

Linear-scaling, tensorially invariant, self-consistent projector **constrained Density Functional Theory in ONETEP**

G. Teobaldi,^a D. D. O'Regan,^b N. D. M. Hine,^c A. A. Mostofi^d

^a*Stephenson Institute for Renewable Energy, Department of Chemistry,
University of Liverpool, UK. Email: g.teobaldi@liv.ac.uk*

^b*Theory and Simulation of Materials, EPFL, Lausanne, Switzerland*

^c*Department of Physics, Cavendish Laboratory, Cambridge University, UK*

^d*Department of Materials and Physics, Imperial College London, UK*



EP/I004483/1
EP/G05567X/1

Motivation: need of atomic-level insight in energy materials & interfaces

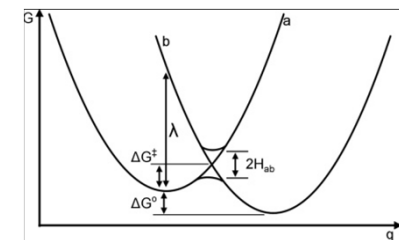
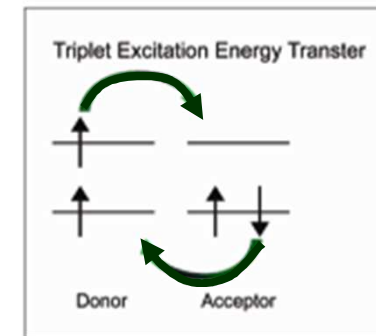
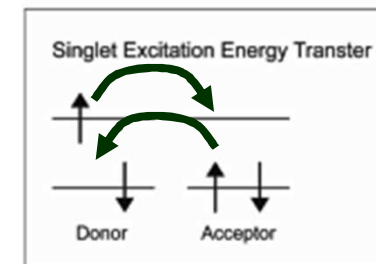
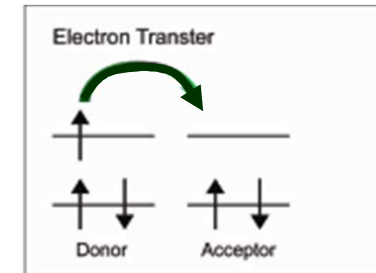
- Electrochemical **energy storage** (B, SCAP)
- Electrochemical **energy conversion** (FC)
- (Bio-)fuel **production**
- e-(h) migration across **PV interfaces**
- **Catalysis & photo-catalysis**
- (Solar) **light-harvesting**

Charge (energy) transfer in **extended, heterogeneous, often buried** interfaces

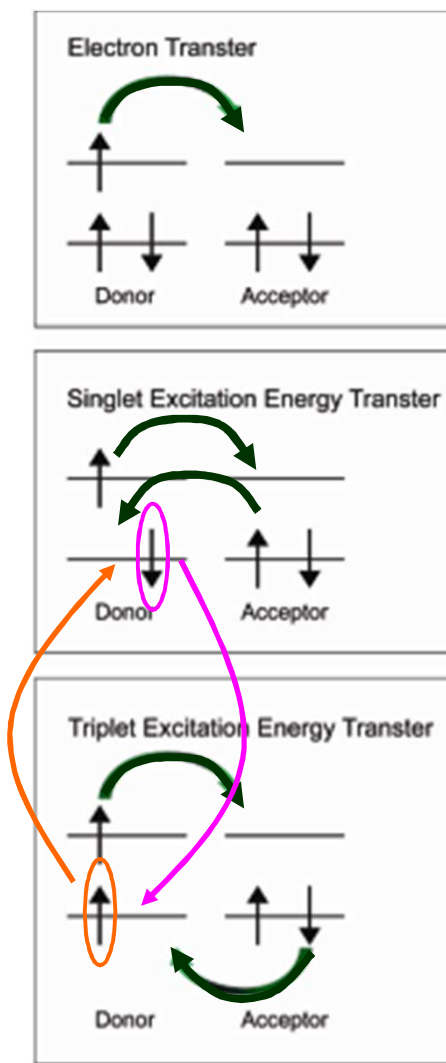


Need to access to the physico-chemical factors governing the **thermodynamics** and **kinetics** of **charge (energy) transfer** in such interfaces

Viable approximations to the physico-chemical factors governing the **thermodynamics** and **kinetics** of **charge (energy) transfer** in such interfaces

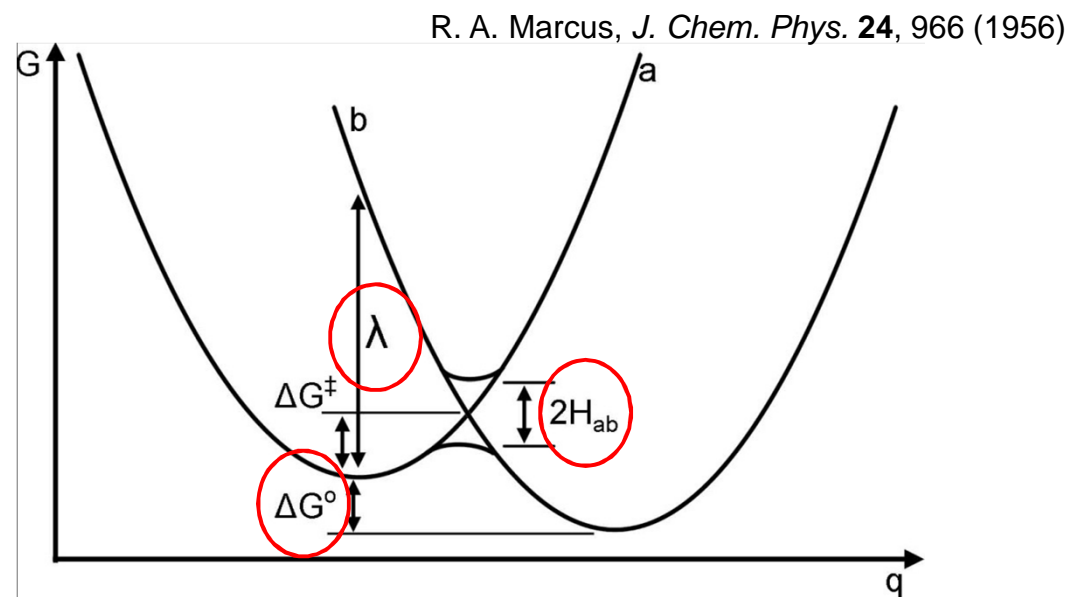


Electron coupling and e-, h-, energy-transfer (in condensed phases)



S \leftrightarrow T inter-system crossing

Acc. Chem. Res. **42**, 509 (2009)



$$k_{a \rightarrow b} = \frac{2\pi}{\hbar} \frac{\langle |H_{ab}|^2 \rangle}{\sqrt{4\pi k_B T \lambda}} e^{-\frac{(\lambda + \Delta G^\circ)}{4\pi k_B T \lambda}}$$

- Selectively localise e/h/e-h pair on 'a' and 'b'
- Optimise (the geometry of the) system on the 'a' and 'b' diabatic) electronic potential energy surfaces \rightarrow evaluate ΔG° , λ
- Approximate many-body electronic wave-functions Ψ_a , Ψ_b
- Approximate non-adiabatic coupling $H_{ab} = \langle \Psi_a | H_{el} | \Psi_b \rangle$ (H_{el} is not diagonal in the {a,b} diabatic representation)

Constrained-DFT [and (approximated) diabatic states: $\tau_{ij} = \langle \psi_i | \nabla_R \psi_j \rangle = 0$; $\nabla \times \tau = \tau \times \tau$]

$$\sum_{\sigma} \int w_k^{\sigma}(\mathbf{r}) \rho_{\sigma}(\mathbf{r}) d\mathbf{r} - N_k = 0$$

$$W[\rho, \{V_k\}] = E[\rho] + \sum_k^m V_k [\sum_{\sigma} \int w_k^{\sigma}(\mathbf{r}) \rho_{\sigma}(\mathbf{r}) d\mathbf{r} - N_k]$$

$$W[\mathbf{P}] = E[\mathbf{P}] + V_c (\text{Tr}\{\mathbf{P}\mathbf{w}_c\} - N_c)$$

$$\begin{aligned} \frac{\partial W}{\partial V_k} &= \sum_{\sigma} \sum_i \left(\frac{\delta W}{\delta \phi_{i\sigma}^*} \frac{\partial \phi_{i\sigma}^*}{\partial V_k} + \text{cc} \right) + \frac{\partial W}{\partial V_k} \\ &= \sum_{\sigma} \int w_k^{\sigma}(\mathbf{r}) \rho_{\sigma}(\mathbf{r}) d\mathbf{r} - N_k \end{aligned}$$

$$\begin{aligned} \frac{\partial^2 W}{\partial V_k \partial V_l} &= \sum_{\sigma} \sum_i \int w_k^{\sigma}(\mathbf{r}) \phi_{i\sigma}^*(\mathbf{r}) \frac{\delta \phi_{i\sigma}(\mathbf{r})}{\delta [V_l w_l^{\sigma}(\mathbf{r}')] } w_l^{\sigma}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \text{cc} \\ &= \sum_{\sigma} \sum_i \int w_k^{\sigma}(\mathbf{r}) \phi_{i\sigma}^*(\mathbf{r}) \sum_{a \neq i} \frac{\phi_{a\sigma}^*(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}'')}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \phi_{a\sigma}(\mathbf{r}) \\ &\quad w_l^{\sigma}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \text{cc} \\ &= 2 \sum_{\sigma} \sum_i \sum_{a > N_{\sigma}} \frac{\langle \phi_{i\sigma} | w_k^{\sigma} | \phi_{a\sigma} \rangle \langle \phi_{i\sigma} | w_l^{\sigma} | \phi_{a\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \end{aligned} \quad (6)$$

$$\nabla_A W = \nabla_A E + V_c \sum_{\lambda v} P_{\lambda v} \nabla_A w_{c\lambda v}$$

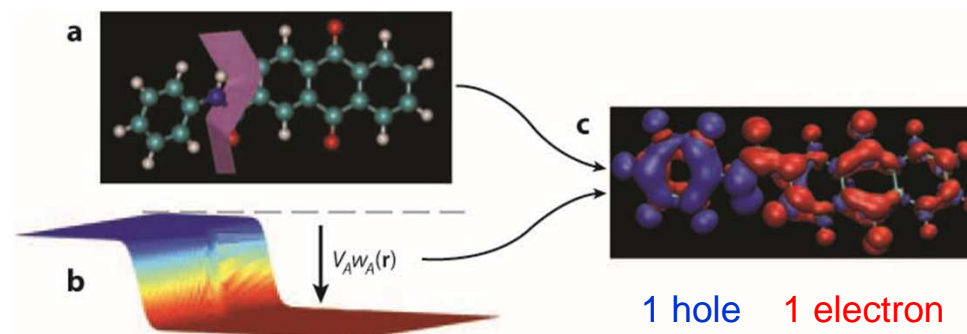
B. Kaduk *et al. Chem. Rev* **112**, 321 (2012)

1. Add constrain on the (e) density
[electron/spin-density localisation...]

2. Build a constrained functional W
[via the Lagrange multipliers V_k]

3. Reformulate W
in terms of the density matrix (P)

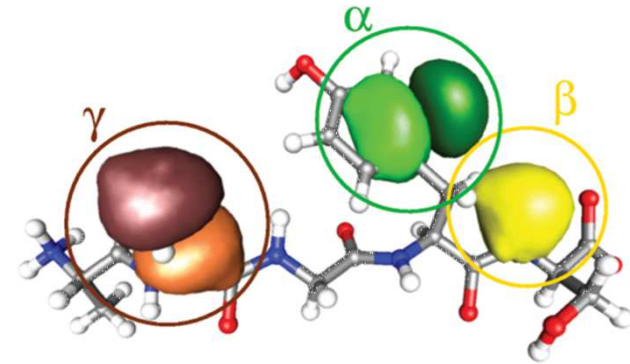
4. Maximize W (concave) WRT P & V_k



5. atomic forces

[various definition of w_c : Löwdin, Becke, Bader, etc population analysis)]

- State-of-the art linear-scaling DFT code, capable of treating tens of thousands of atoms.
- Reformulates Kohn-Sham DFT in terms of the single-particle density matrix.
- Uses localized functions (NGWFs or Non-orthogonal Generalized Wannier Functions).
- Linear scaling is achieved by exploiting
 - the sparsity of the density kernel, and
 - the exponential decay of the density matrix.
 ... by the introduction of spatial cutoffs for the kernel and the NGWFs.
- Achieves near-complete basis set accuracy.
- Fully parallel, portable.



