



Pair-Atomic Resolution-of-the-Identity

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Outline

- The Resolution-of-the-Identity (RI) approximation
- Methods exploiting locality to reach linear-scaling RI
- The PARI approximation
- Results and Analysis of convergence issues
- Conclusion

The RI approximation

The Resolution-of-the-Identity (RI), or the **density-fitting** approximation:

- Speed up calculations (**typically by factor 3-30**) at little loss of chemical accuracy
- Highly successful for **approximating the Coulomb contribution** (in particular in DFT)
- Also used for small- to medium-sized systems for **approximation of the exact exchange** and in correlated treatment - **Scaling wall**
- **Requires an auxiliary basis set**

The RI approximation

- In the most commonly used RI treatments, the four-center two-electron integrals (in the Mulliken notation)

$$(\mu\nu|\gamma\delta) = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi_\mu(\mathbf{r}_1) \psi_\nu(\mathbf{r}_1) \frac{1}{r_{12}} \psi_\gamma(\mathbf{r}_2) \psi_\delta(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2.$$

are approximated by $\widetilde{(\mu\nu|\gamma\delta)}$, according to

$$(\mu\nu|\gamma\delta) \approx \widetilde{(\mu\nu|\gamma\delta)} = \sum_{IJ} (\mu\nu|I)(I|J)^{-1}(J|\gamma\delta)$$

with $\{\mu\}$ the (regular) AO basis set and with an atom-centered auxiliary basis set $\{I\}$

- The Coulomb contribution (up to 10 000 AO basis functions)

$$J_{\mu\nu} = (\mu\nu|\rho) = \sum_{\gamma\delta} (\mu\nu|\gamma\delta) D_{\gamma\delta}$$
$$\approx \tilde{J}_{\mu\nu} = (\mu\nu|\tilde{\rho}) = \sum_I (\mu\nu|I) c_I, \quad \sum_J (I|J) c_J = (J|\rho)$$

RI for the exact exchange (RI-K)

- The (regular) exchange contribution

$$K_{\mu\nu} = \sum_{\gamma\delta} (\mu\gamma|\nu\delta) D_{\gamma\delta} = \sum_i^{\text{occ}} (\mu i|\nu i)$$

approximated according to - Weigend (2002), Polly *et.al* (2004)

$$\tilde{K}_{\mu\nu} = \sum_{\gamma\delta} \sum_{IJ} (\mu\gamma|I)(I|J)^{-1}(J|\nu\delta) D_{\gamma\delta} = \sum_i^{\text{occ}} \sum_{IJ} (\mu i|I)(I|J)^{-1}(J|\nu i)$$

- **Scaling wall** limits this approach to about 1000 AO basis-functions
 - metric matrix $(I|J)$ non-sparse $\rightarrow \mathcal{O}(N^3)$ scaling
 - non-locality of fitting coefficients $c_I^{\mu\nu}$ (for each pair $\mu\nu$)

$$c_I^{\mu\nu} = \sum_J (I|J)^{-1} (J|\mu\nu)$$

- transformation steps, e.g.

$$(I|\mu i) = \sum_{\nu} (I|\mu\nu) L_{\nu i}, \quad \mathcal{O}(N^2 N_{\text{occ}})$$

Methods for linear-scaling RI

Two main approaches for linear-scaling RI:

- the **Partitioning approach**

Partition the density and fit each density in a local region

Gallant and St-Amant (1996), Sodt *et.al* (2006), Sodt and Head-Gordon (2008)

- the **Local Metric approach**

Obtain the fitting coefficients using (w) a local metric (e.g. the overlap metric)

Baerends *et.al* (1973), Vahtras *et.al* (1993), Jung *et.al* (2005), Reine *et.al* (2008)

$$c_I^{\mu\nu} = \sum_J \langle I|w|J \rangle^{-1} \langle J|w|\mu\nu \rangle$$

instead of the Coulomb metric

$$c_I^{\mu\nu} = \sum_J (I|J)^{-1} (J|\mu\nu)$$

Methods for linear-scaling RI

Atomic RI (ARI): an elegant and balanced partitioning approach:

