Fast evaluation of molecular integrals using solid harmonic Gaussian functions

Dorothea Golze

July 11, 2017

Contents

1. Introduction
2. SHG scheme
3. Results and Application
   - Comparison of algorithms
   - Speed-ups
   - Application
4. Conclusions

Motivation

2-center integrals

- RI approaches in KS-DFT
- semi-empirical methods
- QM/MM

Type of integrals

- $(a|\mathcal{O}|b)$ Coulomb, overlap,...
- $(a|r_a^{2n}|b)$ local operator $\mathbf{r}_a = \mathbf{r} - \mathbf{R}_a$
- $(ab\tilde{a})$ three-index integrals

Gaussian-type orbitals

Primitive Cartesian Gaussian

$$\psi(\alpha, \mathbf{l}, \mathbf{r}, \mathbf{R}) = (x - R_x)^{l_x}(y - R_y)^{l_y}(z - R_z)^{l_z} \exp\left[-\alpha(\mathbf{r} - \mathbf{R})^2\right]$$

with $\mathbf{l}=(l_x,l_y,l_z)$

number: $(l+1)(l+2)/2$ $l=l_x+l_y+l_z$

Primitive spherical harmonic Gaussian

$$\Psi_{l,m}(\alpha, \mathbf{r}, \mathbf{R}) = r^l Y_{l,m}(\theta, \phi) \exp\left[-\alpha(\mathbf{r} - \mathbf{R})^2\right]$$

number: $2l+1$

Primitive solid harmonic Gaussian

$$\chi_{l,m}(\alpha, \mathbf{r}) = \sqrt{\frac{4\pi}{2l+1}} r^l Y_{l,m}(\theta, \phi) \exp\left[-\alpha(\mathbf{r} - \mathbf{R})^2\right]$$

number: $2l+1$

Gaussian-type orbitals

Primitive Cartesian Gaussian

$$\psi(\alpha, \mathbf{l}, \mathbf{r}, \mathbf{R}) = (x - R_x)^{l_x}(y - R_y)^{l_y}(z - R_z)^{l_z} \exp\left[-\alpha(\mathbf{r} - \mathbf{R})^2\right]$$

with $\mathbf{l}$=(l_x,l_y,l_z)

number: $(l{+}1)(l{+}2)/2$ $\qquad l{=}l_x{+}l_y{+}l_z$

Primitive spherical harmonic Gaussian

$$\Psi_{l,m}(\alpha, \mathbf{r}, \mathbf{R}) = r^l Y_{l,m}(\theta, \phi) \exp\left[-\alpha(\mathbf{r} - \mathbf{R})^2\right]$$

number: $2l{+}1$

Primitive solid harmonic Gaussian

$$\chi_{l,m}(\alpha, \mathbf{r}) = \sqrt{\frac{4\pi}{2l+1}} r^l Y_{l,m}(\theta, \phi) \exp\left[-\alpha(\mathbf{r} - \mathbf{R})^2\right]$$

number: $2l{+}1$

Gaussian-type orbitals

Primitive solid harmonic Gaussian

$$\chi_{l,m}(\alpha, \mathbf{r}) = \sqrt{\frac{4\pi}{2l+1}} r^l Y_{l,m}(\theta, \phi) \exp\left[-\alpha(\mathbf{r} - \mathbf{R})^2\right]$$

number: $2l{+}1$

Contracted spherical harmonic Gaussian function

$$\varphi_{l,m}(\mathbf{r}) = N_l \sum_{\alpha \in A} c_\alpha \chi_{l,m}(\alpha, \mathbf{r}),$$

N_l...normalization constants

"Traditional" Obara-Saika (OS) scheme

OS scheme for molecular integrals

- recursive integral scheme based on Cartesian Gaussians
- popular scheme, also used for libint

Steps in CP2K

1. evaluation of integrals of primitive Cartesian Gaussians
2. transformation to spherical Gaussian integrals
3. contraction of spherical integrals

