

# Hartree-Fock Exchange and Hybrid Exchange-Correlation Functionals

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# Exchange energy

- Electrons are fermions, so Pauli's exclusion principle applies.
- This imposes the antisymmetry requirement on the wavefunction:

$$\mathbf{x}_i = \{\mathbf{r}_i, s_i\}$$

$$\Psi(\dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots) = -\Psi(\dots, \mathbf{x}_j, \dots, \mathbf{x}_i, \dots)$$

- Even though the electrons do not interact explicitly, they still feel the presence of each other, because they are quantum-mechanical in nature.
- At the HF level of theory, this interaction is represented by the following exchange energy expression:

$$E_X^{HF} = - \sum_{ij} f_i f_j \iint \frac{\psi_i^*(\mathbf{r}_1) \psi_i(\mathbf{r}_2) \psi_j^*(\mathbf{r}_2) \psi_j(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

# Exchange (and correlation) energy in DFT

- The exact functional for exchange and correlation is not known, so we resort to approximations.

– LDA:

$$E_{XC}^{\text{DFT}}[n] = \int \epsilon_{XC}(n)n(\vec{r})d^3r.$$

– LSDA:

$$E_{XC}^{\text{DFT}}[n_{\uparrow}, n_{\downarrow}] = \int \epsilon_{XC}(n_{\uparrow}, n_{\downarrow})n(\vec{r})d^3r.$$

– GGA:

$$E_{XC}^{\text{DFT}}[n_{\uparrow}, n_{\downarrow}] = \int \epsilon_{XC}(n_{\uparrow}, n_{\downarrow}, \vec{\nabla}n_{\uparrow}, \vec{\nabla}n_{\downarrow})n(\vec{r})d^3r.$$

- A convincing argument can be made (using the concept of adiabatic connection [1-2]), that a good description of the exchange and correlation can be obtained by:

$$E_{xc} = (1 - a)E_{xc}^{\text{DFT}} + aE_x^{\text{HF}}.$$

# Hybrid exchange

- This observation is the inspiration for hybrid functionals, which replace a portion of the DFT exchange with HF exchange.

PBE0:

$$E_{xc}^{PBE0} = E_{xc}^{PBE} + 0.25 (E_x^{HF} - E_x^{PBE})$$

B3LYP:

$$E_{xc}^{B3LYP} = E_{xc}^{LDA} - a_0 (E_x^{HF} - E_x^{LDA}) + a_x \Delta E_x^{\text{Becke88}} + a_c (E_c^{LYP} - E_c^{LDA})$$

with  $a_0 = 0.20$ ,  $a_x = 0.72$  and  $a_c = 0.81$ .

# Advantages of hybrid functionals

- ▶ More accurate bond energies

Method	Mean Abs Error (kcal mol <sup>-1</sup> )
B3LYP	4.93
Hartree-Fock	211.54
LDA	121.85
PBE	22.22

Table: mean absolute errors for the 223 enthalpies of formation of the G3/99 set of complexes [3].

- ▶ Superior geometries

Method	Mean Abs Error (Å)
B3LYP	0.0104
Hartree-Fock	0.0249
LDA	0.0131
PBE	0.0159

Table: mean absolute errors of bond lengths from the T-96R set of complexes [3].

# Advantages of hybrid functionals

- ▶ Improved accuracy of calculated band gaps for many solids, in particular metal oxides

Method	Band Gap (eV)
Experiment	3.75
B3LYP	3.89
Hartree-Fock	12.33
LDA	2.36
PBE	2.35

Table: ( $\Gamma - \Gamma$ ) band gaps calculated for SrTiO<sub>3</sub> perovskites structures [4].

## Motivation for including HF exchange in ONETEP

- To be able to utilize hybrid functionals, such as B3LYP.
- To perform Hartree-Fock calculations.
- To lay groundwork for future implementation of other wavefunction methods, such as MP2.

# How to calculate it?

- HF exchange energy in terms of molecular orbitals:

$$E_X^{HF} = - \sum_{ij} f_i f_j \iint \frac{\psi_i^*(\mathbf{r}_1) \psi_i(\mathbf{r}_2) \psi_j^*(\mathbf{r}_2) \psi_j(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

- HF exchange energy in terms of NGWFs:

$$E_X^{HF} = - \sum_{\alpha\beta\gamma\delta} K^{\alpha\beta} K^{\gamma\delta} \iint \frac{\phi_\alpha^*(\mathbf{r}_1) \phi_\beta(\mathbf{r}_2) \phi_\gamma^*(\mathbf{r}_2) \phi_\delta(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

- Hartree energy in terms of molecular orbitals:

$$E_H = - \sum_{ij} f_i f_j \iint \frac{\psi_i^*(\mathbf{r}_1) \psi_i(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \psi_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

- Hartree energy in terms of NGWFs:

$$E_H = - \sum_{\alpha\beta\gamma\delta} K^{\alpha\beta} K^{\gamma\delta} \iint \frac{\phi_\alpha^*(\mathbf{r}_1) \phi_\beta(\mathbf{r}_1) \phi_\gamma^*(\mathbf{r}_2) \phi_\delta(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