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

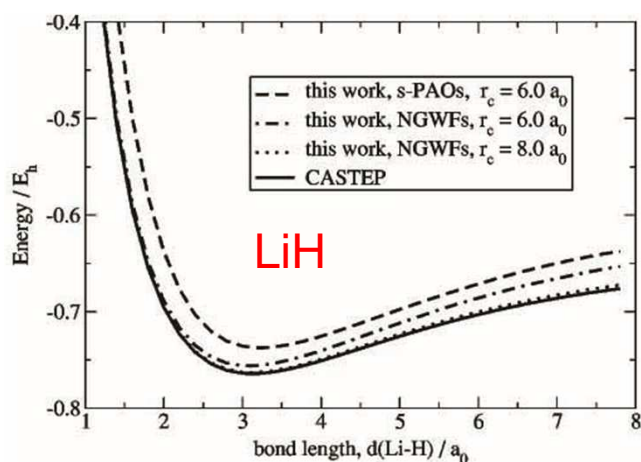
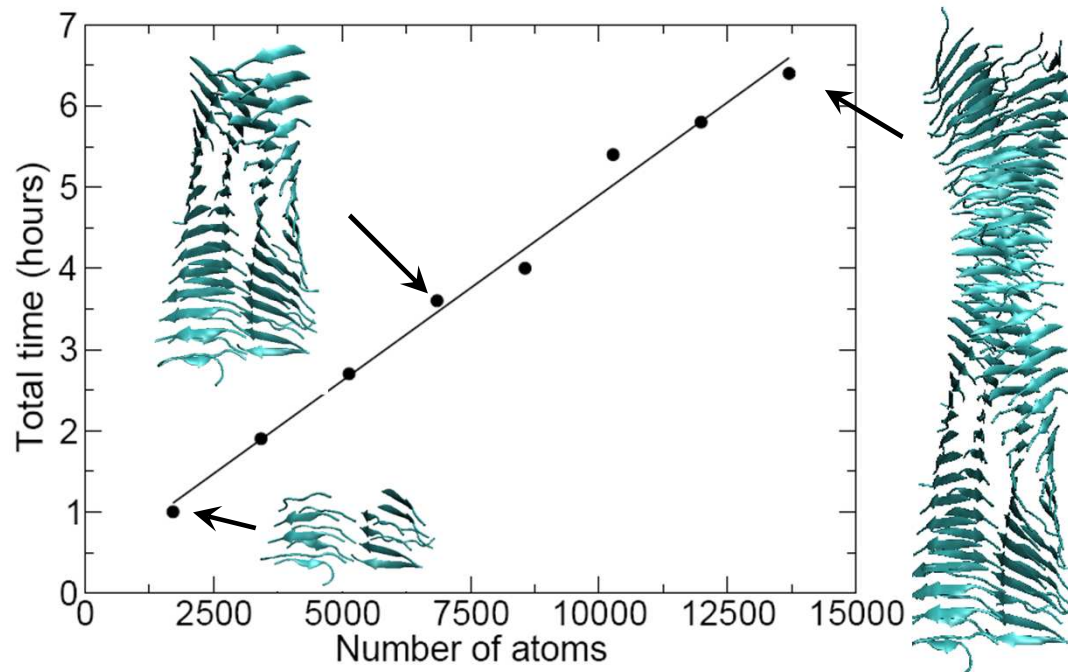
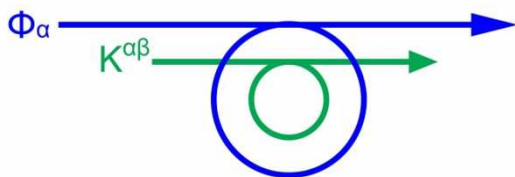
$$\rho(\mathbf{r}, \mathbf{r}') \rightarrow 0 \text{ as } |\mathbf{r} - \mathbf{r}'| \rightarrow \infty$$

$$\phi_{\alpha}(\mathbf{r}) = \sum_i D_i(\mathbf{r}) C_{i,\alpha}$$

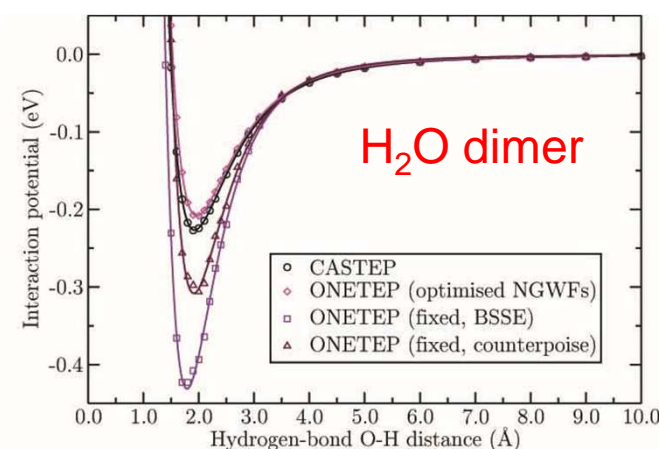
↑
psinc functions,
equivalent to plane waves

Single-point energy calculation
for an amyloid fibril protein,
run on 256 cores of Iridis3
(University of Southampton)

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



Near-complete
basis set accuracy



Projector constrained-DFT in ONETEP

1. For each spin-channel σ , and cDFT-site I , augment the DFT energy by the difference from the **targeted electronic population** $[(\Delta)N_{(I)(\sigma)}]$ times the **constraining potential** ($U_{q/s}$)

$$E_{cDFT} = E_{DFT} + \sum_{I=1}^{N_{sites}} \sum_{\sigma=1}^2 \underline{U_q^{(I)(\sigma)}} \left(Tr [n^{(I)(\sigma)}] - \underline{N_{(I)(\sigma)}} \right) + \sum_{I=1}^{N_{sites}} \underline{U_s^{(I)}} \left(Tr [n^{(I)(\uparrow)}] - Tr [n^{(I)(\downarrow)}] - \underline{\Delta N_{(I)}} \right)$$

where the tensorially invariant¹ subspace occupancy of the I^{th} cDFT-site reads:

$$n^{(I)(\sigma)} = n^{(I)(\sigma)m}_{m'} = O^{(I)mm''} \langle \varphi_{m''}^{(I)} | \phi_{\alpha} \rangle K^{(\sigma)\alpha\beta} \langle \phi_{\beta} | \varphi_{m'}^{(I)} \rangle$$

with

$$O_{mm'}^{(I)} = \langle \varphi_m^{(I)} | \varphi_{m'}^{(I)} \rangle, \quad | \varphi^{(I)m} \rangle = | \varphi_{m'}^{(I)} \rangle O^{(I)m'm}, \quad O_{mm''}^{(I)} O^{(I)m''m'} = \delta_m^{m'}$$

2. Augment (σ -dependent) DFT Hamiltonian with (σ -dependent) cDFT contributions, calculated as derivative of the cDFT correction with respect to an arbitrary density Kernel:

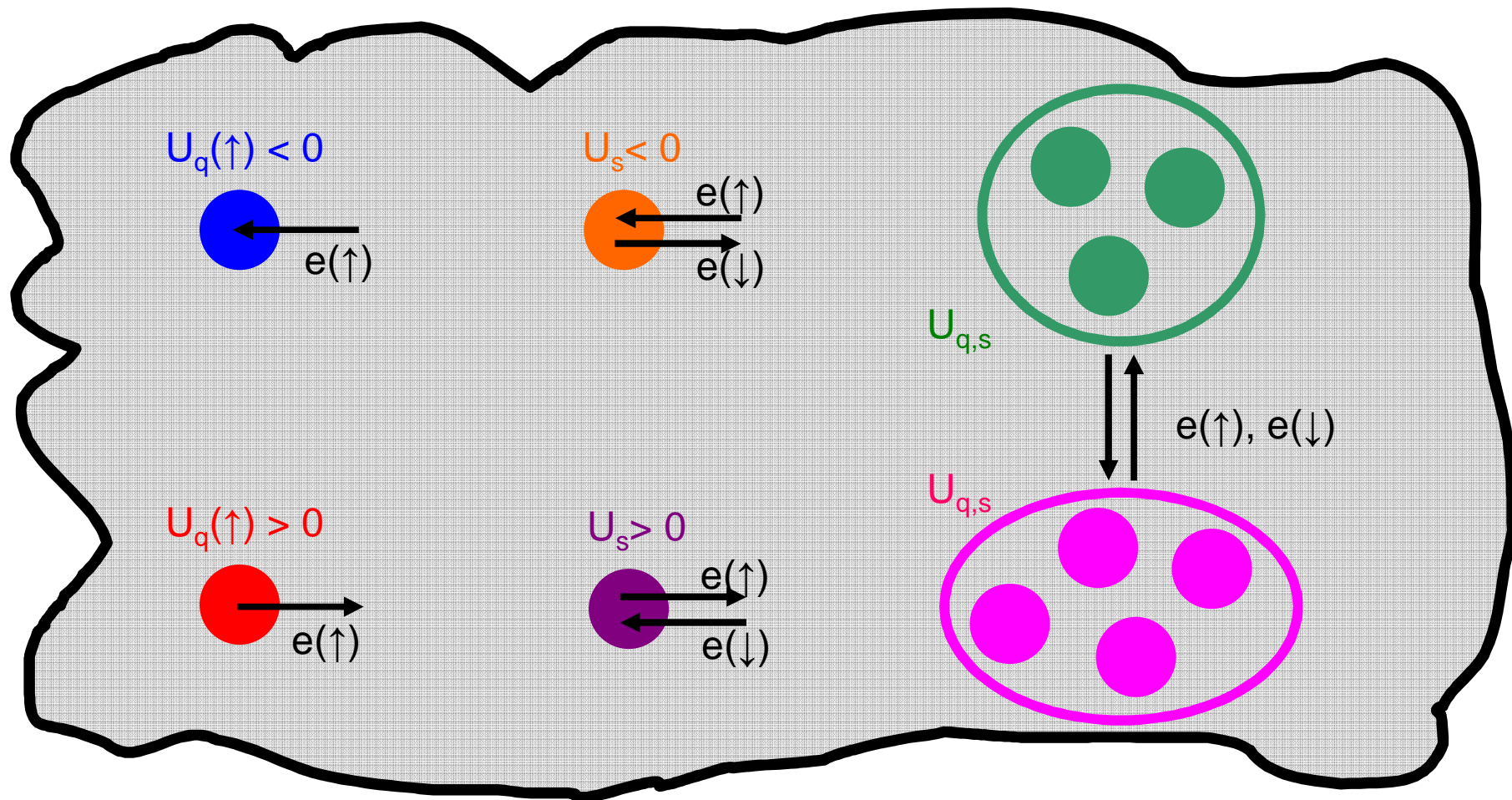
$$H_{\beta\alpha}^{cDFT(\sigma)} = \left[\underline{U_q^{(\sigma)}} + (-1)^{1+\sigma} \underline{U_s} \right] \left[\frac{\partial n_m^{(\sigma)}}{\partial K^{\alpha\beta(\sigma)}} \right] = \left[\underline{U_q^{(\sigma)}} + (-1)^{1+\sigma} \underline{U_s} \right] \left[V_{\beta m} O^{mm''} W_{m''\alpha} \right]$$

$$V_{\beta m} = \langle \phi_{\beta} | \varphi_m \rangle, \quad W_{m''\alpha} = V_{\alpha m''}^{\dagger} = \langle \varphi_{m''} | \phi_{\alpha} \rangle$$

[1] a) D. D. O'Regan *et al.*, *Phys. Rev. B* **82**, 081102 (2010); b) D. D. O'Regan *et al.*, *ibid.* **83**, 245124 (2011); c) D. D. O'Regan *et al.*, *ibid.* **85**, 085108 (2012).