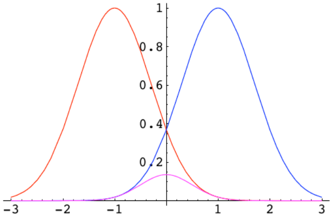
Cartesian Gaussians - Properties

Gaussian product rule

$$\psi_A = \exp(-\alpha r_A^2)$$

$$\psi_B = \exp(-\beta r_B^2)$$

$$\psi_{AB} = \underbrace{\exp(-\mu R_{AB}^2)}_{\textit{prefactor}} \; \underbrace{\exp(-p r_P^2)}_{\textit{product Gaussian}}$$



where

$$p = \alpha + \beta \qquad \leftarrow \text{total exponent}$$

$$\mu = \frac{\alpha\beta}{\alpha + \beta} \qquad \leftarrow \text{reduced exponent}$$

$$\mathbf{R}_{AB} = \mathbf{R}_A - \mathbf{R}_B \qquad \leftarrow \text{relative separation}$$

$$\mathbf{R}_P = \frac{\alpha \mathbf{R}_A + \beta \mathbf{R}_B}{\alpha + \beta} \qquad \leftarrow \text{“center of mass”}$$

- greatly simplifies integral evaluation
- two-center integrals reduced to one-center int.

Contents

1 Introduction

2 SHG scheme

3 Results and Application
- Comparison of algorithms
- Speed-ups
- Application

4 Conclusions

Solid harmonic Gaussians (SHGs)

Complex solid harmonics

$$C_{l,m}(\mathbf{r}) = \sqrt{\frac{4\pi}{2l+1}} r^l Y_{l,m}(\theta, \phi),$$

Solid harmonic Gaussian

$$\chi_{l,m}(\alpha, \mathbf{r}) = C_{l,m}(\mathbf{r}) \exp\left(-\alpha r^2\right)$$

Reformulation of SHG

$$\chi_{l,m}(\alpha, \mathbf{r}_a) = \frac{C_{l,m}(\nabla_a) \exp\left(-\alpha r_a^2\right)}{(2\alpha)^l},$$

$C_{l,m}(\nabla_a)$...Spherical Tensor Gradient Operator (STGO)

Integrals $(a|\mathcal{O}|b)$

Two-center integrals

$$(a|\mathcal{O}|b) = \iint \varphi_{l_a,m_a}(\mathbf{r}_1 - \mathbf{R}_a)\mathcal{O}(\mathbf{r}_1 - \mathbf{r}_2)\varphi_{l_b,m_b}(\mathbf{r}_2 - \mathbf{R}_b)d\mathbf{r}_1 d\mathbf{r}_2$$

Coulomb: $\mathcal{O}(\mathbf{r}) = 1/r$, Overlap: $\mathcal{O}(\mathbf{r}) = \delta(\mathbf{r})$

Reformulation in terms of STGO

$$(a|\mathcal{O}|b) = C_{l_a,m_a}(\nabla_a)C_{l_b,m_b}(\nabla_b)O_{l_a,l_b}(R^2_{ab})$$

Final integral expression[I]

$$(a|\mathcal{O}|b) = \sum_{j=0}^{\min(l_a,l_b)} O^{(l_a+l_b-j)}_{l_a,l_b}(R^2_{ab})\tilde{Q}^{c/s,c/s}_{l_a,\mu_a,l_b,\mu_b,j}(\mathbf{R}_{ab})$$

with $\mu = |m|$

[I] T. Giese, D. York, *J. Chem. Phys.*, **2008**, 128, 064104

Integrals $(a|\mathcal{O}|b)$

Two-center integrals

$$(a|\mathcal{O}|b) = \iint \varphi_{l_a,m_a}(\mathbf{r}_1 - \mathbf{R}_a)\mathcal{O}(\mathbf{r}_1 - \mathbf{r}_2)\varphi_{l_b,m_b}(\mathbf{r}_2 - \mathbf{R}_b)d\mathbf{r}_1 d\mathbf{r}_2$$

Coulomb: $\mathcal{O}(\mathbf{r}) = 1/r$, Overlap: $\mathcal{O}(\mathbf{r}) = \delta(\mathbf{r})$

Reformulation in terms of STGO

$$(a|\mathcal{O}|b) = C_{l_a,m_a}(\nabla_a)C_{l_b,m_b}(\nabla_b)O_{l_a,l_b}(R_{ab}^2)$$