# How to calculate it?

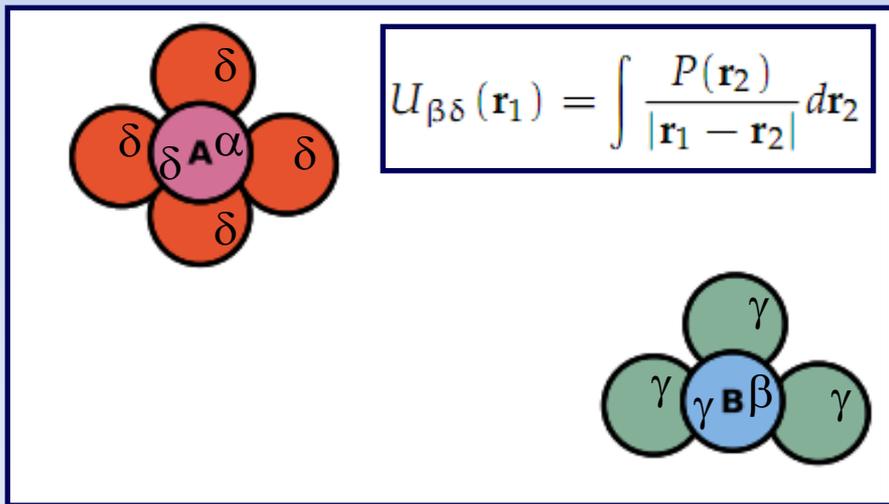
- HF exchange energy in terms of NGWFs:

$$E_X^{HF} = - \sum_{\alpha\beta\gamma\delta} K^{\alpha\beta} K^{\gamma\delta} \iint \frac{\phi_\alpha^*(\mathbf{r}_1) \phi_\beta(\mathbf{r}_2) \phi_\gamma^*(\mathbf{r}_2) \phi_\delta(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

- HF exchange energy in terms of the exchange matrix:

$$E_X^{HF} = - \sum_{\alpha\beta} K^{\alpha\beta} X_{\alpha\beta}.$$

$$X_{\alpha\beta} = \sum_{\substack{\gamma\delta \\ S_{\alpha\delta} \neq 0 \\ S_{\beta\gamma} \neq 0}} \int \phi_\alpha^*(\mathbf{r}_1) \phi_\delta(\mathbf{r}_1) \int \frac{\phi_\beta(\mathbf{r}_2) K^{\gamma\delta} \phi_\gamma^*(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 d\mathbf{r}_1,$$



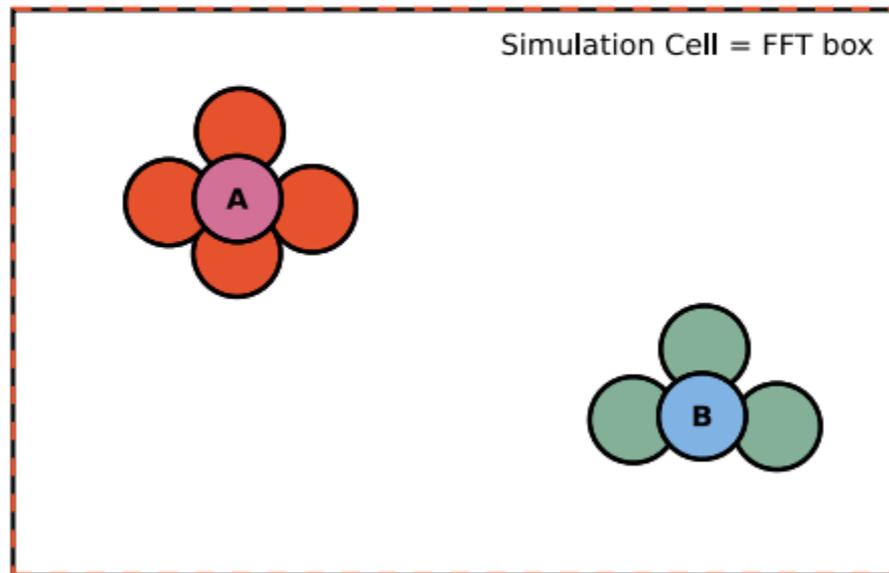
$$U_{\beta\delta}(\mathbf{r}_1) = \int \frac{P(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2$$

$$P(\mathbf{r}_2) = \sum_{\substack{\gamma \\ S_{\beta\gamma} \neq 0}} \phi_\beta(\mathbf{r}_2) K^{\gamma\delta} \phi_\gamma^*(\mathbf{r}_2)$$

$$X_{\alpha\beta} = \sum_{\substack{\delta \\ S_{\alpha\delta} \neq 0}} \int \phi_\alpha^*(\mathbf{r}_1) \phi_\delta(\mathbf{r}_1) \int \frac{P(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 d\mathbf{r}_1$$