- In the ARI approach of Sodt *et.al* each charge distribution $|\mu\nu\rangle$ is first associated with a center C , and is fitted using auxiliary functions $|I\rangle$ centered on the atoms in some buffer zone $[C]$ around C

$$|\mu\nu\rangle = \sum_I c_I^{\mu\nu} |I\rangle, \quad |I\rangle \in [C]$$

- fixed buffer-zone size - **system dependent**
- the set $|I\rangle$ includes the **auxiliary functions centered on several atoms**
- Jung *et.al* explored the decay behavior of the two-center fitting coefficients $c_I^{\mu\nu}$.
 - Coulomb metric fit - the asymptotic decay of $c_I^{\mu\nu}$ was as slow as $\frac{1}{r}$
 - local (**overlap/attenuated Coulomb**) metric fit - **exponential decay** with distance
 - But the fitting errors ≈ 10 times smaller in the Coulomb than in the overlap metric

The PARI approach

We propose the pair-atomic resolution-of-the-identity (PARI):

- fit each charge distribution $|\mu\nu\rangle$ with auxiliary functions $|I\rangle$ centered on the two parent atoms A and B of the basis functions $|\mu\rangle$ and $|\nu\rangle$

$$|\widetilde{\mu\nu}\rangle = \sum_{I \in A \cup B} c_I^{\mu\nu} |I\rangle, \quad c_I^{\mu\nu} = \sum_{J \in A \cup B} (I|J)^{-1} (J|\mu\nu)$$

instead of the (regular) RI approx.

$$|\widetilde{\mu\nu}\rangle = \sum_{I \in \mathcal{M}} c_I^{\mu\nu} |I\rangle, \quad c_I^{\mu\nu} = \sum_{J \in \mathcal{M}} (I|J)^{-1} (J|\mu\nu)$$

- replace all $(\mu\nu|\gamma\delta)$ by **robust** and **variational** $(\widetilde{\mu\nu}|\gamma\delta)$ given by

$$\begin{aligned} (\widetilde{\mu\nu}|\gamma\delta) &= (\mu\nu|\widetilde{\gamma\delta}) + (\widetilde{\mu\nu}|\gamma\delta) - (\widetilde{\mu\nu}|\widetilde{\gamma\delta}) \\ &= (\mu\nu|\gamma\delta) - (\mu\nu - \widetilde{\mu\nu}|\gamma\delta - \widetilde{\gamma\delta}) \end{aligned}$$

- Pros/Cons:

- highly local
- removes scaling bottleneck
- decreases accuracy \rightarrow larger auxiliary basis sets

PARI for the Coulomb contribution (PARI-J)

$$\begin{aligned}
 \tilde{J}_{\mu\nu} &= \sum_{\gamma\delta} (\widetilde{\mu\nu|\gamma\delta}) D_{\gamma\delta} = \sum_{\gamma\delta} \left[(\widetilde{\mu\nu|\gamma\delta}) + (\mu\nu|\widetilde{\gamma\delta}) - (\widetilde{\mu\nu}|\widetilde{\gamma\delta}) \right] D_{\gamma\delta} \\
 &= \sum_{\gamma\delta} \left[\sum_{I \in A \cup B} c_I^{\mu\nu} (I|\gamma\delta) + \sum_{J \in C \cup D} (\mu\nu|J) c_J^{\gamma\delta} - \sum_{I \in A \cup B, J \in C \cup D} c_I^{\mu\nu} (I|J) c_J^{\gamma\delta} \right] D_{\gamma\delta} \\
 &= \sum_{I \in A \cup B} c_I^{\mu\nu} (I|\rho) + \sum_{J \in C \cup D} (\mu\nu|J) c_J - \sum_{I \in A \cup B} c_I^{\mu\nu} (I|\tilde{\rho}), \text{ with } c_J = \sum_{\gamma\delta} c_J^{\gamma\delta} D_{\gamma\delta} \\
 &= \sum_{J \in C \cup D} (\mu\nu|J) c_J + \sum_{I \in A \cup B} c_I^{\mu\nu} (I|\rho - \tilde{\rho}), \text{ with } |\tilde{\rho}\rangle = \sum_J c_J |J\rangle, \sum_J (I|J) c_J = (J|\rho) \\
 &= \sum_I (\mu\nu|I) c_I + \sum_{I \in A \cup B} C_I^{\mu\nu} (I|\rho - \tilde{\rho})
 \end{aligned}$$