Final integral expression[I]

$$(a|\mathcal{O}|b) = \sum_{j=0}^{\min(l_a,l_b)} O_{l_a,l_b}^{(l_a+l_b-j)}(R_{ab}^2)\tilde{Q}_{l_a,\mu_a,l_b,\mu_b,j}^{c/s,c/s}(\mathbf{R}_{ab})$$

with $\mu = |m|$

[I] T. Giese, D. York, *J. Chem. Phys.*, **2008**, 128, 064104

Integrals $(a|\mathcal{O}|b)$

Two-center integrals

$$(a|\mathcal{O}|b) = \iint \varphi_{l_a,m_a}(\mathbf{r}_1 - \mathbf{R}_a)\mathcal{O}(\mathbf{r}_1 - \mathbf{r}_2)\varphi_{l_b,m_b}(\mathbf{r}_2 - \mathbf{R}_b)d\mathbf{r}_1 d\mathbf{r}_2$$

Coulomb: $\mathcal{O}(\mathbf{r}) = 1/r$, Overlap: $\mathcal{O}(\mathbf{r}) = \delta(\mathbf{r})$

Reformulation in terms of STGO

$$(a|\mathcal{O}|b) = C_{l_a,m_a}(\nabla_a)C_{l_b,m_b}(\nabla_b)O_{l_a,l_b}(R_{ab}^2)$$

Final integral expression[I]

$$(a|\mathcal{O}|b) = \sum_{j=0}^{\min(l_a,l_b)} O_{l_a,l_b}^{(l_a+l_b-j)}(R_{ab}^2)\tilde{Q}_{l_a,\mu_a,l_b,\mu_b,j}^{c/s,c/s}(\mathbf{R}_{ab})$$

with $\mu = |m|$

[I] T. Giese, D. York, *J. Chem. Phys.*, **2008**, 128, 064104

Integrals $(a|\mathcal{O}|b)$

Derivative of contracted s type integral

$$O^{(k)}_{l_a,l_b}(R^2_{ab}) = N_{l_a} N_{l_b} \sum_{\alpha\in A}\sum_{\beta\in B} \frac{c_\alpha c_\beta}{(2\alpha)^{l_a}(2\beta)^{l_b}} \left(\frac{\partial}{\partial R^2_{ab}}\right)^k (0_a|\mathcal{O}|0_b). \tag{1}$$

- dependent on exponents
- dependent on l, but not m quantum number

Angular dependent part

- $\tilde{Q}^{c/s,c/s}_{l_a,\mu_a,l_b,\mu_b,j}(\mathbf{R}_{ab})$ constructed from regular scaled solid harmonics $R_{l,m}$
- $R_{l,m}$ obtained recursively
- no dependence on exponents!

Integrals $(a|\mathcal{O}|b)$

Derivative of contracted s type integral

$$O^{(k)}_{l_a,l_b}(R^2_{ab}) = N_{l_a} N_{l_b} \sum_{\alpha \in A} \sum_{\beta \in B} \frac{c_\alpha c_\beta}{(2\alpha)^{l_a}(2\beta)^{l_b}} \left(\frac{\partial}{\partial R^2_{ab}} \right)^k (0_a|\mathcal{O}|0_b). \tag{1}$$

- dependent on exponents
- dependent on l, but not m quantum number

Angular dependent part

- $\tilde{Q}^{c/s,c/s}_{l_a,\mu_a,l_b,\mu_b,j}(\mathbf{R}_{ab})$ constructed from regular scaled solid harmonics $R_{l,m}$
- $R_{l,m}$ obtained recursively
- no dependence on exponents!

Integrals $(a|r_a^{2n}|b)$ and $(ab\tilde{a})$

Integral $(a|r_a^{2n}|b)$

$$(a|r_a^{2n}|b) = \int \varphi_{l_a,m_a}(\mathbf{r}_a) r_a^{2n} \varphi_{l_b,m_b}(\mathbf{r}_b) d\mathbf{r}$$

Derivation of expression in terms of $C_{l,m}(\nabla_a)$ for[II]

$$\chi_{l,m}(\alpha, \mathbf{r}_a) r_a^{2n} = C_{l,m}(\mathbf{r}_a) \exp\left(-\alpha r_a^2\right) r_a^{2n}$$

Integral $(ab\tilde{a})$

$$(ab\tilde{a}) = \int \varphi_{l_a,m_a}(\mathbf{r}_a) \varphi_{\tilde{l}_a,\tilde{m}_a}(\mathbf{r}_a) \varphi_{l_b,m_b}(\mathbf{r}_b) d\mathbf{r}$$

Derivation of STGO expression for $\chi_{l,m}(\alpha, \mathbf{r}_a)\chi_{\tilde{l},\tilde{m}}(\tilde{\alpha}, \mathbf{r}_a)$ based on $(a|r_a^{2n}|b)$