# Approach 1: calculating the electrostatic integral in reciprocal space

$$X_{\alpha\beta} = \sum_{\substack{\gamma\delta \\ S_{\alpha\delta} \neq 0 \\ S_{\beta\gamma} \neq 0}} \int \Phi_{\alpha}^*(\mathbf{r}_1) \Phi_{\delta}(\mathbf{r}_1) \int \frac{\Phi_{\beta}(\mathbf{r}_2) K^{\gamma\delta} \Phi_{\gamma}^*(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 d\mathbf{r}_1,$$



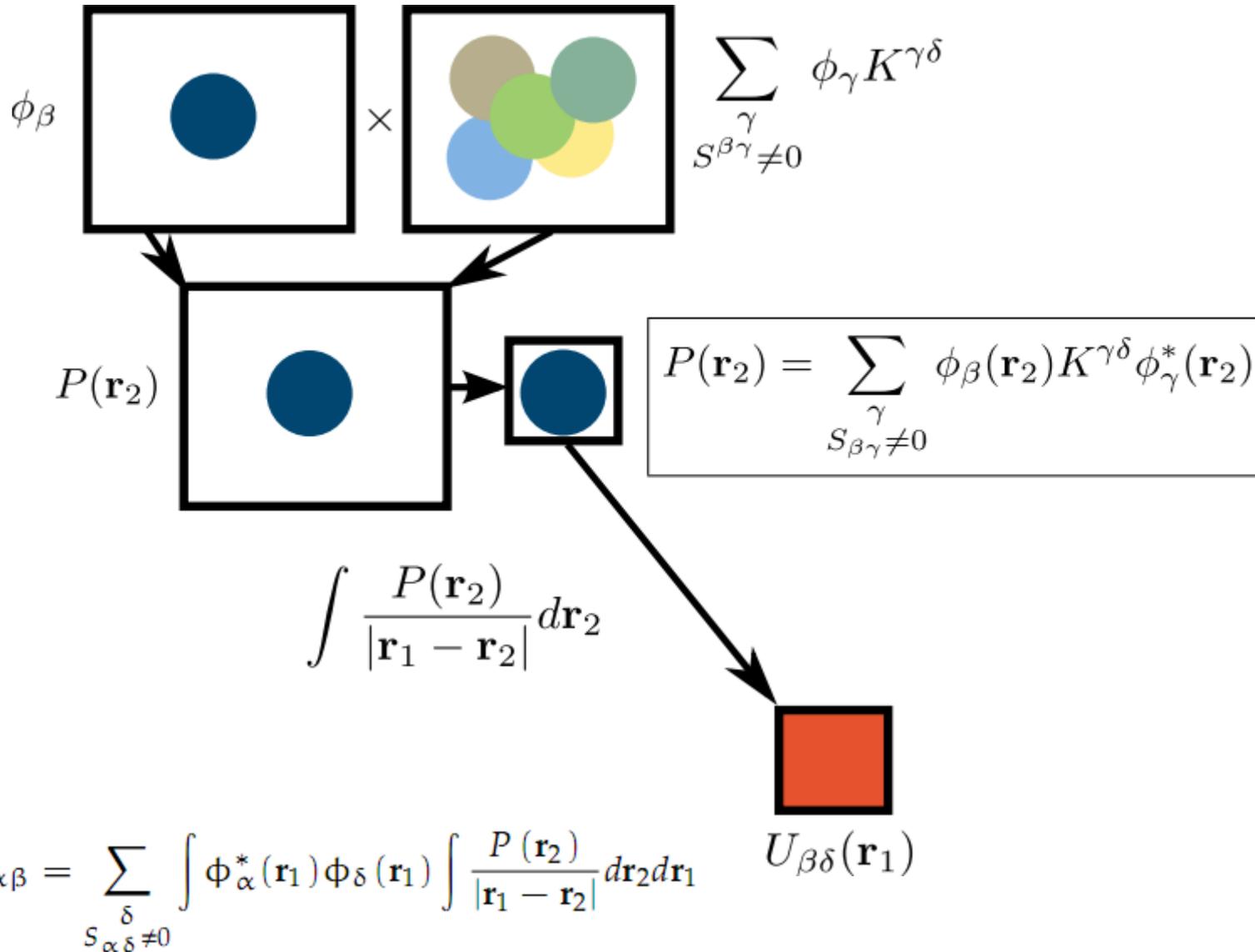
- Evaluation of the inner potential integral by FFTs would require several FFTs of the entire simulation cell for each pair of atoms. Result: quadratic scaling.