- straightforwardly linear scaling using screening and FMM

PARI-K

PARI for the Exact-Exchange contribution (PARI-K)

- split fitting coefficients into the two parent atoms

$$|\widetilde{\mu\nu}\rangle = |\widetilde{\underline{\mu}\nu}\rangle + |\widetilde{\underline{\mu}\underline{\nu}}\rangle, \quad |\widetilde{\underline{\mu}\nu}\rangle = \sum_{I \in A} c_I^{\mu\nu} |I\rangle, \quad |\widetilde{\underline{\mu}\underline{\nu}}\rangle = \sum_{J \in B} c_J^{\mu\nu} |J\rangle$$

- leads to a splitting of $(\widetilde{\mu\nu|\gamma\delta})$ into eight parts - four involving three-center and four two-center integrals
- collect terms in order to calculate each integral only once and select contraction pathway in order to reduce cost
- exploit symmetry of integrals and density matrix

An example three-center term:

$$K_{\mu\gamma}^{\pm} \triangleq \sum_{I\delta} d_{I,\delta}^{\mu} (I|\gamma\delta), \quad I, \mu \in A, \gamma \in C, \delta \in M, \quad d_{I,\gamma}^{\mu} = \sum_{\nu} c_I^{\mu\nu} D_{\nu\gamma}$$

- ignoring screening each of these terms scale $\mathcal{O}(N^3 n^3 a)$
number of atoms N , of regular/auxiliary basis functions per atom n, a
- to be compared with the $\mathcal{O}(N^4 n^2 a^2)$ scaling of conventional RI

Outline of PARI-K algorithm

Three-center contributions

Loop A

Calculate the fitting coefficients $c_l^{\mu\nu}$, $l, \mu \in A, \nu \in M$
and density coefficients $d_{l,\gamma}^\mu$

Loop C

Loop $D \geq C$

Calculate $(l|\gamma\delta)$, $l \in A, \gamma \in C, \delta \in D$

Make contractions

$$\tilde{K}_{\mu\gamma} \pm \sum_{l\delta} d_{l,\delta}^\mu (l|\gamma\delta), \quad \mathcal{O}(N^3 n^3 a)$$

$$\tilde{K}_{\mu\delta} \pm \sum_{l\gamma} d_{l,\gamma}^\mu (l|\gamma\delta), \quad \mathcal{O}(N^3 n^3 a)$$

$$X_{l,\gamma}^\mu = \sum_{\delta} (l|\gamma\delta) D_{\mu\delta}, \quad \mathcal{O}(N^3 n^3 a)$$

$$X_{l,\delta}^\mu = \sum_{\gamma} (l|\gamma\delta) D_{\mu\gamma}, \quad \mathcal{O}(N^3 n^3 a)$$

Make contractions

$$\tilde{K}_{\nu\gamma} \pm \sum_{l,\mu} c_l^{\mu\nu} X_{l,\gamma}^\mu, \quad \mathcal{O}(N^3 n^3 a)$$

$$\tilde{K}_{\nu\delta} \pm \sum_{l,\mu} c_l^{\mu\nu} X_{l,\delta}^\mu, \quad \mathcal{O}(N^3 n^3 a)$$

Symmetrized or anti-symmetrized **K**

Results and Analysis of convergence issues

G2/G3 Benchmark set (358 molecules), B3LYP, 6-31G/df-def2

	$\delta(dfJ)$	$\delta(pariJ)$	$\delta(dfK)$	$\delta(pariK)$	$\delta(dfJK)$	$\delta(pariJK)$
μ	-2.14e-05	-7.40e-05	8.04e-06	-3.21e-05	-1.33e-05	-5.34e-05
σ	9.11e-06	4.82e-05	-1.11e-06	3.48e-05	8.00e-06	4.39e-05
σ^{max}	5.14e-05	2.05e-04	1.45e-05	1.35e-04	3.68e-05	1.86e-04