[II] D. Golze, N. Benedikter, M. Iannuzzi, J. Wilhelm, J. Hutter, *J. Chem. Phys.*, **2017**, 146, 034105

Implementation

Table: `DZVP-MOLOPT-GTH` for oxygen

	Contraction coefficients				
Exponents	*s*	*s*	*p*	*p*	*d*
12.015954705512	-0.060190841200	0.065738617900	0.036543638800	-0.034210557400	0.014807054400
5.108150287385	-0.129597923300	0.110885902200	0.120927648700	-0.120619770900	0.068186159300
2.048398039874	0.118175889400	-0.053732406400	0.251093670300	-0.213719464600	0.290576499200
0.832381575582	0.462964485000	-0.572670666200	0.352639910300	-0.473674858400	1.063344189500
0.352316246455	0.450353782600	0.186760006700	0.294708645200	0.484848376400	0.307656114200
0.142977330880	0.092715833600	0.387201458600	0.173039869300	0.717465919700	0.318346834400
0.046760918300	-0.000255945800	0.003825849600	0.009726110600	0.032498979400	-0.005771736600

Implementation

For each atomic kind:

  Calculate contraction matrix: $C_{l_a,\alpha} = N_{l_a} c_\alpha / (2\alpha)^{l_a}$

$l_{\max} = \mathrm{MAX}(l_{a,\max}, l_{b,\max})$

For all $0 \le l \le l_{\max}$:

  Tabulate $R^c_{l,m}(\mathbf{R}_{ab})$ and $R^s_{l,m}(\mathbf{R}_{ab})$

For all $0 \le l_{a/b} \le l_{a/b,\max}$:

  Calculate $\widetilde{Q}^{c/s,c/s}_{l_a,\mu_a,l_b,\mu_b,j}(\mathbf{R}_{ab})$

  If derivatives required:

   Calculate $\frac{\partial}{\partial R_{a,i}} \widetilde{Q}^{c/s,c/s}_{l_a,\mu_a,l_b,\mu_b,j}(\mathbf{R}_{ab}), \quad i = x, y, z$

For all sets a/b:

  $n_{\max} = l_{a,\mathrm{max\_set}} + l_{b,\mathrm{max\_set}}$

  If derivatives required:

   $n_{\max} = n_{\max} + 1$

  For all exponents in set a/b:

   Calculate $(0_a|\mathcal{O}|0_b)^{(k)}, \qquad 0 \le k \le n_{\max}$

   For all shells in set a/b:

    Contract: $O^{(k)}_{l_a,l_b}(R^2_{ab}) = \sum_\alpha \sum_\beta C_{l_a,\alpha} C_{l_b,\beta} (0_a|\mathcal{O}|0_b)^{(k)}$

  For all shells in set a/b:

   For all $-l_{a/b} \le m_{a/b} \le l_{a/b}$:

    Calculate $(a|\mathcal{O}|b) = \sum_j O^{(l_a+l_b-j)}_{l_a,l_b}(R^2_{ab}) \widetilde{Q}^{c/s,c/s}_{l_a,\mu_a,l_b,\mu_b,j}(\mathbf{R}_{ab})$

    If derivatives required:

     Calculate $\frac{\partial}{\partial R_{a,i}}(a|\mathcal{O}|b), \qquad i = x, y, z$