So, what are we doing in practice?

...(just) adding attractive/repulsive potentials to **constrain** subspace **populations**, **population differences**, and/or **magnetic moments (differences)**



$$E_{cDFT} = E_{DFT} + \sum_{I=1}^{N_{sites}} \sum_{\sigma=1}^2 \underline{U_q^{(I)(\sigma)}} (Tr [n^{(I)(\sigma)}] - \underline{N_{(I)(\sigma)}}) + \sum_{I=1}^{N_{sites}} \underline{U_s^{(I)}} (Tr [n^{(I)(\uparrow)}] - Tr [n^{(I)(\downarrow)}] - \underline{\Delta N_{(I)}})$$

Choosing the projectors for the cDFT-subspaces

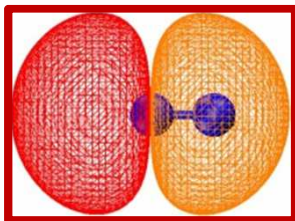
- The cDFT functional is constructed using the occupancy matrix (n) of the localised cDFT-projectors φ_m

$$n^{(I)(\sigma)} = n^{(I)(\sigma)m}_{m'} = O^{(I)mm''} \langle \varphi_{m''}^{(I)} | \phi_\alpha \rangle K^{(\sigma)\alpha\beta} \langle \phi_\beta | \varphi_{m'}^{(I)} \rangle$$

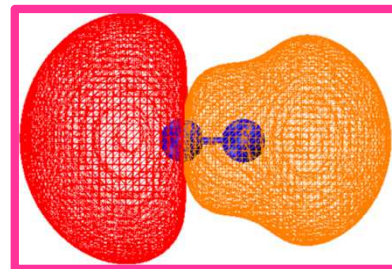
$$O^{(I)}_{mm'} = \langle \varphi_m^{(I)} | \varphi_{m'}^{(I)} \rangle, \quad | \varphi^{(I)m} \rangle = | \varphi_{m'}^{(I)} \rangle O^{(I)m'm}, \quad O^{(I)}_{mm''} O^{(I)m''m'} = \delta_m^{m'}$$

- What to use as cDFT-projectors?**

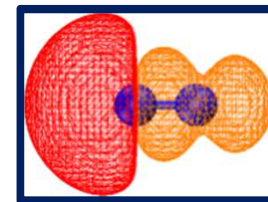
LCAO basis function, **valence pseudo-orbitals**, hydrogenic wavefunctions, Maximally Localised Wannier Function (MLWF), **in situ optimised DFT-NGWFs**, **in situ optimised cDFT-NWGFs**, **self-consistent cDFT-NGWFs**?



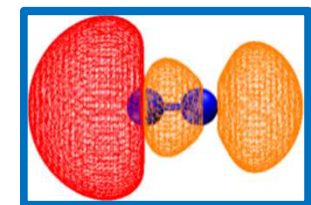
PAO- φ_m



$\varphi_m = \text{DFT-} \phi_\alpha$

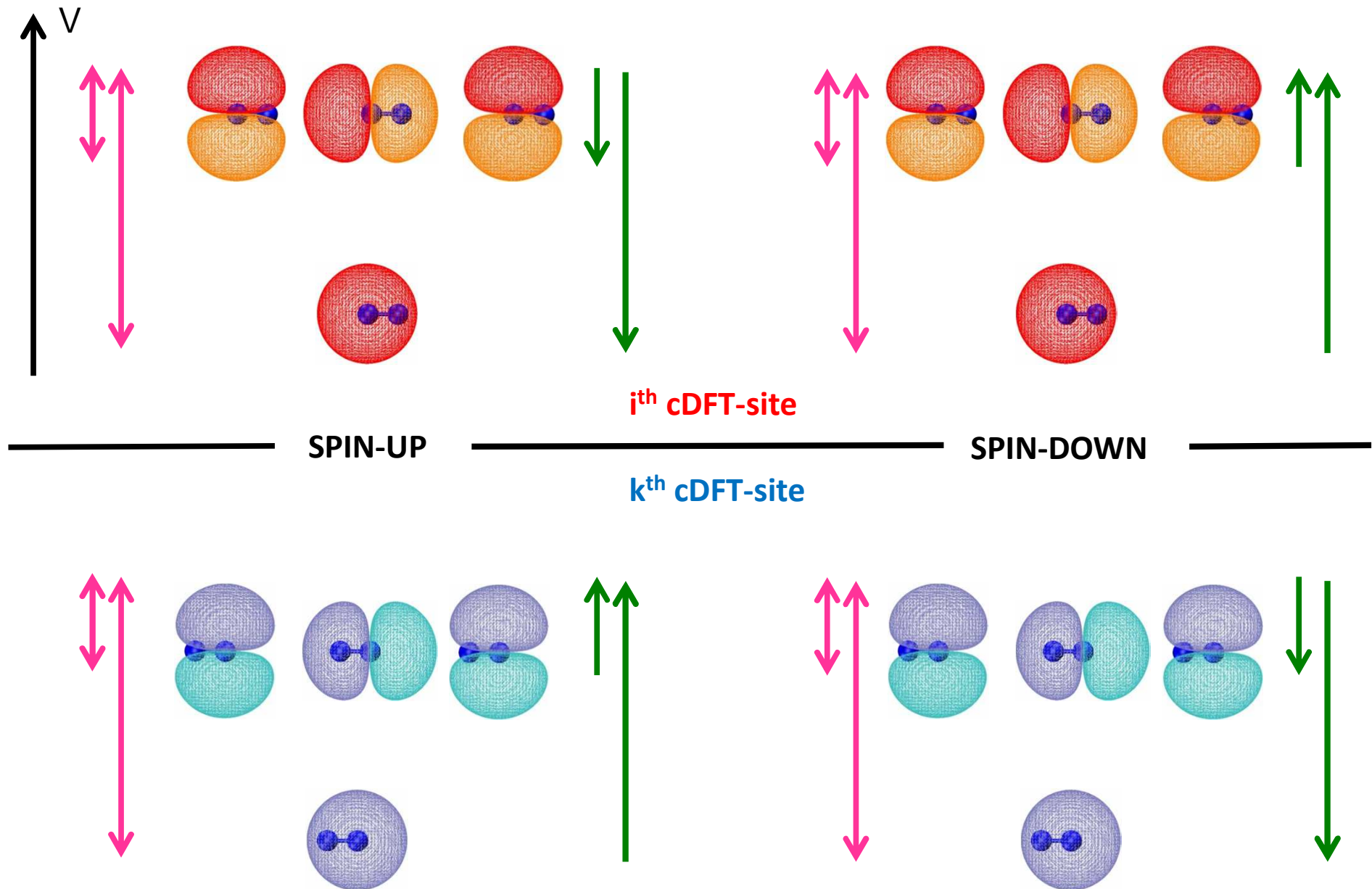


$\varphi_m = \text{cDFT-} \phi_\alpha$



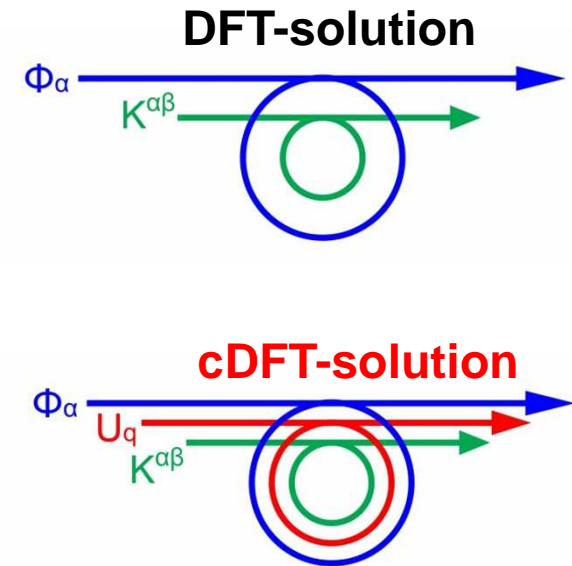
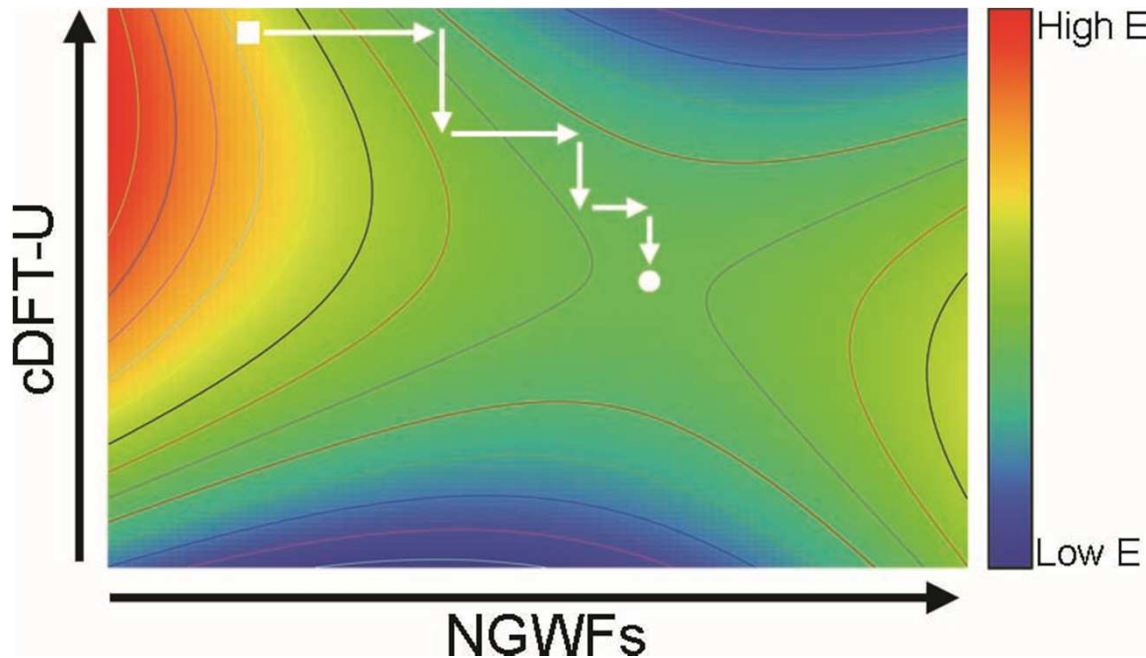
SC- φ_m

Choosing between the implemented ($8 \times 2 \times 2 = 32$) flavours of cDFT



How to optimise the cDFT-potentials with just one NGWFs-optimisation...