# Approach 1 – conclusions

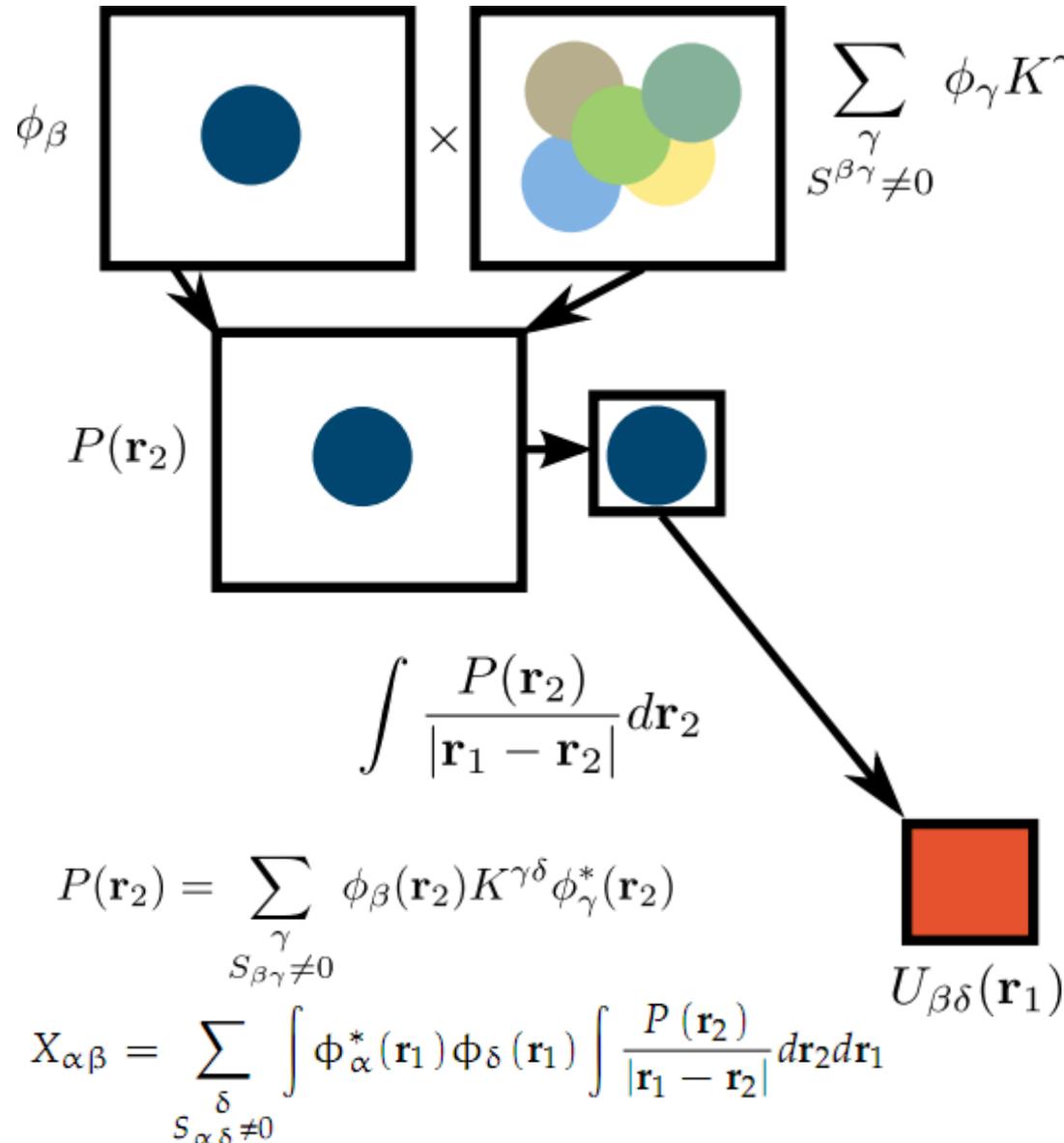
- Already available in ONETEP since 2.3.0, in main branch.
- Requires manual adjustment of the FFT box to coincide with the simulation cell.
- Scales as  $O(N^2)$ , vacuum is not free, large prefactor.
- Cannot obtain results in reasonable time beyond 20 atoms.

System	# of atoms	Time of 1 LNV iteration [s]	on $N$ cores, $N=$
H <sub>2</sub> O	3	640	2
Si <sub>16</sub>	16	1405	16
benzene	12	28647	8

# Let's try something different

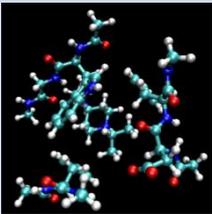


# Approach 2: Direct numerical integration



- The integral  $U_{\beta\delta}(\mathbf{r}_1)$  must be evaluated anew for every "interesting" point  $\mathbf{r}_1$ .
- ... that is everywhere, where  $\phi_\alpha^*(\mathbf{r}_1)\phi_\delta(\mathbf{r}_1)$  is nonzero.
- What is more, the integral depends on both  $\beta$  and  $\delta$ .
- It all boils down to a 6D integration, where for every block of the  $X$  matrix, the potential integral over all points of one tightbox must be calculated for every point in another tightbox.

