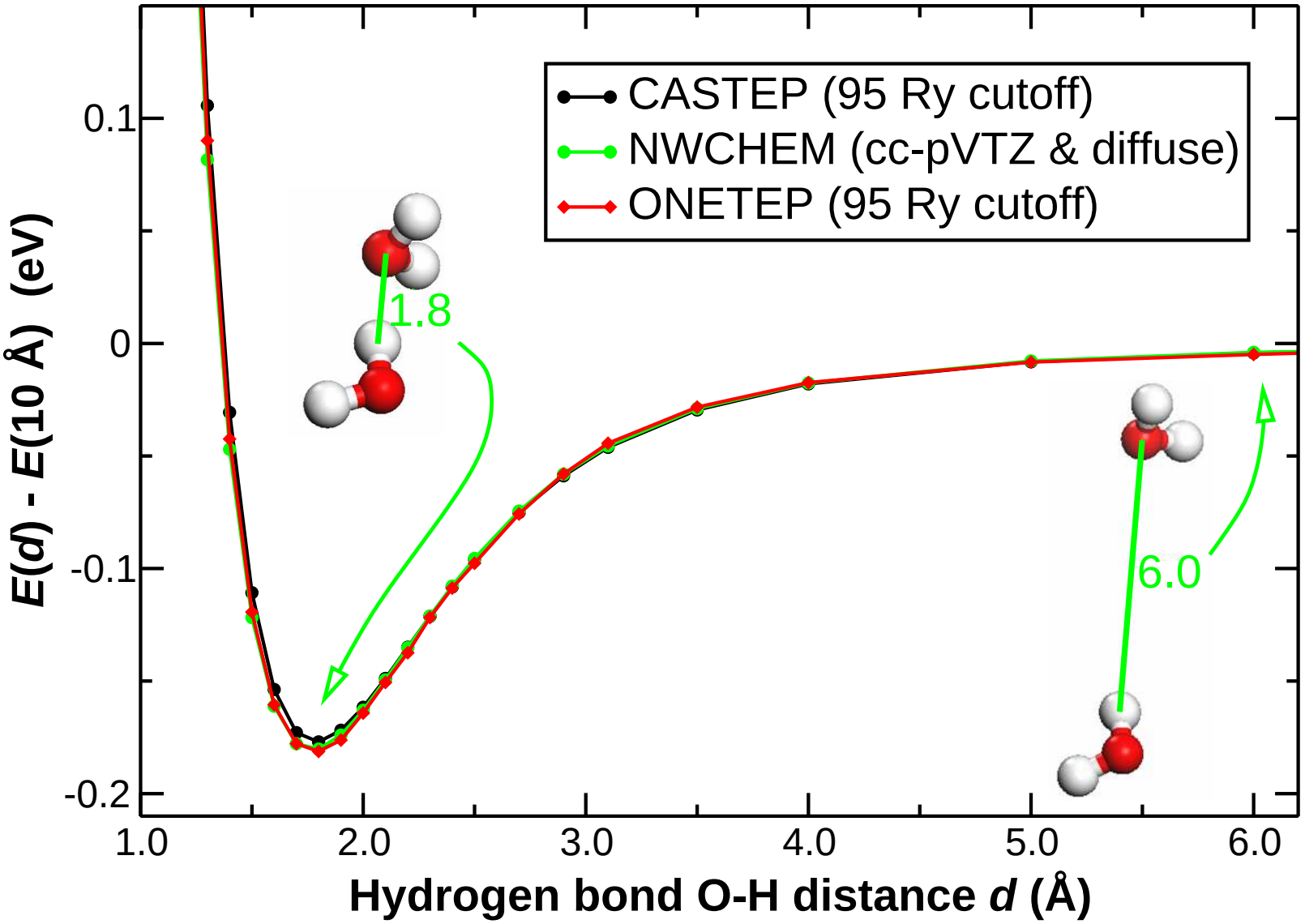
Energy differences

Comparison with a traditional plane−wave code

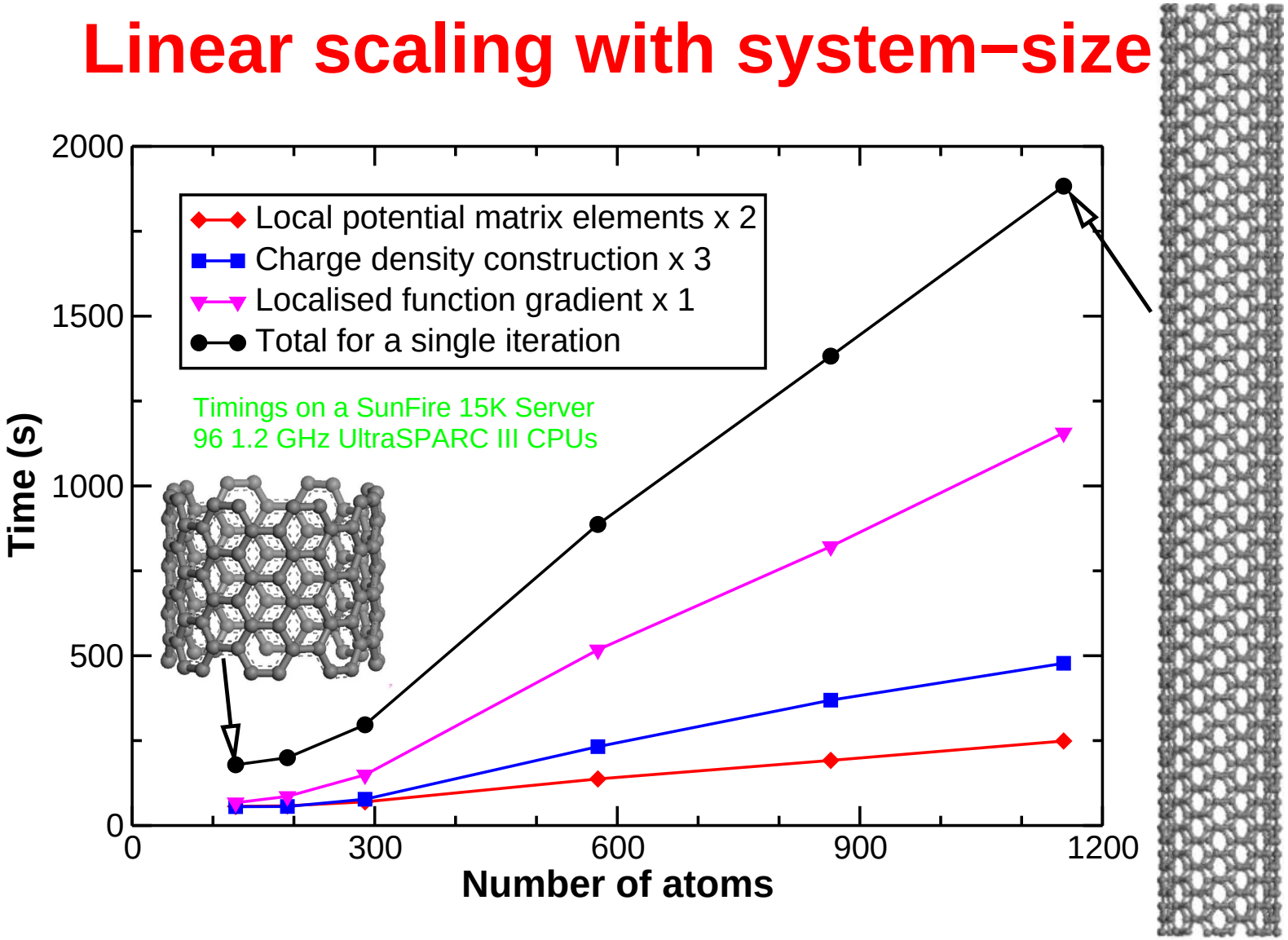
Energy differences between nonionic and zwitterionic forms	CASTEP	**ONETEP**
Gly 	1.21 eV (28.0 kcal mol^{-1})	1.20 eV (27.7 kcal mol^{-1})
 AlaSerGlyTyrSer	1.07 eV (24.7 kcal mol^{-1})	1.08 eV (24.9 kcal mol^{-1})