Some convergence issues:

- some molecules have a diverging negative energy during SCF
- we observed the non-positive definiteness of the PARI approx.
- this may come from the non-uniformity of the PARI operator,
- leading to discontinuities of the Potential Energy Surface

Results and Analysis of convergence issues

Timings for 6-31G_df-def2 (in sec. per iteration)

	<i>regJ</i>	<i>pariJ</i>	<i>dfJ</i>	<i>LinK</i>	<i>pariK</i>	<i>dfK</i>
PA_oligomer_2	1.89	1.18	0.68	2.88	9.5	11.11
PA_oligomer_3	0.24	0.28	0.12	0.37	1.18	0.63
PA_oligomer_4	0.63	0.51	0.27	0.97	3.21	2.02
PA_oligomer_5	1.18	0.81	0.43	1.98	6.15	5.07
PP	2.71	1.48	0.84	4.83	11.34	12.33
acene_1	1.93	1.08	0.61	3.35	6.9	5.76
acene_2	4.33	2.18	1.29	7.89	18.85	19.23
acene_3	8.69	3.46	1.92	15.91	34.93	-
acene_4	11.83	4.27	2.89	22.11	56.25	-
acene_5	19.82	5.69	3.96	38.14	76.0	-
beta-dipeptide	2.19	1.42	0.75	4.51	10.8	11.57
co	0.01	0.08	0.01	0.01	0.09	0.03
dipeptide	1.58	1.17	0.59	3.38	8.66	7.77
dmabn	2.66	1.54	0.88	5.63	12.03	13.26
h2co	0.02	0.12	0.02	0.03	0.22	0.07
hcl	0.01	0.13	0.01	0.01	0.14	0.03
n2	0.01	0.06	0.01	0.01	0.08	0.03
tripeptide	3.42	1.98	1.14	7.17	20.64	18.24

Results and Analysis of convergence issues

Timings for cc-pVTZ_cc-pVTZdenfit (in sec. per iteration)

	<i>regJ</i>	<i>pariJ</i>	<i>dfJ</i>	<i>LinK</i>	<i>pariK</i>	<i>dfK</i>
PA_oligomer_2	138.00	10.80	5.18	395.00	148.00	202.87
PA_oligomer_3	13.53	2.09	0.80	36.60	15.54	11.48
PA_oligomer_4	41.06	4.33	1.86	116.00	38.99	40.04
PA_oligomer_5	81.00	7.44	3.45	291.00	89.00	143.84
PP	210.00	13.33	6.62	675.00	157.00	295.73
acene_1	173.00	10.87	5.53	477.00	131.00	204.18
acene_2	423.00	20.55	11.22	1199.00	287.00	-
acene_3	799.00	33.21	18.35	2363.00	554.00	-
acene_4	1295.00	48.32	28.88	3746.00	1064.00	-
acene_5	1797.00	64.00	39.59	5555.00	1659.00	-
beta-dipeptide	162.00	12.29	6.19	573.00	168.00	210.43
co	0.22	0.28	0.05	0.53	0.55	0.29
dipeptide	106.00	9.91	4.66	378.00	123.00	132.06
dmabn	221.00	15.26	7.04	854.00	183.00	231.08
h2co	0.78	0.59	0.12	2.26	1.87	0.93
hcl	0.18	0.43	0.04	0.40	0.63	0.17
n2	0.22	0.24	0.05	0.53	0.53	0.28
tripeptide	279.00	18.47	9.12	952.00	291.00	-

Conclusion and future perspective

- We have presented the PARI scheme for efficient calculation of the Coulomb and exchange contributions to DFT
- The PARI method can in general be used for any method involving four-center two-electron integrals
- Linear scaling in nature, relatively small errors
- Allows differentiated treatment by adding Lagrangian multipliers
- The method has some inherent problems, but highly promising

Thank you for your attention!