# Approach 2: Direct numerical integration

System	# of atoms	Time of 1 LNV iteration [s]	on $N$ cores, $N=$
H <sub>2</sub> O	3	136	1
benzene dimer	24	7814	16
P4_2BOH	36	17872	24
DTQGY	71	98000	32
	156	689000	48

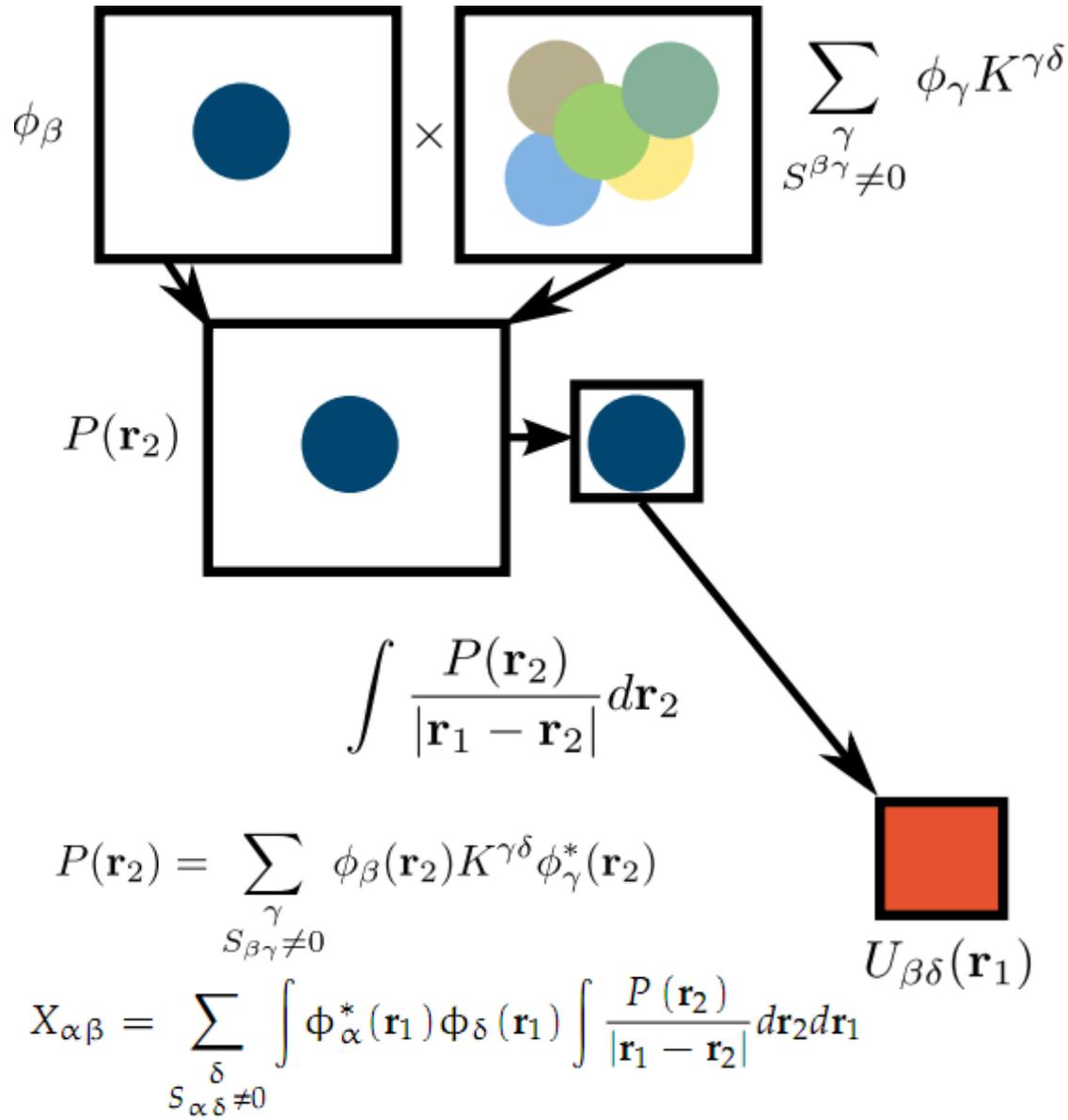
**Way too slow!**

# Approach 2: Direct numerical integration

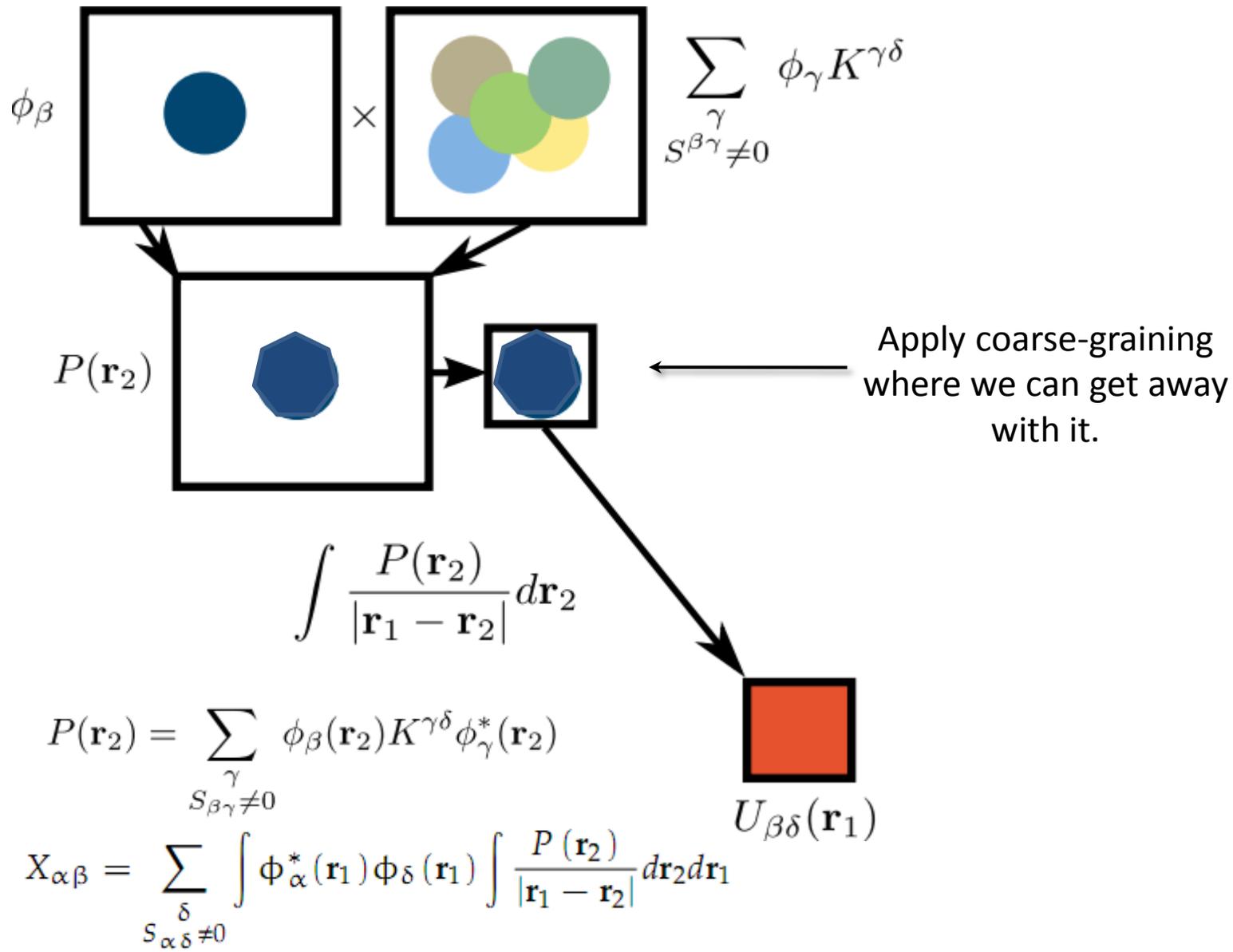
System	# of atoms	Time of 1 LNV iteration [s]		on $N$ cores, $N=$
		original	optimized	
H <sub>2</sub> O	3	136	38	1
benzene dimer	24	7814	705	16
P4_2BOH	36	17872	1451	24
DTQGY	71	98000	17135	32
	156	689000	42311	48

**Still way too slow!**

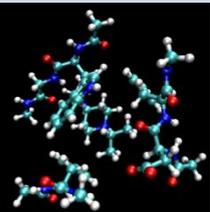
# Approach 2: Direct numerical integration



# Approach 2: Direct numerical integration



## Approach 2: Direct numerical integration

System	# of atoms	Time of 1 LNV iteration [s]			on $N$ cores, $N=$
		original	optimized	cg'ed	
H <sub>2</sub> O	3	136	38	38	1
benzene dimer	24	7814	705	714	16
P4_2BOH	36	17872	1451	1364	24
DTQGY	71	98000	17135	16613	32