Contents

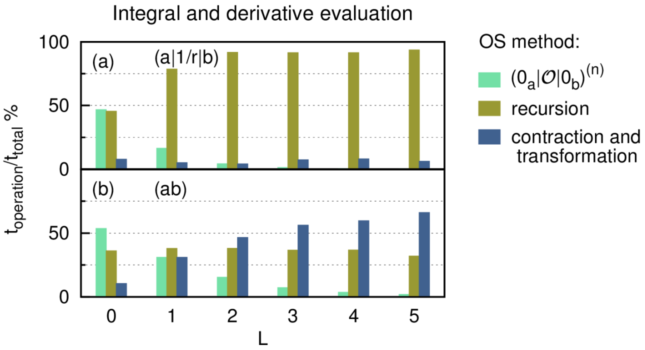
1 Introduction

2 SHG scheme

3 Results and Application
- Comparison of algorithms
- Speed-ups
- Application

4 Conclusions

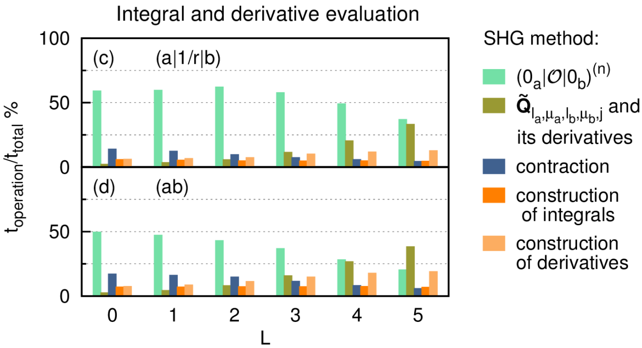
Timings Obara-Saika method



Most expensive step

- (a|1/r|b): recursion of primitive Cartesian integrals
- (ab): contraction+transformation to contracted spherical Gaussian

Timings SHG method



Most expensive step

- evaluation of fundamental (s-type) $(0_a|\mathcal{O}|0_b)^{(n)}$ integrals + their scalar derivatives

Comparison of contraction steps

Table: Number of matrix elements that need to be contracted for $(a|O|b)$

Integral method	H-DZVP		O-DZVP	
	Int.	Int.+Dev.	Int.	Int.+Dev.
OS	784	3136	3969	15876
SHG	147	196	245	294

Integrals

- SHG: contraction of $(0_a|\mathcal{O}|0_b)^{(n)}$ with $n = l_{a,max} + l_{b,max}$
- OS: contraction of each primitive spherical Gaussian integral $(A|\mathcal{O}|B)$

Comparison of contraction steps

Table: Number of matrix elements that need to be contracted for $(a|O|b)$

Integral method	H-DZVP		O-DZVP	
	Int.	Int.+Dev.	Int.	Int.+Dev.
OS	784	3136	3969	15876
SHG	147	196	245	294

Integrals + derivatives

- SHG: contraction of $(0_a|\mathcal{O}|0_b)^{(n)}$ with $n = l_{a,max} + l_{b,max} + 1$
- OS: contraction of $(A|\mathcal{O}|B)$ and $\partial(A|\mathcal{O}|B)/\partial x$, $\partial(A|\mathcal{O}|B)/\partial y$, $\partial(A|\mathcal{O}|B)/\partial z$

Comparison of recursive part

- recursion for each primitive integral $(A|\mathcal{O}|B)$
- recursion only once for $\widetilde{\mathbf{Q}}_{l_a,\mu_a,l_b,\mu_b,j}(\mathbf{R}_{ab})$ for $0 \leq l_a/l_b \leq l_{a/b,\max}$

Comparison of recursive part

Example

- SHG: 243 matrix elements $\widetilde{\mathbf{Q}}_{l_a,\mu_a,l_b,\mu_b,j}(\mathbf{R}_{ab})$
- OS: 4900 primitive Cartesian integrals, where $l_{\max} = 2$

Table: `DZVP-MOLOPT-GTH` for oxygen

	Contraction coefficients				
Exponents	*s*	*s*	*p*	*p*	*d*
12.015954705512	-0.060190841200	0.065738617900	0.036543638800	-0.034210557400	0.014807054400
5.108150287385	-0.129597923300	0.110885902200	0.120927648700	-0.120619770900	0.068186159300
2.048398039874	0.118175889400	-0.053732406400	0.251093670300	-0.213719464600	0.290576499200
0.832381575582	0.462964485000	-0.572670666200	0.352639910300	-0.473674858400	1.063344189500
0.352316246455	0.450353782600	0.186760006700	0.294708645200	0.484848376400	0.307656114200
0.142977330880	0.092715833600	0.387201458600	0.173039869300	0.717465919700	0.318346834400
0.046760918300	-0.000255945800	0.003825849600	0.009726110600	0.032498979400	-0.005771736600

Advantages of the SHG scheme

	OS scheme	SHG scheme
• contraction	for each primitive integral $(A\|\mathcal{O}\|B)$	only for s-overlap and its $l_{a,max} + l_{b,max}$ scalar derivatives
• derivatives	recursion up to $l_{max} + 1$	recursion up to l_{max}
• contraction of derivatives	for $(A\|\mathcal{O}\|B)$ and its Cartesian derivatives	only for one more derivative of the s overlap
• transformation	required	not required