- Kohn-Sham DFT: **minimum** of E_{DFT} with respect to **NGWFs** for idempotent $K^{\alpha\beta}$
- cDFT: **maximum** of E_{cDFT} with respect to constraining potentials ($U_{q/s}$)

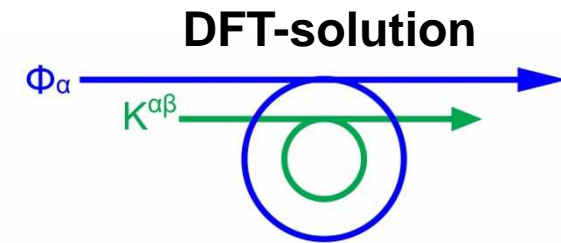


- Can the problem be solved by **alternating NGWFs and $U_{q/s}$ optimisation steps?** (having 'only' $\partial E_{\text{cDFT}}/\partial \Phi_\alpha$, $\partial E_{\text{cDFT}}/\partial K^{\alpha\beta}$, and $\partial E_{\text{cDFT}}/\partial U_{q/s}$ available)

$$\frac{\partial E_{\text{cDFT}}}{\partial U_s^{(I)}} = \text{Tr} [n^{(I)(\uparrow)}] - \text{Tr} [n^{(I)(\downarrow)}] - \Delta N_{(I)}$$

$$\frac{\partial E_{\text{cDFT}}}{\partial U_q^{(I)(\sigma)}} = \text{Tr} [n^{(I)(\sigma)}] - N_{(I)(\sigma)}$$

More on alternate NGWFs-cDFT line search [1/2]



NGWFs-OPT Loop ($E_{\text{DFT}+U_{q/s}}$ minimisation)

• NGWFs_0

[Dens Kern-OPT Loop ($E_{\text{DFT}+U_{q/s}}$ minimisation, **fixed** $U_{q/s}$)

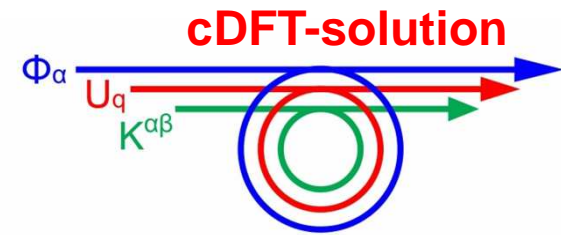
• NGWFs_1 (**fixed** $U_{q/s}$)

[Dens Kern-OPT Loop ($E_{\text{DFT}+U_{q/s}}$ minimisation, **fixed** $U_{q/s}$)

• Extrapolate NGWFs_new (NGWFs_0, NGWFs_1)

NGWFs line-search

More on alternate NGWFs-cDFT line search [2/2]



NGWFs-OPT Loop ($E_{\text{DFT}+U_{q/s}}$ minimisation)

- NGWFs_0

- $U_{q/s}$ -OPT Loop ($E_{\text{DFT}} + E_c = E_{\text{cDFT}}$ MAXIMISATION)

- Denskernel-OPT Loop ($E_{\text{DFT}+U_{q/s}}$ minimisation, **fixed** $U_{q/s}$)

- NGWFs_1 (**fixed** $U_{q/s}$, optimised for NGWFs_0)

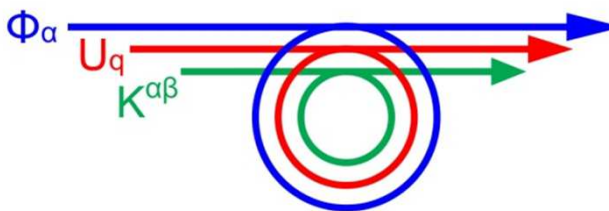
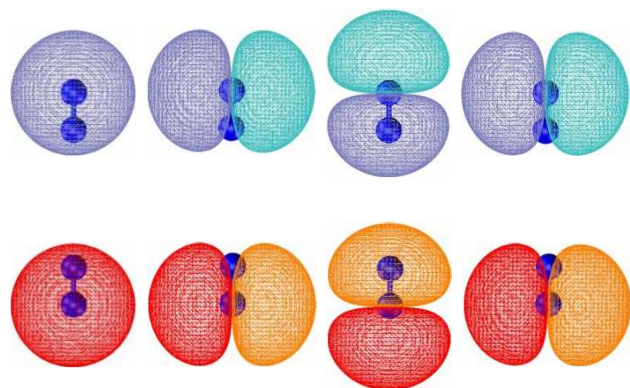
- Denskernel-OPT Loop ($E_{\text{DFT}+U_{q/s}}$ minimisation, **fixed** $U_{q/s}$)

- Extrapolate NGWFs_new (NGWFs_0, NGWFs_1)

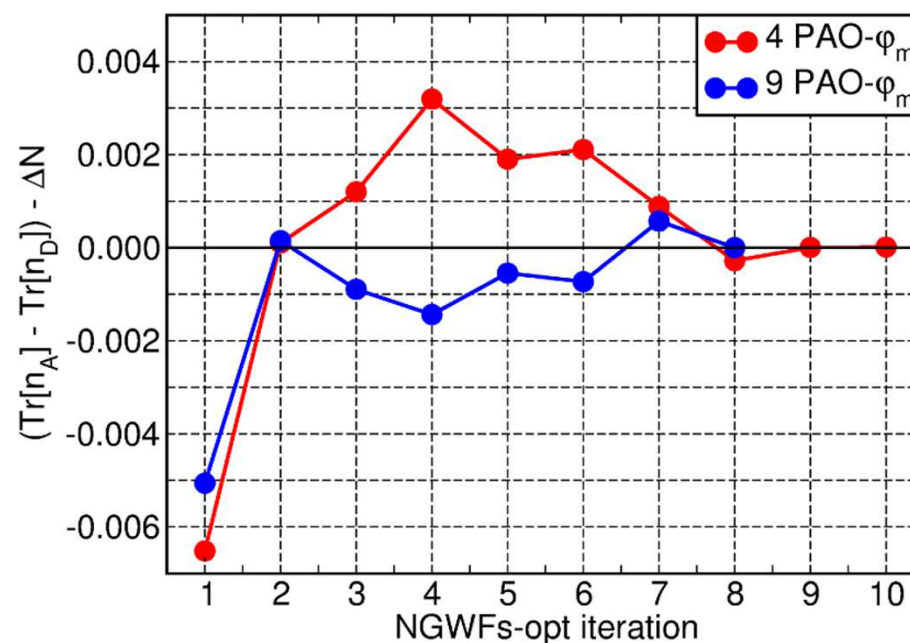
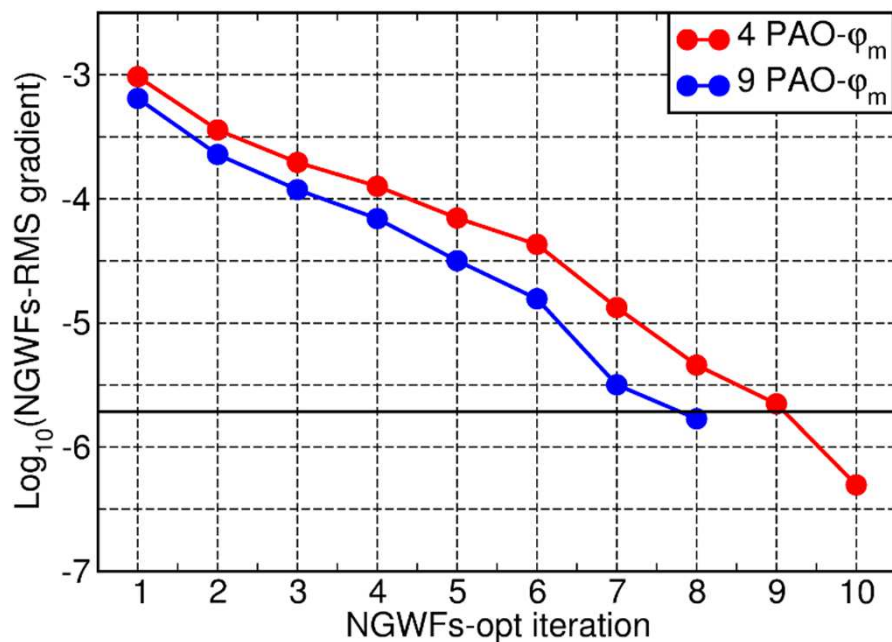
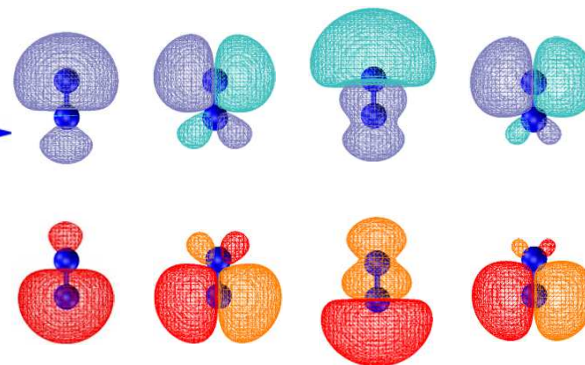
NGWFs line-search

In action on $N^{(+)}=N^{(-)}$ (1.1 Å)