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

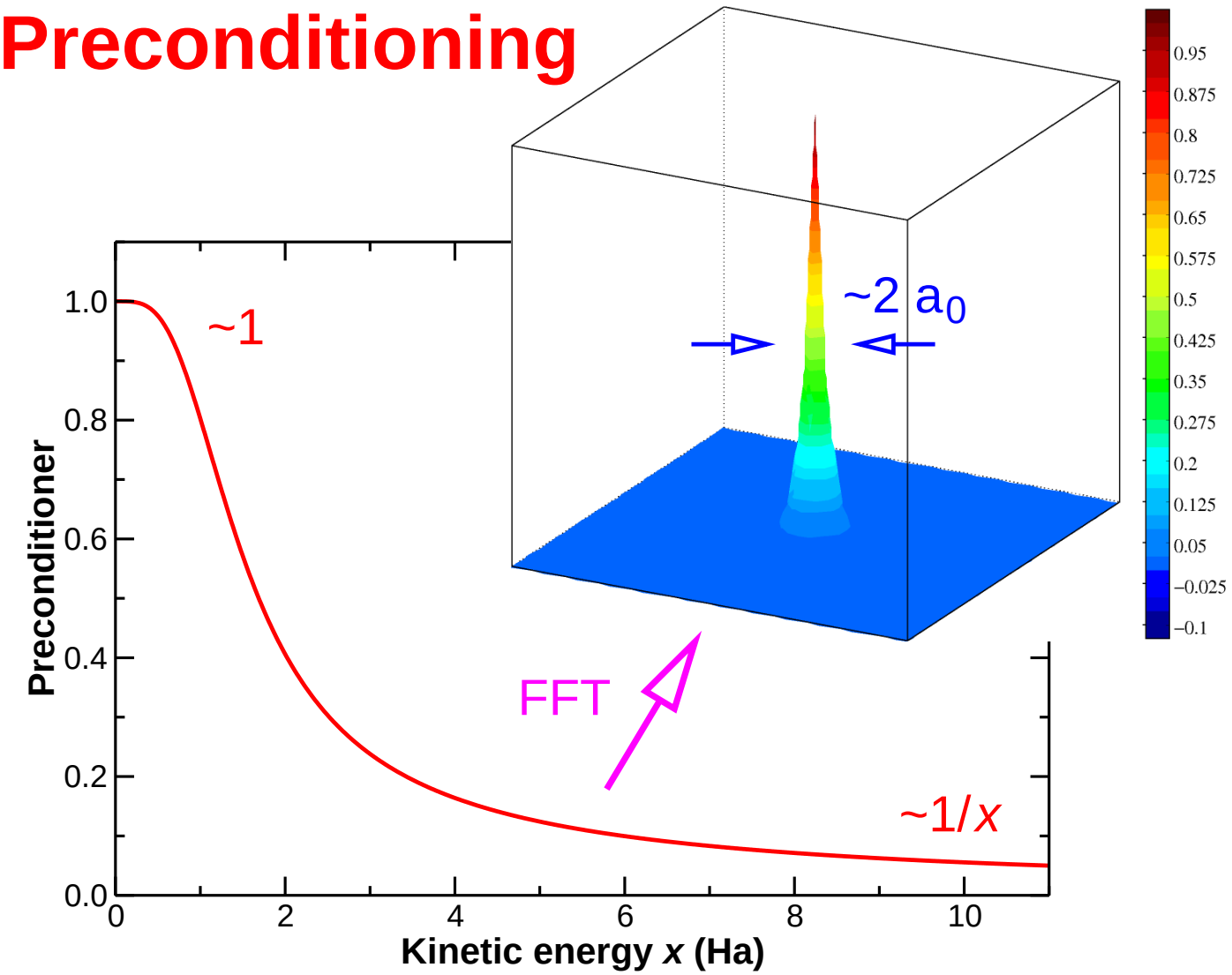
Hydrogen bonds



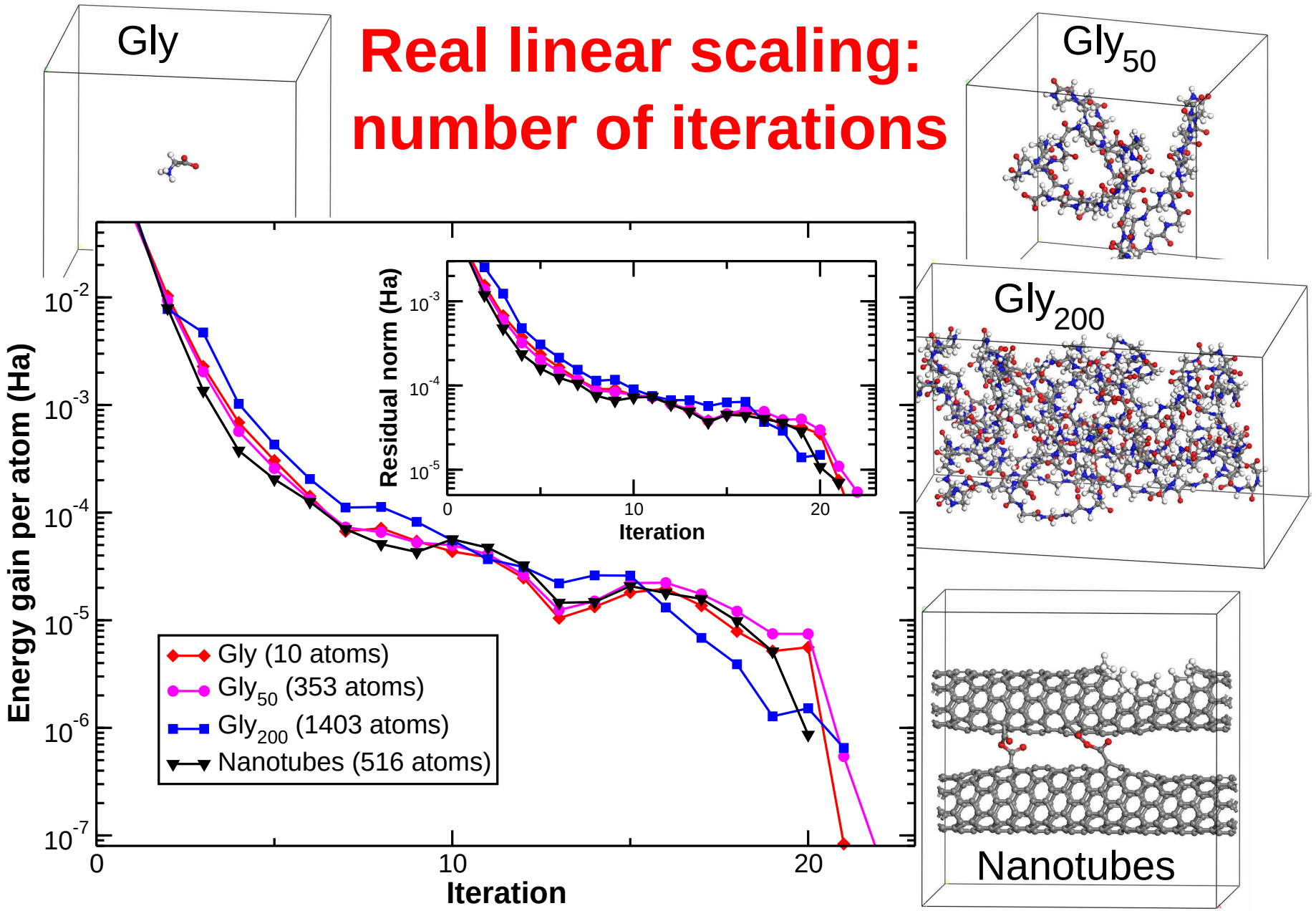