Advantages of the SHG scheme

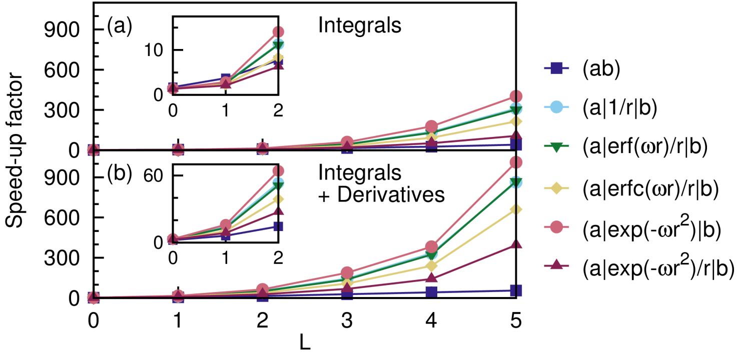
	OS scheme	SHG scheme
• contraction	for each primitive integral $(A\|\mathcal{O}\|B)$	only for s-overlap and its $l_{a,max} + l_{b,max}$ scalar derivatives
• derivatives	recursion up to $l_{max} + 1$	recursion up to l_{max}
• contraction of derivatives	for $(A\|\mathcal{O}\|B)$ and its Cartesian derivatives	only for one more derivative of the s overlap
• transformation	required	not required

SHG scheme efficient for

- ▷ large contraction lengths
- ▷ large angular momentum
- ▷ derivatives

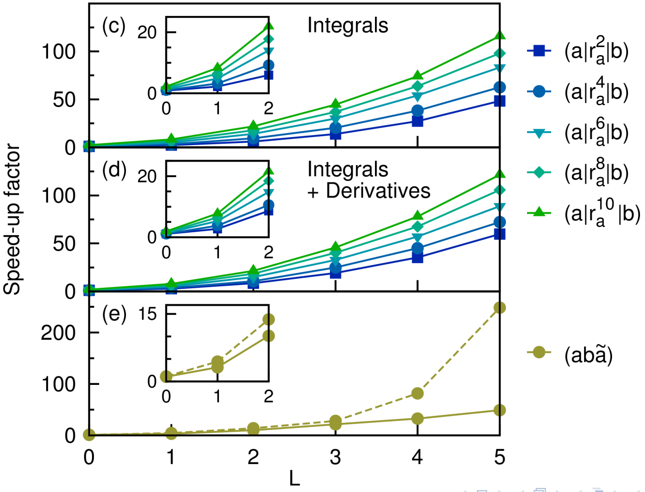
Speed-up dependent on l quantum number

- speed-up with respect to Obara-Saika method
- Contraction length set to $K = 7$



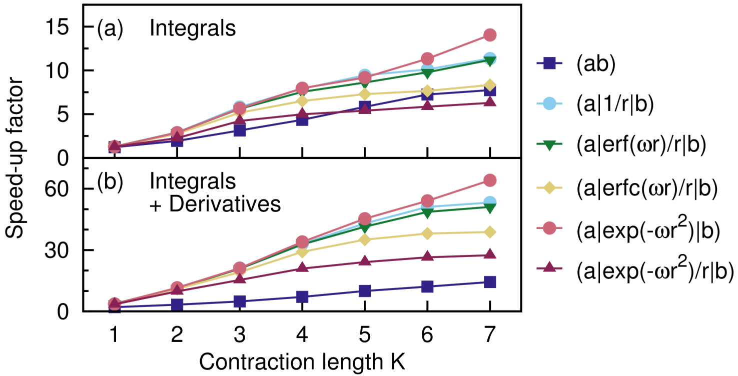
Speed-up dependent on l quantum number

- Contraction length set to $K = 7$



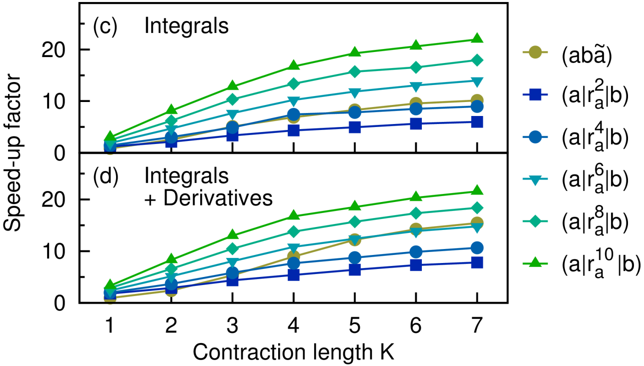
Speed-up dependent on contraction length