Initial PAO NGWFs (Φ_α) & cDFT- φ_m

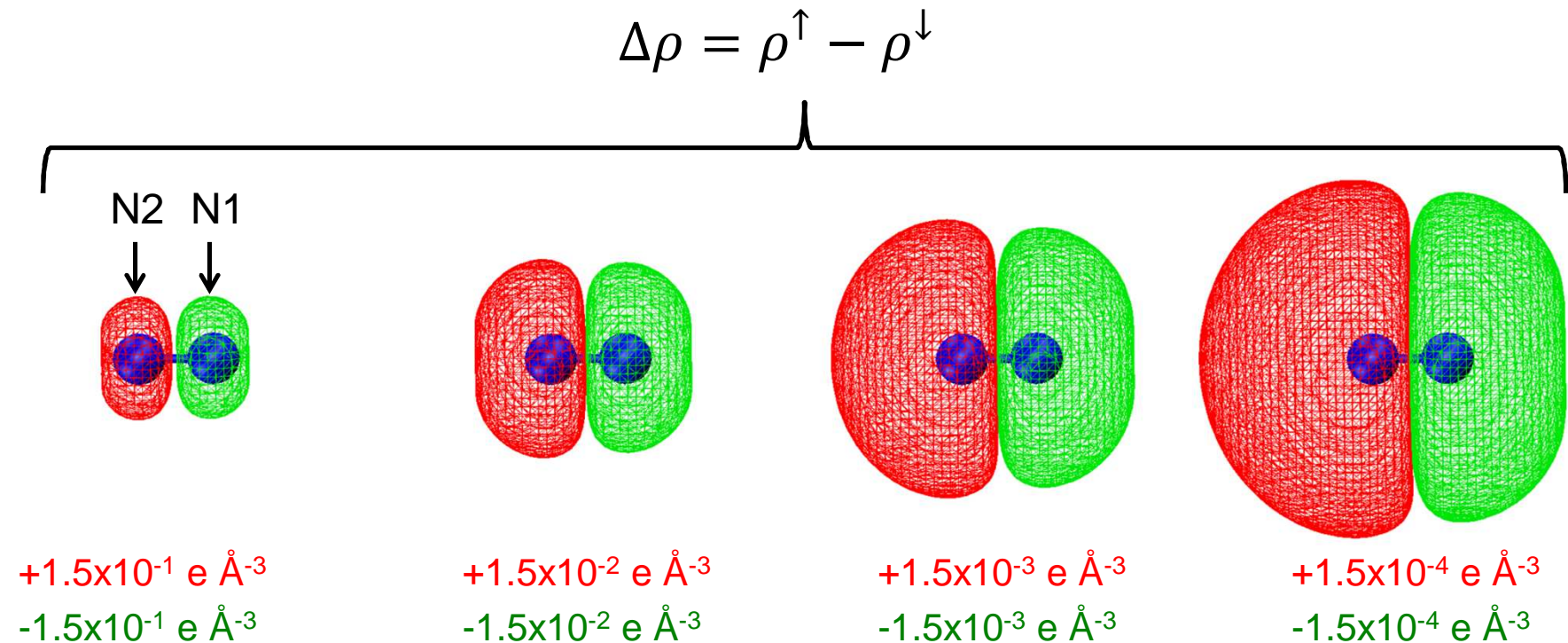


Final cDFT-optimised NGWFs (Φ_α)

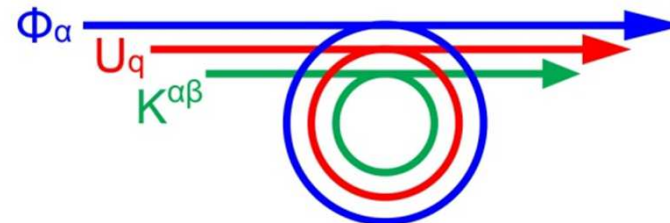


Fast convergence within the requested 2×10^{-6} (NGWFs-RMS) and 10^{-5} (cDFT-RMS) thresholds

Do we actually end up with $\uparrow N^{(+)} = \uparrow N^{(-)}$ (1.1 Å)? [YES]



- Noticeably **sharp separation** of ρ^\uparrow and ρ^\downarrow in spite of 5Å-radius NGWFs and PAO- φ_m
- How is it possible? Because $K^{\alpha\beta}$, the NGWFs $\{\Phi_\alpha\}$, and U_q have **been optimised for the given cDFT-problem**.



(Fixed- ϕ_m) cDFT atomic-forces

Instantaneous cDFT-site population

$$E_{cDFT} = E_{DFT} + U_q(Tr[n] - N)$$

cDFT-potential

Targeted population

$$\mathbf{F} = -\frac{\partial E_{cDFT}}{\partial \mathbf{R}} = -\nabla_{\mathbf{R}} E_{cDFT} = -\nabla_{\mathbf{R}} E_{DFT} - \nabla_{\mathbf{R}} U_q(Tr[n] - N) =$$

$$= -\nabla_{\mathbf{R}} E_{DFT} - (\nabla_{\mathbf{R}} U_q)(Tr[n] - N) - U_q \nabla_{\mathbf{R}} Tr[n] + U_q Tr[n] \nabla_{\mathbf{R}} N =$$

→0 after cDFT-solution

=0 (N is constant)

$$= -\nabla_{\mathbf{R}} E_{DFT} - U_q \nabla_{\mathbf{R}} Tr[n]$$

↑
[1]

↑
[2]



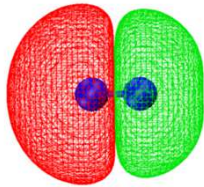
!!! Tight cDFT-convergence is necessary !!!

[1] a) N. D. M. Hine *et al.*, *Phys. Rev. B* **83**, 195102 (2011);

b) A. Ruiz-Serrano *et al.*, *J. Chem. Phys.* **136**, 234101 (2012).

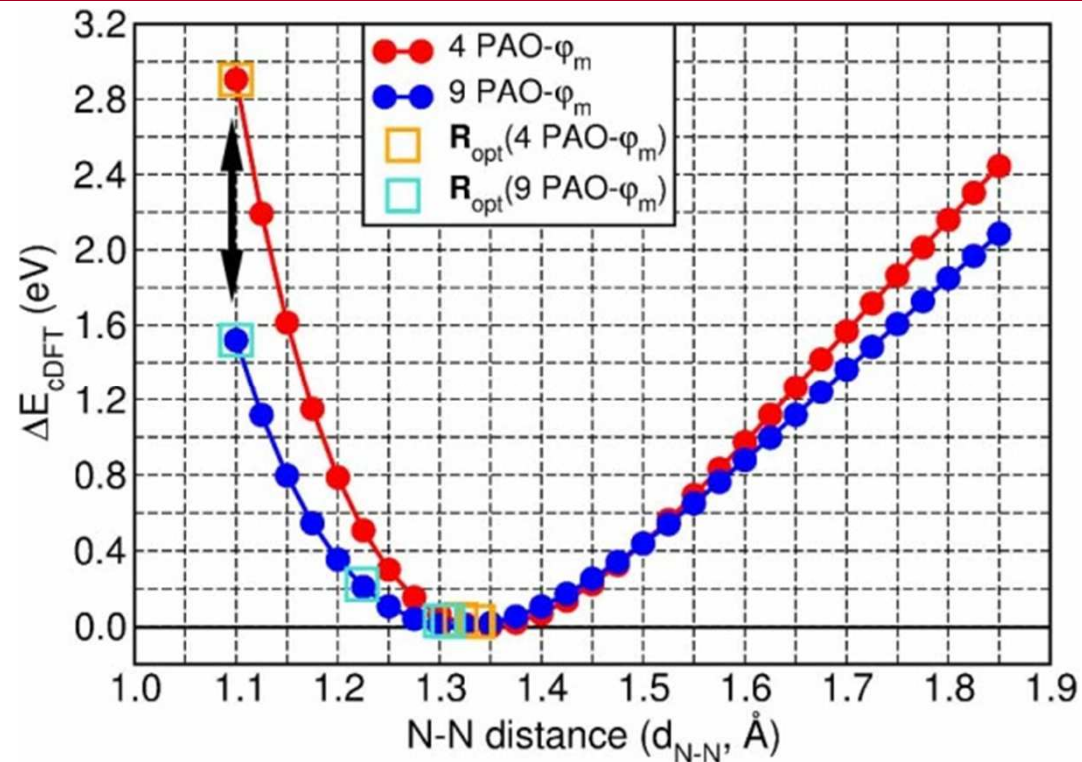
[2] D. D. O'Regan *et al.*, *Phys. Rev. B* **85**, 085107 (2012) and references therein.

(Fixed- φ_m) cDFT atomic-forces and geometry optimisation for $N^{(+)}=N^{(-)}$



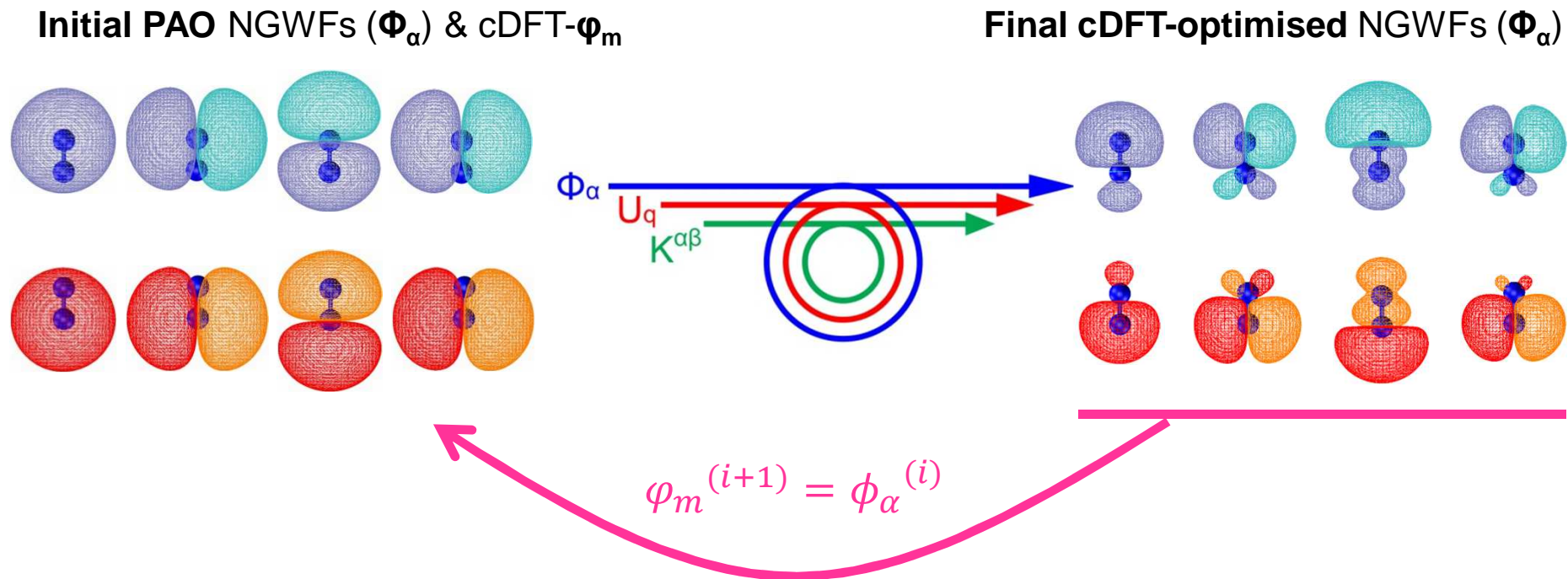
$$\rho^{\uparrow}-\rho^{\downarrow} = +1.5 \times 10^{-3} \text{ e } \text{\AA}^{-3}$$

$$\rho^{\uparrow}-\rho^{\downarrow} = -1.5 \times 10^{-3} \text{ e } \text{\AA}^{-3}$$