	156	689000	42311	25757	48

**Still way too slow!**

## Approach 2 – conclusions

- Working linear-scaling approach, but the prefactor is so huge, we'll never get to the linear-scaling regime.
- Implemented in the Southampton development version since 2.4.12 (but not available in the main branch).
- Can serve as a reference calculation.
- Useless beyond ca. 80 atoms.

# Approach 3: expanding $P(\mathbf{r}_2)$

$$X_{\alpha\beta} = \sum_{\substack{\gamma\delta \\ S_{\alpha\delta} \neq 0 \\ S_{\beta\gamma} \neq 0}} \int \phi_{\alpha}^*(\mathbf{r}_1) \phi_{\delta}(\mathbf{r}_1) \int \frac{\phi_{\beta}(\mathbf{r}_2) K^{\gamma\delta} \phi_{\gamma}^*(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 d\mathbf{r}_1,$$

Solution: expand the NGWF product in an auxiliary basis set,

$$P(\mathbf{r}_2) = \sum_{\substack{\gamma \\ S_{\beta\gamma} \neq 0}} \phi_{\beta}(\mathbf{r}_2) K^{\gamma\delta} \phi_{\gamma}^*(\mathbf{r}_2) = \sum_i^{N_{\text{fit}}} f_i(\mathbf{r}_2) c_i$$