- angular momentum set to $l = 2$



Speed-up dependent on contraction length

- angular momentum set to $l = 2$

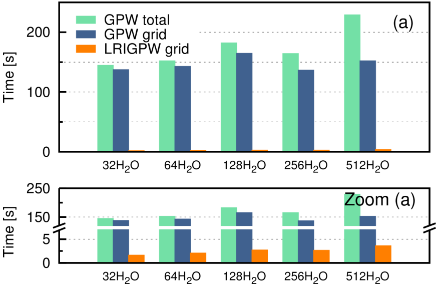


Speed-up for MOLOPT basis sets

Table: Speed-up for DZVP/TZV2PX-MOLOPT-GTH for O and DZVP-MOLOPT-SR-GTH for Cu

Integral type	O-DZVP		O-TZV2PX		Cu-DZVP	
	Int.	Int.+Dev.	Int.	Int.+Dev.	Int.	Int.+Dev.
(ab)	6.2	5.5	11.4	10.3	8.9	8.3
$(a\|1/r\|b)$	5.9	18.4	16.8	31.6	14.6	26.0
$(a\|\mathrm{erf}(\omega r)/r\|b)$	5.8	18.4	16.6	31.7	14.4	26.0
$(a\|\mathrm{erfc}(\omega r)/r\|b)$	5.2	16.3	14.9	29.5	12.9	24.8
$(a\|\exp(-\omega r^2)\|b)$	6.4	19.7	18.0	32.5	16.0	27.4
$(a\|\exp(-\omega r^2)/r\|b)$	4.4	14.1	12.3	25.4	10.8	22.0
$(a\|r_a^2\|b)$	9.7	8.8	22.9	18.6	19.7	15.8
$(a\|r_a^4\|b)$	16.0	14.0	39.4	29.3	34.7	25.2
$(a\|r_a^6\|b)$	25.3	21.6	59.5	44.3	56.1	38.9
$(a\|r_a^8\|b)$	34.7	29.6	79.3	61.4	73.4	54.6
$(a\|r_a^{10}\|b)$	44.7	36.7	105.2	79.9	97.5	72.2
$(ab\tilde{a})$	10.1	8.7	7.5	7.2	7.2	10.5

Local resolution of identity (LRI) in GPW



GPW grid-operations

- collocation of $\rho(\mathbf{r})$
- integration of $\int [V_{\rm H}(\mathbf{r}) + V_{\rm xc}(\mathbf{r})]\, \chi_\mu \chi_\nu \, d\mathbf{r}$
  - ▷ dominant

$\Rightarrow$ LRIGPW[III] : reduction of prefactor for grid-operations

[III] D. Golze, M. Iannuzzi, J. Hutter, *JCTC*, **2017**, 13 (5), 2202

Local density fitting

Pair density approximation

$$\rho(\mathbf{r}) = \sum_{AB} \underbrace{\sum_{\mu\nu} P_{\mu\nu}\chi_\mu^A(\mathbf{r})\chi_\nu^B(\mathbf{r})}_{\rho_{AB}} \approx \sum_{AB} \underbrace{\left[\sum_i a_i^A f_i^A(\mathbf{r}) + \sum_j a_j^B f_j^B(\mathbf{r})\right]}_{\tilde{\rho}_{AB}} \quad (2)$$

Minimization of D_{AB}

$$D_{AB} = \int |\rho_{AB} - \tilde{\rho}_{AB}|^2 d\mathbf{r} \quad (3)$$

with constraint

$$N_{AB} = \int \rho_{AB} d\mathbf{r} = \int \tilde{\rho}_{AB} d\mathbf{r}. \quad (4)$$

Why this type of fitting?