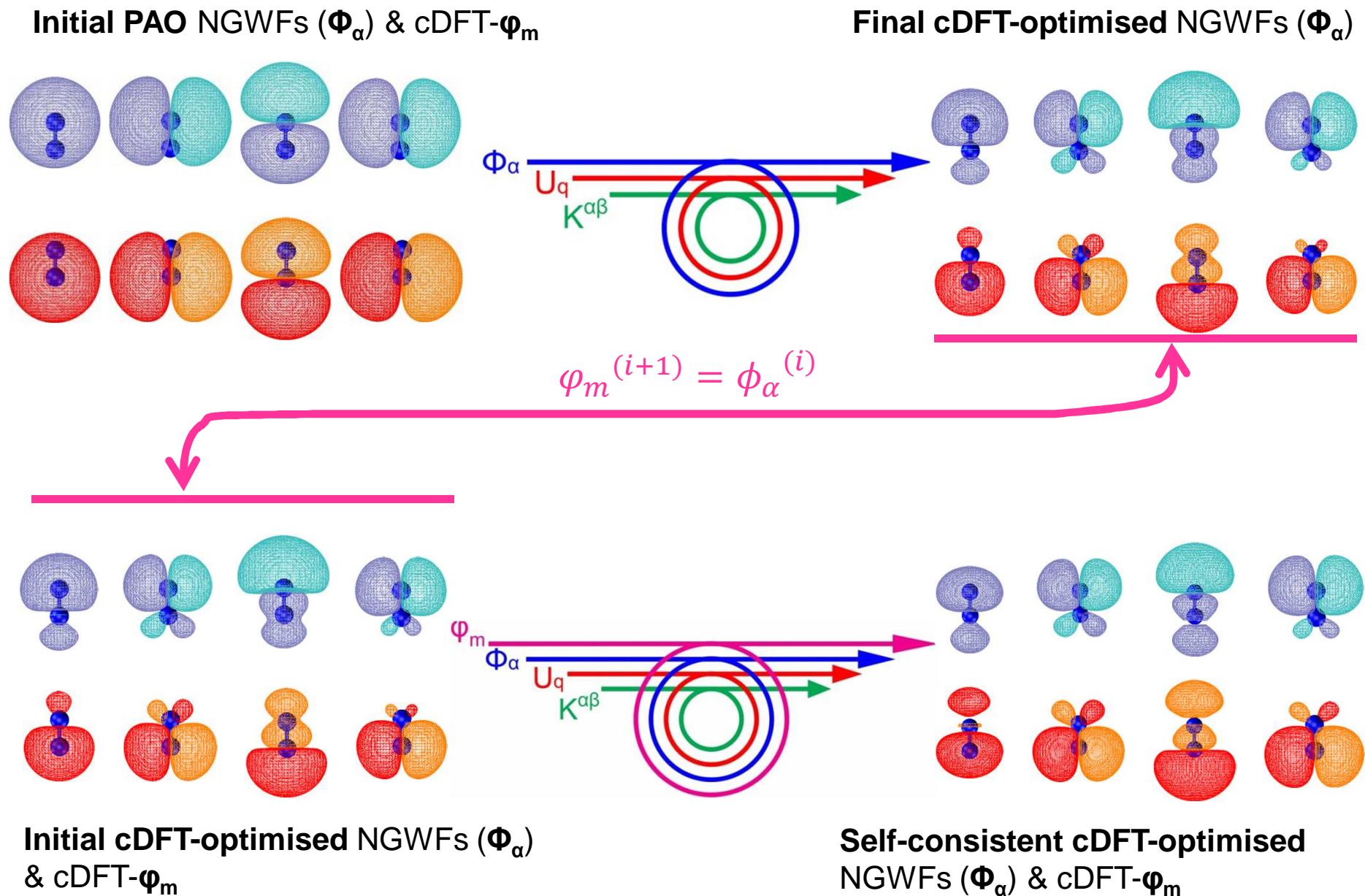
- **Fast-convergence** of BFGS optimisation algorithm: $F_{\max} < 0.01 \text{ eV/\AA}$ in 4 BFGS iterations
- **Spin-decoupling** of two π -electrons in $^{\uparrow}N^{(+)}=^{\uparrow}N^{(-)} \rightarrow$ **elongation** of optimum **bond-distance**
- **4 PAO- φ_m** : $1.10 \text{ \AA} \rightarrow 1.35 \text{ \AA}$
- **9 PAO- φ_m** : $1.10 \text{ \AA} \rightarrow 1.33 \text{ \AA}$
- **Different** set of cDFT-projectors (φ_m) \rightarrow **different constraints** \rightarrow **different cDFT-solutions**
- **How to reduce cDFT-ambiguities?**

Optimised cDFT-NGWFs (Φ_α) as new cDFT-projectors (φ_m)

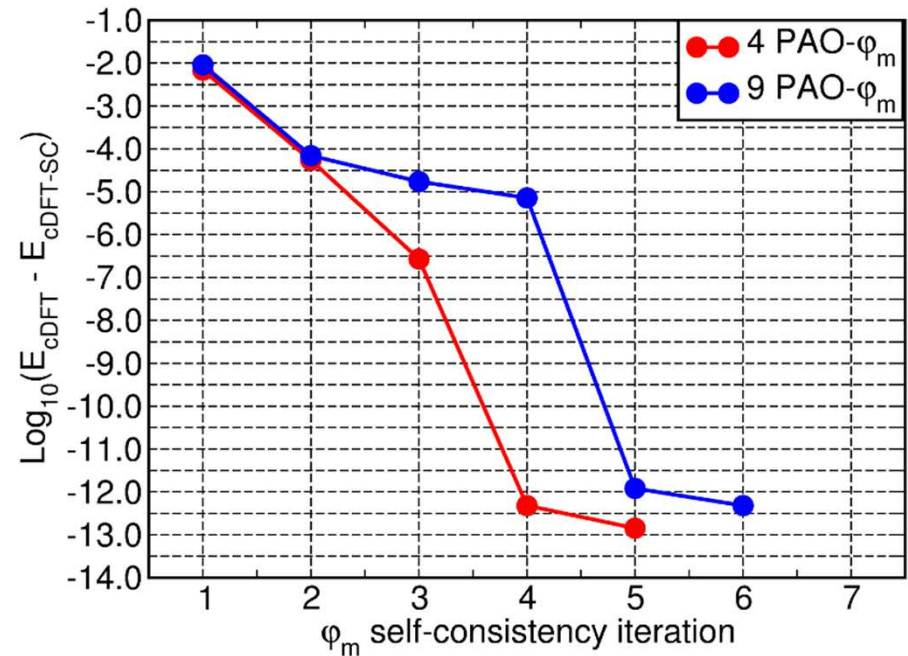
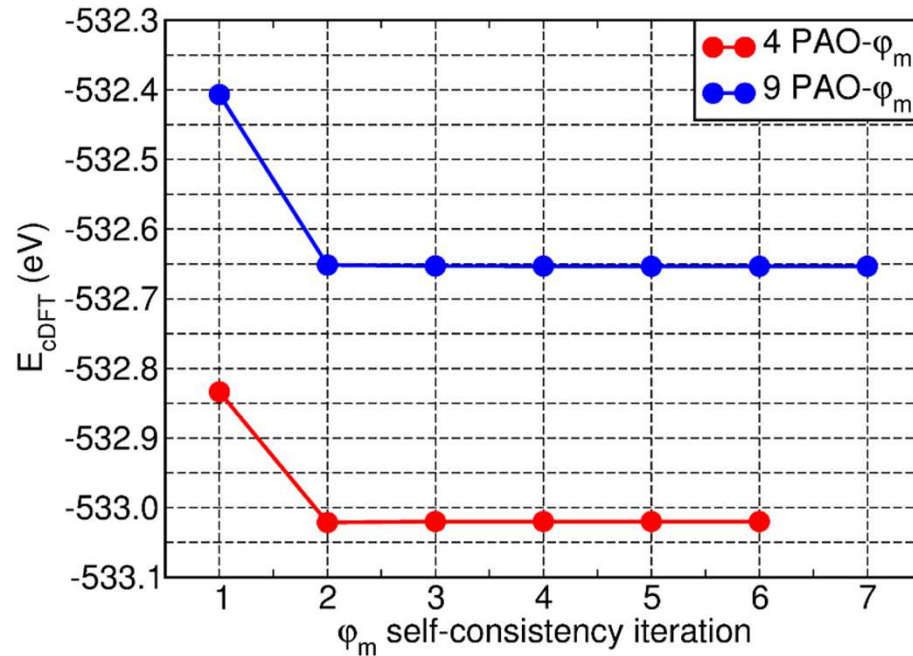


- Use **cDFT-optimised NGWFs (Φ_α)** at iteration (i) as **new cDFT-projectors (φ_m)** for iteration (i+1), and **re-solve** the cDFT problem by **optimising the cDFT-NGWFs (Φ_α)** for iteration (i+1).
- **Iterate until** E_{cDFT} (i.e. Φ_α , $K^{\alpha\beta}$, and φ_m) do not change within given threshold.

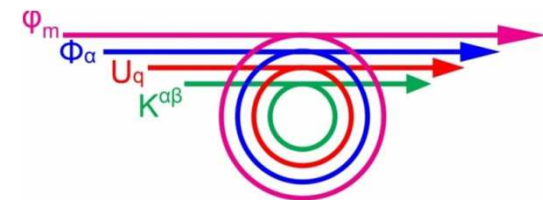
Optimised cDFT-NGWFs (Φ_α) as new cDFT-projectors (ϕ_m)



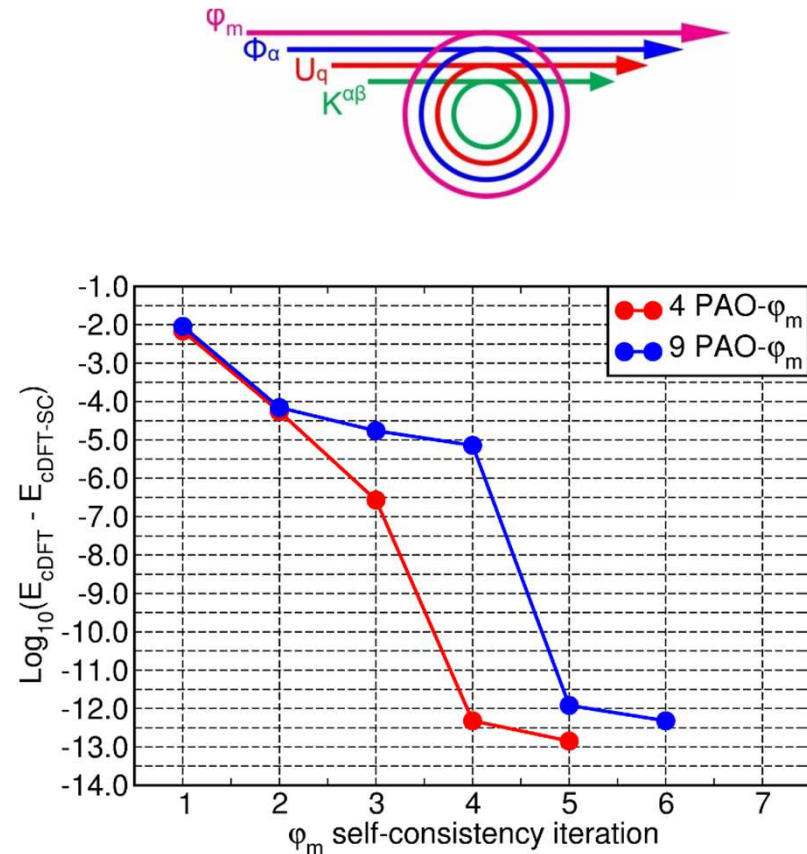
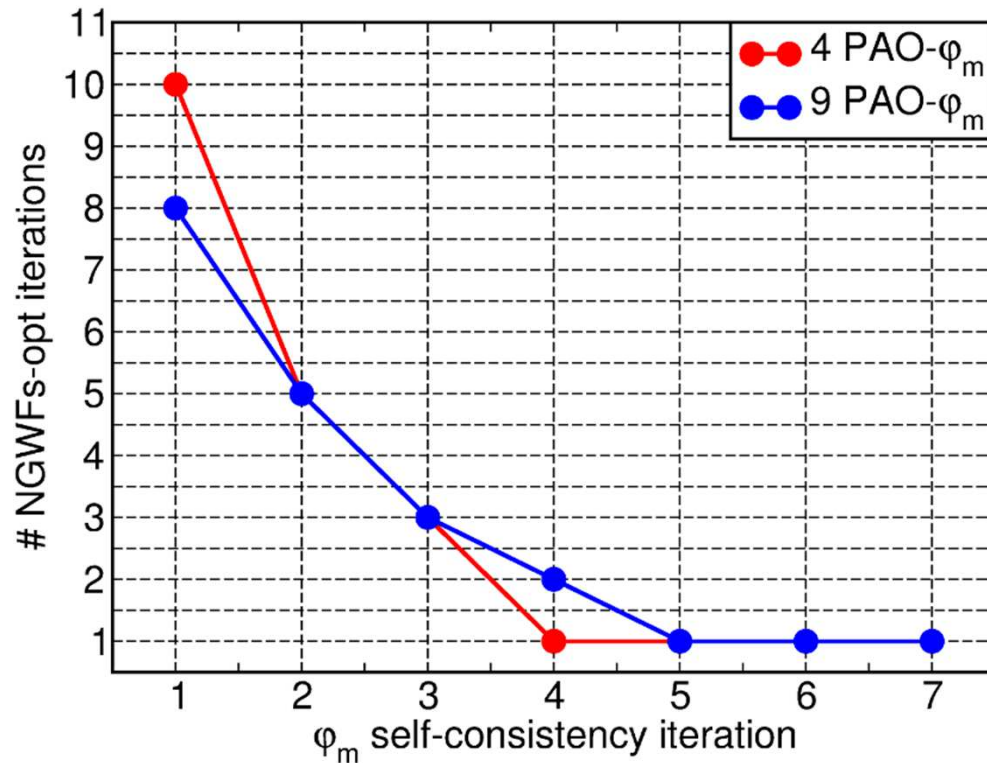
How fast/tight is the convergence of the cDFT-projectors (φ_m)?