Requirements:

- ▶ Potential (inner) integral can be evaluated analytically

$$U_{\beta\delta}(\mathbf{r}_1) = \int \sum_{\substack{\gamma \\ S_{\beta\gamma} \neq 0}} \frac{\phi_{\beta}(\mathbf{r}_2) K^{\gamma\delta} \phi_{\gamma}^*(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 = \int \sum_i^{N_{\text{fit}}} \frac{f_i(\mathbf{r}_2) c_i}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2$$

- ▶ Cost per  $X_{\alpha\beta}$  matrix element independent of system size
- ▶ Must represent product accurately

# Approach 3: expanding $P(\mathbf{r}_2)$ in terms of spherical waves

## Free particle Schrödinger (Helmholtz) Equation

$$(\nabla^2 + q^2) \psi = 0$$

Particle in a box with periodic boundary conditions:

- ▶ Solutions are plane waves ( $e^{i\mathbf{g}\cdot\mathbf{r}}$ )

Particle in a sphere (of radius  $a$ ):

- ▶ Solutions are truncated spherical waves

$$\psi(\mathbf{r}) = \begin{cases} j_l(qr) Z_{lm}(\hat{\mathbf{r}}) & r < a \\ 0 & r \geq a \end{cases}$$

- $j_l(qr)$  is a spherical Bessel function
- $Z_{lm}(\hat{\mathbf{r}})$  is a real spherical harmonic
- $E = \frac{1}{2}q^2 \Rightarrow q_{\max} = \sqrt{2E_{\max}}$

[ Haynes and Payne. *Chem. Phys. Comm.*, **102** 17, (1997)]

## Approach 3: expanding $P(\mathbf{r}_2)$ in terms of spherical waves

- It's possible to analytically evaluate the inner potential integral in constant time, so, with kernel truncation,  $O(N)$  scaling possible.
- However, we need the expansion coefficients,  $\{c_i\}$ :

$$P(\mathbf{r}_2) = \sum_{\substack{\gamma \\ S_{\beta\gamma} \neq 0}} \phi_{\beta}(\mathbf{r}_2) K^{\gamma\delta} \phi_{\gamma}^*(\mathbf{r}_2) = \sum_i^{N_{\text{fit}}} f_i(\mathbf{r}_2) c_i$$

- These can be obtained by calculating and inverting the  $V$  matrix.

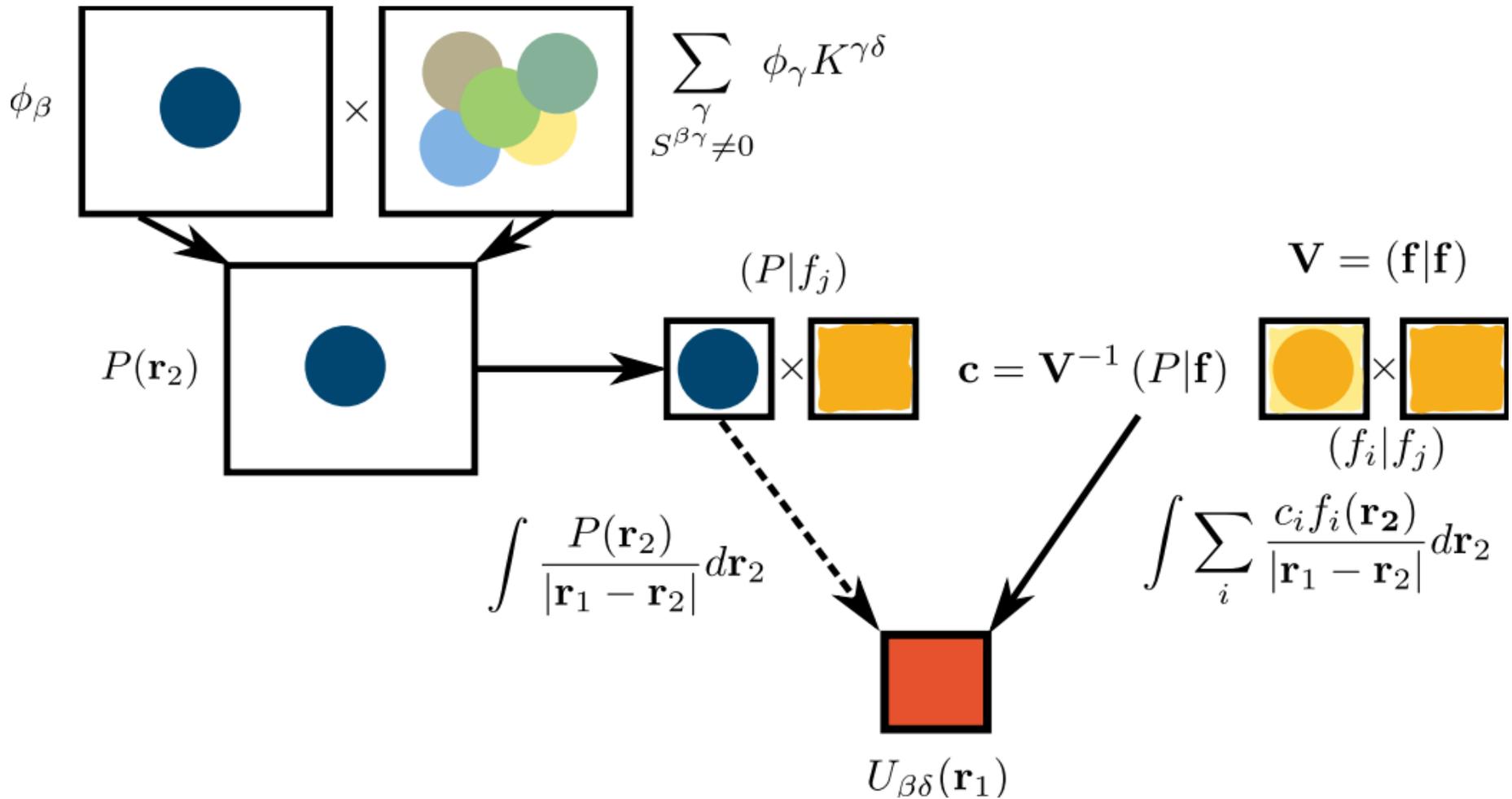
spherical waves centered on atoms A and B.