Linear scaling with system−size



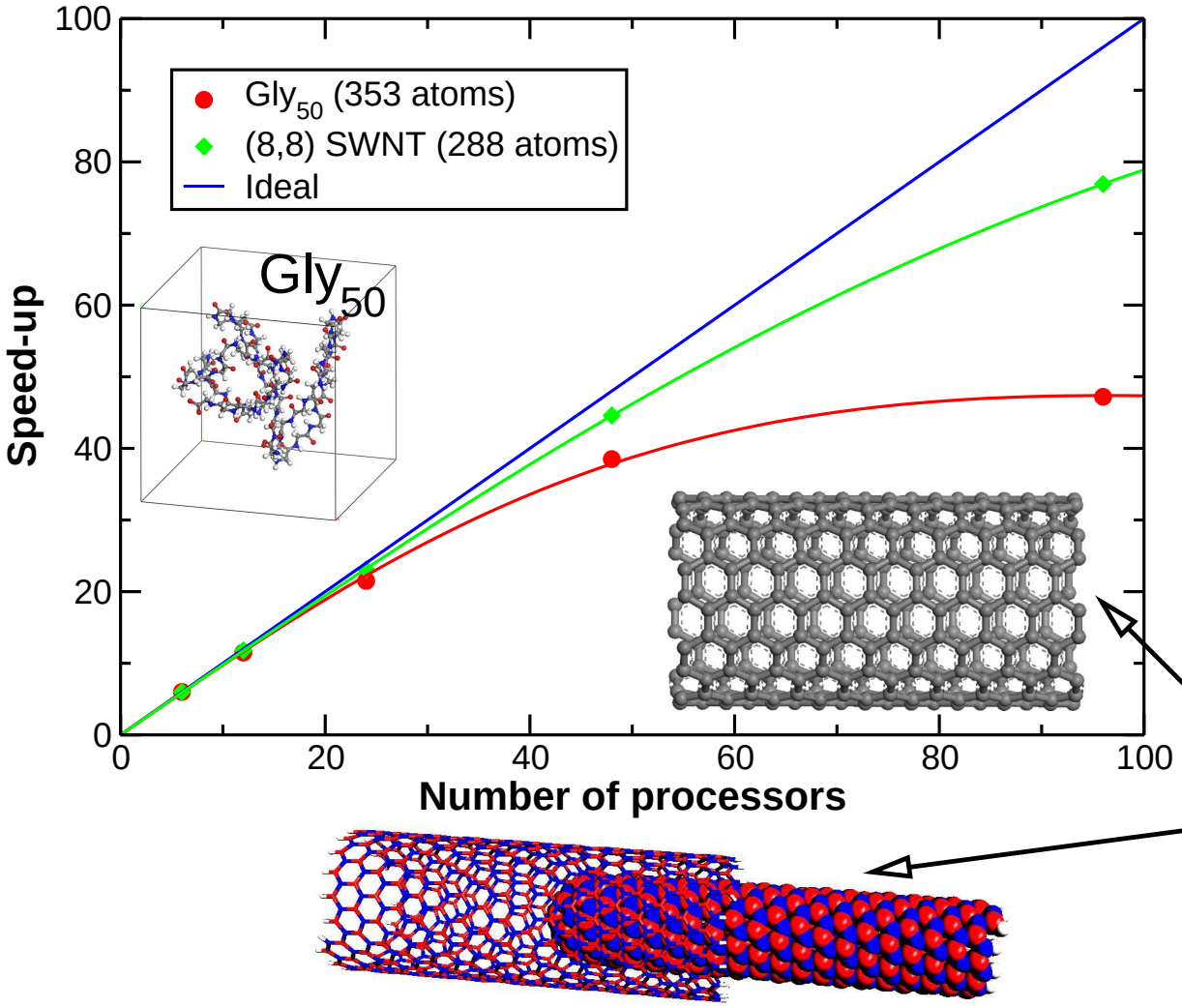
Preconditioning



Real linear scaling: number of iterations



Parallel scalability



System	Number of atoms	Speed−up on 96 procs
Gly_{50}	353	47.2
Gly_{100}	703	88.8
Gly_{200}	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)