- **Fast convergence** (≤ 7 iterations), even for a tightly-constrained problem [N-N: 1.35 Å (1.33 Å)]
- **Tight convergence** ($\leq 10^{-12}$ eV), even for reasonable kinetic-energy cutoffs (1000 eV)
- As the cDFT-projectors (φ_m) reach self-consistency, **energy of cDFT-solution is lowered**
- **Best cDFT-projectors** as those yielding the **lowest-energy cDFT solution** [for the same targeted constraint]



How large is the computational overhead?



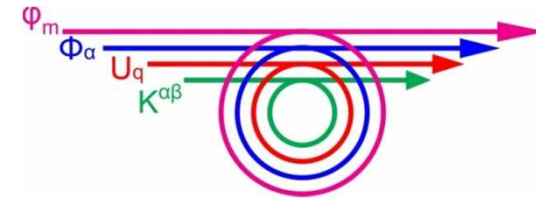
- **4 PAO- φ_m** . 1st cDFT-solution: **10** NWGFS-opt iterations; sc- φ_m procedure: **12**
- **9 PAO- φ_m** . 1st cDFT-solution: **8** NGWFs-opt iterations; sc- φ_m procedure: **13**



- **~x2 increase** of computation cost, for a convergence tighter than **10^{-12} eV**
- **~x0.5 increase** of computation cost, for a convergence tighter than **10^{-4} eV**

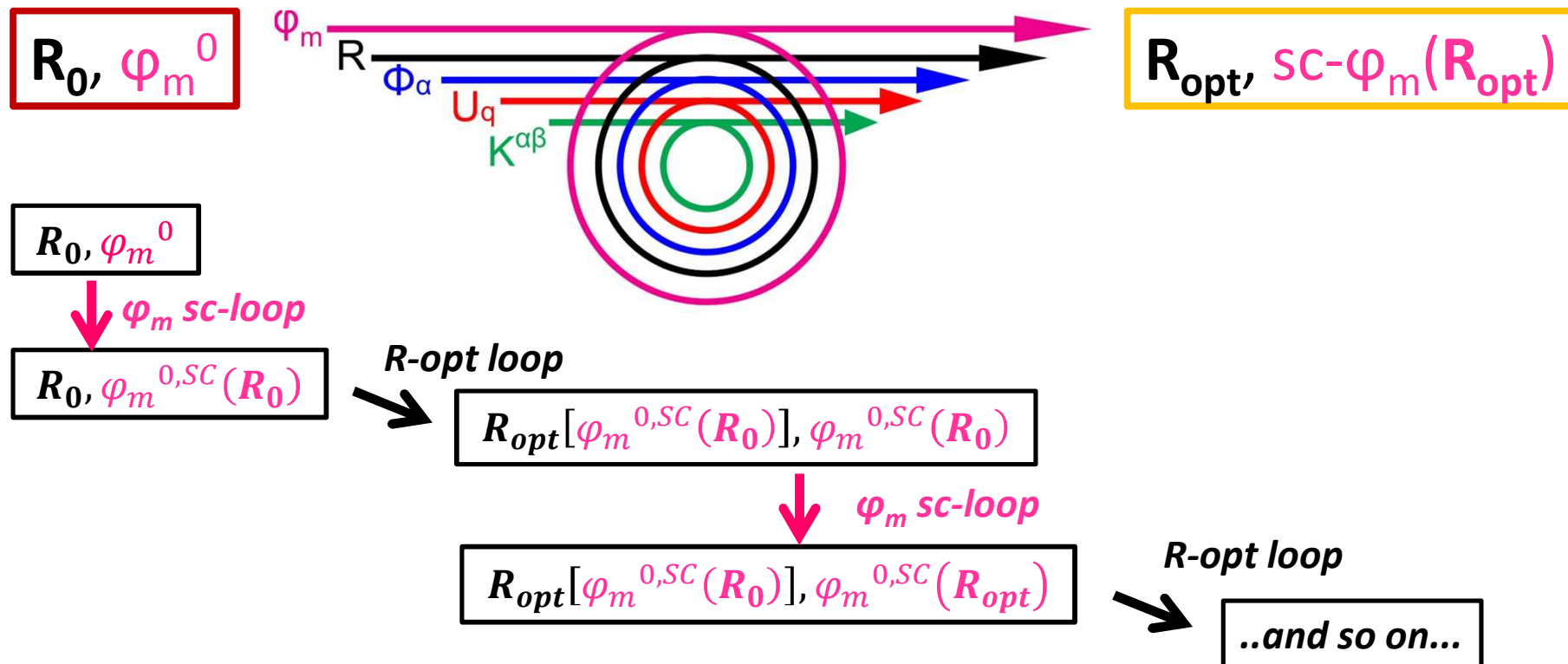
Self-consistency of system-geometry (\mathbf{R}) and cDFT-projectors (φ_m)

- sc-cDFT-projectors ($\text{sc-}\varphi_m$) depend on system-geometry \mathbf{R}

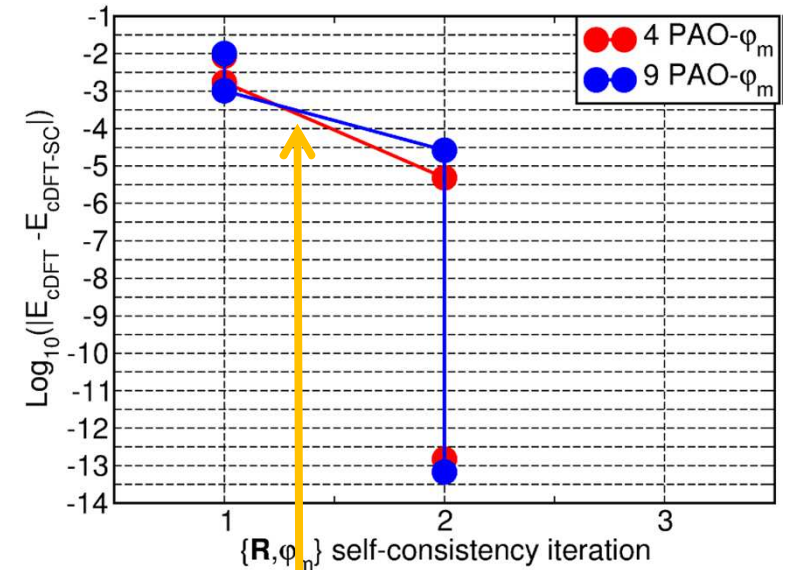
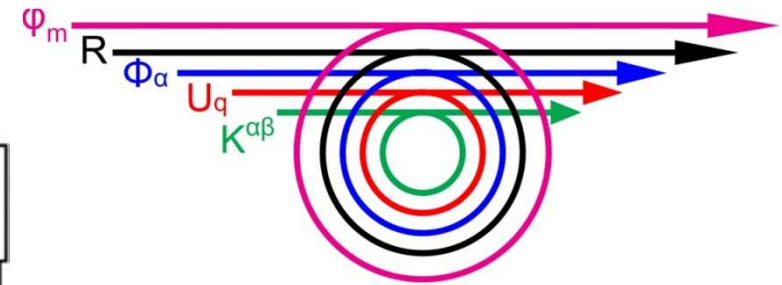
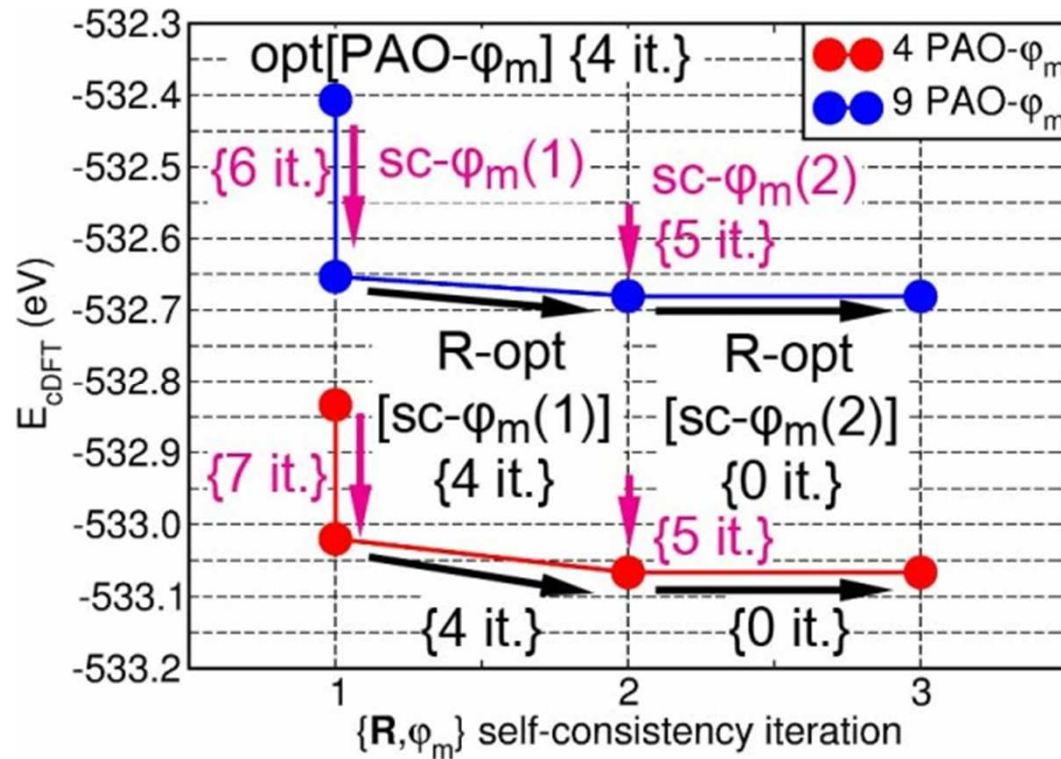


- $\frac{\partial \varphi_m^{SC}}{\partial \mathbf{R}}$??? **no idea(!)**

- **'Solution'**: perform optimisation of both φ_m and \mathbf{R} , **alternating** self-consistency cDFT-projector (φ_m) optimisation (at **fixed- \mathbf{R}**) and geometry (\mathbf{R}) optimisation (with **fixed-sc- φ_m**) loops.