$$(a|b) = \iint \frac{a(\mathbf{r}_1)b(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 d\mathbf{r}_1$$

$$\mathbf{c} = \mathbf{V}^{-1} (P|\mathbf{f})$$

$$V_{ij} = (f_i|f_j)$$

# Approach 3: the procedure



## Approach 3 – conclusions

- Algebraically sound and clever.
- Appears very sensitive to the accuracy of the  $V$  matrix.
- At current state has difficulties converging density kernel.
- Needs more analysis.
- Currently trying to compute  $\mathbf{v} = (\mathbf{f}|\mathbf{f})$  by integrating on a radial grid, instead of a Cartesian grid in tightboxes, to improve accuracy and, hopefully, get convergence.
- Initial results encouraging, but remaining bugs need to be squashed.

## Conclusions: current state of affairs

- B1LYP, B1PW91, B3LYP, B3PW91, PBE0 and X3LYP already implemented in ONETEP, but only usable for the smallest systems.
- Approaches 1 (FFT-based) and 2 (direct brute-force integration) work, but can only serve as benchmarks.
- Approach 3 (SW-expansion-based) still somewhat broken, but looks promising.

## Future outlook

- Implement newer hybrid functionals, which use the modified (truncated, decaying) Coulomb operator.
- Implement more advanced wavefunction methods (MP2, etc.).
- Working exchange potential can be easily adapted to the calculation of the Hartree potential, yielding a new way to calculate the Hartree energy with open boundary conditions.

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  - Nicholas Zonias
  - Chris Pittock
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    - my grant "*Development of wide-ranging functionality in ONETEP*".
  - iSolutions, the guys who manage our PCs.
  - Iridis3 and HECToR, the parallel machines.

# References

1. Langreth and Perdew, *Solid State Comm.* **17** (1975).
2. Gunnarsson and Lundqvist, *Phys. Rev.* **13** (1976).
3. Staroverov, Scuseria, Tao, and Perdew, *J. Chem. Phys.* **119** (2003);  
erratum in: **121** (2004).
4. Piskunov, Heifets, Eglitis and Borstel, *Comp. Mater. Sci.* **29** (2004).

# Backup slide: overlap vs. electrostatic metric

$$P(\mathbf{r}_2) = \sum_{\substack{\gamma \\ S_{\beta\gamma} \neq 0}} \phi_{\beta}(\mathbf{r}_2) K^{\gamma\delta} \phi_{\gamma}^*(\mathbf{r}_2) = \sum_i^{N_{\text{fit}}} f_i(\mathbf{r}_2) c_i$$

Overlap metric

$$\langle a|b \rangle = \int a^*(\mathbf{r}_1) b(\mathbf{r}_1) d\mathbf{r}_1$$

$$\mathbf{c} = \mathbf{V}^{-1} \langle P|\mathbf{f} \rangle$$

$$V_{ij} = \langle f_i|f_j \rangle$$

if  $i \neq j \Rightarrow \langle f_i|f_j \rangle = 0$  then

$$c_i = \frac{\langle P|f_i \rangle}{\langle f_i|f_i \rangle}$$

$f_i$  centred on atom B.

Electrostatic metric

$$\langle a|b \rangle = \iint \frac{a(\mathbf{r}_1) b(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 d\mathbf{r}_1$$

$$\mathbf{c} = \mathbf{V}^{-1} \langle P|\mathbf{f} \rangle$$

$$V_{ij} = \langle f_i|f_j \rangle$$

$f_i$  centred on atoms A and B.