- local: retain linear scaling
- overlap metric: $\tilde{\rho}$ also used for XC potential
- easy to parallelize

Local density fitting

Pair density approximation

$$\rho(\mathbf{r}) = \sum_{AB} \underbrace{\sum_{\mu\nu} P_{\mu\nu} \chi_\mu^A(\mathbf{r}) \chi_\nu^B(\mathbf{r})}_{\rho_{AB}} \approx \sum_{AB} \underbrace{\left[\sum_i a_i^A f_i^A(\mathbf{r}) + \sum_j a_j^B f_j^B(\mathbf{r}) \right]}_{\tilde{\rho}_{AB}} \quad (2)$$

Minimization of D_{AB}

$$D_{AB} = \int |\rho_{AB} - \tilde{\rho}_{AB}|^2 d\mathbf{r} \quad (3)$$

with constraint

$$N_{AB} = \int \rho_{AB} d\mathbf{r} = \int \tilde{\rho}_{AB} d\mathbf{r}. \quad (4)$$

Why this type of fitting?

- local: retain linear scaling
- overlap metric: $\tilde{\rho}$ also used for XC potential
- easy to parallelize

Fit equations

Linear set of equations for pair AB

$$\mathbf{Sa} = \mathbf{t} + \lambda \mathbf{n} \quad (5)$$

→ one set of equations for each pair
→ solved in every SCF step

<u>Calculated prior to SCF</u>

$$S_{ij} = \int f_i^A f_j^B d\mathbf{r}$$

$$n_i = \int f_i^{A/B} d\mathbf{r}$$

$$T_{\mu\nu i} = \int \chi_\mu^A \chi_\nu^B f_i^{A/B} d\mathbf{r}$$

<u>Constructed in every SCF step</u>

$$t_i = \sum_{\mu \in A, \nu \in B} P_{\mu\nu} T_{\mu\nu i}$$

$$\lambda = \frac{N_{AB} - \mathbf{n}^T \mathbf{S}^{-1} \mathbf{t}}{\mathbf{n}^T \mathbf{S}^{-1} \mathbf{n}}$$

$\{f_i\}$... auxiliary functions
$\{\chi_\nu\}$...orbital basis functions

Fit equations

Linear set of equations for pair AB

$$\mathbf{S}\mathbf{a} = \mathbf{t} + \lambda \mathbf{n} \tag{5}$$

→ one set of equations for each pair
→ solved in every SCF step

Calculated prior to SCF

$$S_{ij} = \int f_i^A f_j^B d\mathbf{r} = (ab)$$

$$n_i = \int f_i^{A/B} d\mathbf{r}$$

$$T_{\mu\nu i} = \int \chi_\mu^A \chi_\nu^B f_i^{A/B} d\mathbf{r} = (ab\tilde{a})$$

Constructed in every SCF step

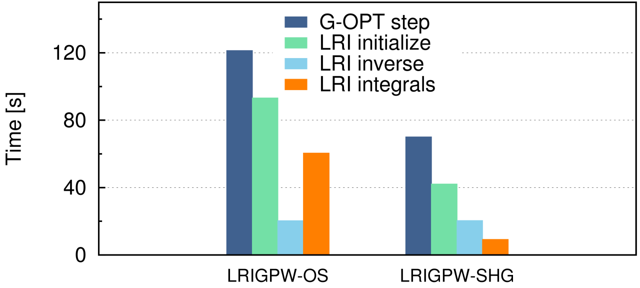
$$t_i = \sum_{\mu \in A, \nu \in B} P_{\mu\nu} T_{\mu\nu i}$$

$$\lambda = \frac{N_{AB} - \mathbf{n}^T \mathbf{S}^{-1} \mathbf{t}}{\mathbf{n}^T \mathbf{S}^{-1} \mathbf{n}}$$

$\{f_i\}$... auxiliary functions
$\{\chi_\nu\}$...orbital basis functions

Timings LRI integrals

- geometry optimization of molecular crystal (urea)



Other applications

RI for hybrid density functionals

- $(a|1/r|b)$ for PBE0, B3LYP
- $(a|erfc(\omega r)/r|b)$ for HSE06
- $(a|erf(\omega r)/r|b)$, $(a|\exp(-\omega r^2)|b)$ for MCY3

Usage

- package shg_int
- called in module library_tests
- routines return integrals of contracted spherical Gaussian functions

Contents

1 Introduction

2 SHG scheme

3 Results and Application
- Comparison of algorithms
- Speed-ups
- Application

4 Conclusions

Conclusions

SHG scheme

- solid harmonic Gaussian functions
- available for two-center integrals
  - $(a|\mathcal{O}|b)$
  - $(a|r_a^{2n}|b)$
  - $(ab\tilde{a})$
- up to three orders of magnitude faster than OS scheme
- especially efficient for highly contracted basis sets with large angular momentum, derivatives