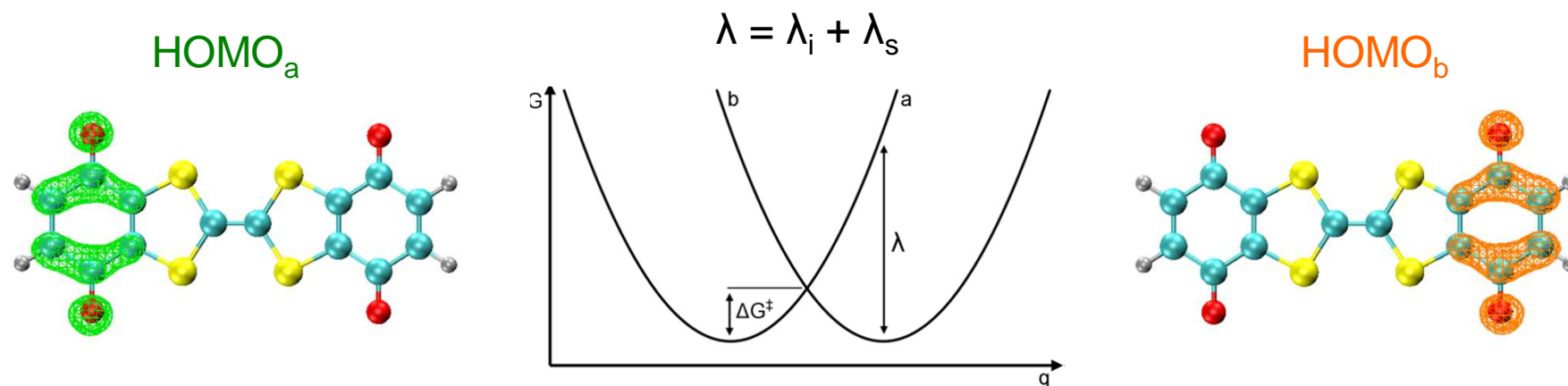


How large is the computational overhead?



- **4 ϕ_m :** 1st sc- ϕ_m loop: **22** NGWFs optimisation iterations
2nd sc- ϕ_m loop: **7** NGWFs optimisation iterations
- **9 ϕ_m :** 1st sc- ϕ_m loop: **21** NGWFs optimisation iterations
2nd sc- ϕ_m loop: **6** NGWFs optimisation iterations
- **Largest computational overhead from extra R_{opt} loop (4 BFGS-iterations)**
[if interested in improving convergence of E_{cDFT} from 10^{-3} to 10^{-5} eV]

Intra-molecular e-transfer in Q-TTF-Q⁽⁻⁾

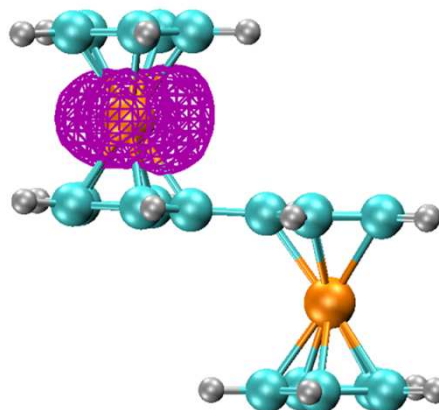
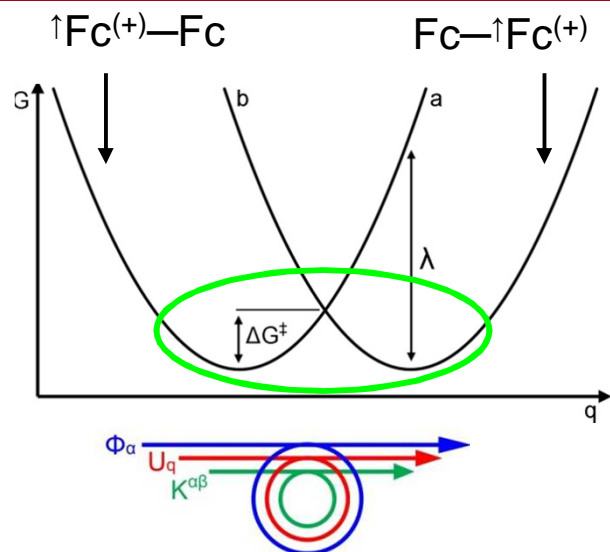


- 0.03 eV Å⁻¹ geometry optimisation threshold (Pulay corrected¹)
- $\lambda_{i, \text{ONETEP}}(\text{BLYP}, \phi_m: \text{DFT}-\phi_\alpha) =$ **16.5 kcal/mol**

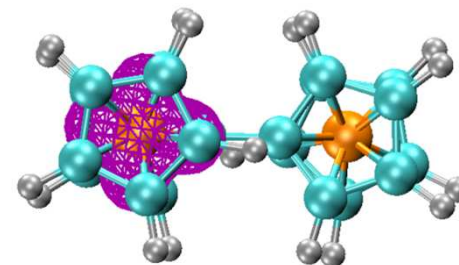
- $\langle \lambda_i \rangle (\text{BLYP}, \text{PW}, \text{Hirshfeld})^{2a} =$ **5.1 kcal/mol**
[averaged over MD trajectory in H₂O]
- $\lambda_i (\text{B3LYP}/6\text{-}31\text{+G(d)}, \text{Löwdin population})^{2b} =$ **13.1 kcal/mol**
- $\lambda_i (\text{B3LYP}/6\text{-}31\text{+G(d)}, \text{Becke population})^{2c} =$ **16.9 kcal/mol**
- $\lambda_{\text{exp}}(\text{ethyl acetate}:\text{t-butyl alcohol } 10:1) = \lambda_i + \lambda_s \sim$ **22 kcal/mol^{2b}**

[1] A. Ruiz-Serrano *et al.*, *J. Chem. Phys.* **136**, 234101 (2012); [2] a) H. Oberhofer *et al.*, *J. Chem. Phys.* **133**, 244105 (2010);
b) Q. Wu *et al.*, *J. Phys. Chem. A* **110**, 9212 (2006); c) Q. Wu *et al.*, *J. Phys. Chem.* **125**, 164105 (2006)

e-transfer in metal-organic systems: Ferrocenium-Ferrocene complexes



$\uparrow\text{Fc}^{(+)}-\text{Fc}$; Fc: $\text{Fe}(\text{C}_5\text{H}_5)_2$



$$\Delta\rho = \rho^\uparrow - \rho^\downarrow = 10^{-2} \text{ e } \text{\AA}^{-3}$$

- 0.05 eV \AA^{-1} geometry optimisation threshold (Pulay corrected¹)

- $\Delta G^\ddagger_{\text{ONETEP}}(\text{PBE}, \phi_m: \text{DFT-}\phi_\alpha) =$ **5.1 kcal/mol**

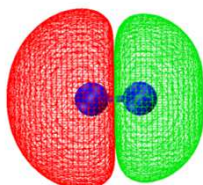
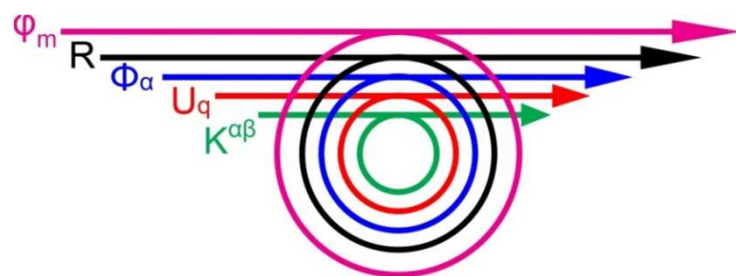
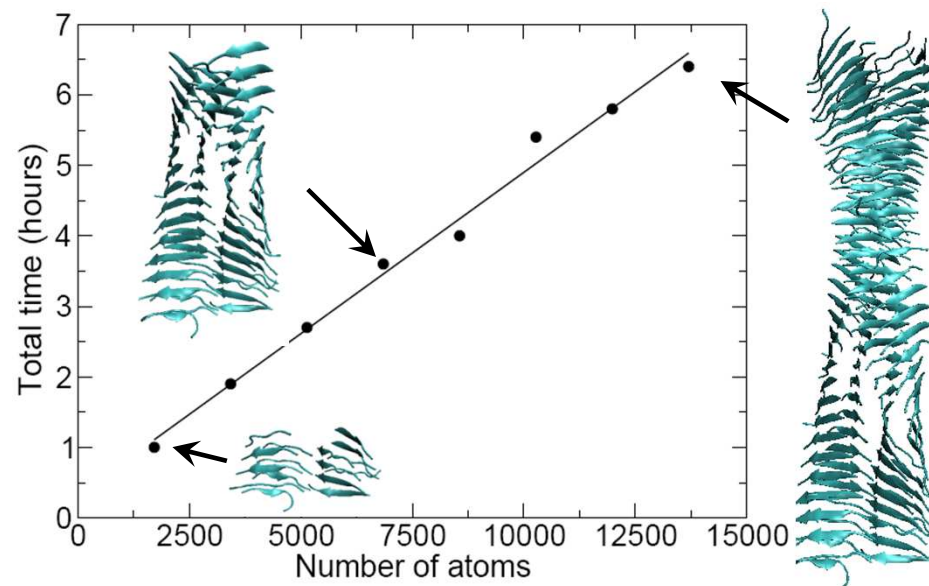
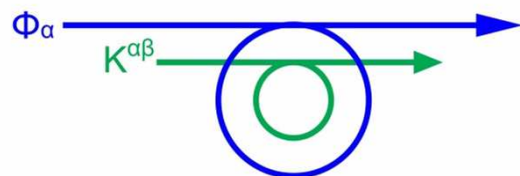
- $\Delta G^\ddagger(\text{B3LYP}/6\text{-}31\text{G}^{**}/\text{LANL2DZ}, \text{Becke population})^2 =$ **7.5 kcal/mol**

$\uparrow\text{Fc}^{(+)}-\text{CH}_2-\text{CH}_2-\text{Fc}$; Fc: $\text{Fe}(\text{C}_5\text{H}_5)_2$

- $\Delta G^\ddagger_{\text{ONETEP}}(\text{PBE}, \phi_m: \text{DFT-}\phi_\alpha) =$ **1.7 kcal/mol**

- $\Delta G^\ddagger(\text{B3LYP}/6\text{-}31\text{G}^{**}/\text{LANL2DZ}, \text{Becke population})^2 =$ **1.4 kcal/mol**

To summarise



$$\rho^\uparrow - \rho^\downarrow > 0$$

$$\rho^\uparrow - \rho^\downarrow < 0$$

