Multiscale Methods in Electronic Structure Calculations

Heinz-Jürgen Flad

Institut für Informatik, Universität zu Kiel

In collaboration with:

- Reinhold Schneider (Universität zu Kiel)
- Hongjun Luo (MPI Leipzig)
- Sambasiva Rao Chinnamsetty (MPI Leipzig)
- Boris N. Khoromskij (MPI Leipzig)
- Wolfgang Hackbusch (MPI Leipzig)

DFG Priority Program:

Modern and Universal First-Principle-Methods for Many-Electron Systems in Chemistry and Physics

Outline of the talk

- Multiresolution analysis in a nutshell.
- Best N-term approximation of pair-correlation functions.

  1. Cusp conditions.
  2. RPA Jastrow factor.
  3. Wavelets versus GTO bases.

- Fast computation of two-electron integrals via tensor products.

  1. Density-fitting scheme using tensor product approximation.
  2. Tensor product quadrature for Coulomb potential.
  3. Wavelet compression of univariate components.

Wavelet multiresolution analysis in $L^2(\mathbb{R})$

Decomposition of $L^2(\mathbb{R})$ into a nested sequence of subspaces

$$L^2(\mathbb{R}) = \text{closure}\left(\bigcup_{l\in\mathbb{Z}} V_l\right) \qquad \cdots \subset V_{j-1} \subset V_j \subset V_{j+1} \subset \cdots$$

Scaling functions $\{\varphi_{j,k}\}_{k\in\mathbb{Z}}$ provide a (bi)orthogonal basis in V_j.

Wavelets $\{\psi_{j,k}\}_{k\in\mathbb{Z}}$ span complement W_j of V_j, i.e., $V_{j+1} = W_j \bigoplus V_j$

Multiscale decomposition: $L^2(\mathbb{R}) = V_{l_0} \bigoplus_{l\geq l_0} W_l$

Scaling functions and wavelets are constructed via dilation and translation

$$\varphi_{j,k}(x) := 2^{j/2}\varphi(2^j x - k), \quad \psi_{j,k}(x) := 2^{j/2}\psi(2^j x - k), \quad j,k \in \mathbb{Z}$$

Refinement relations: $\varphi(x) = 2\sum_a h_a \varphi(2x-a), \quad \psi(x) = 2\sum g_k \varphi(2x-k)$

Any function f in $L^2(\mathbb{R})$ can be expanded in an orthogonal wavelet basis

$$f(x) = \underbrace{\sum_a \langle \varphi_{l_0,a} | f \rangle \, \varphi_{l_0,a}(x)}_{V_{l_0}} + \underbrace{\sum_{j=l_0}^{\infty} \sum_a \langle \psi_{j,a} | f \rangle \, \psi_{j,a}(x)}_{\bigoplus_{l_0 \le j} W_j},$$

Norm equivalences with Sobolev and more general Besov function spaces

$$\| f \|_{H^s}^2 \sim \sum_a \left| \langle \varphi_{l_0,a} | f \rangle \right|^2 + \sum_{j=l_0}^{\infty} 2^{2sj} \sum_a \left| \langle \psi_{j,a} | f \rangle \rangle \right|^2$$

Vanishing moments: $\int dx \, x^k \, \psi(x) = 0$, for $k = 0, \ldots, n-1$.

Estimates for wavelet coefficients from Taylor series

$$f(x) = c_0 + \cdots + c_{n-1}(x - 2^{-j}a)^{n-1} + R_{n-1}(x)(x - 2^{-j}a)^n$$

$$\left| \langle \psi_{j,a} | f \rangle \right| \le \| f^{(n)} \|_{L^\infty(\mathrm{supp}\psi_{j,a})} 2^{-j(n+1/2)} \int dx \, |x^n \psi(x)|$$

Bounds on derivatives $f^{(n)}$ are important for approximation theory.

Tensor product wavelet bases in higher dimensions

Isotropic 3d-wavelets:

$$
\begin{aligned}
\gamma^{(0)}_{j,\mathbf{a}}(\mathbf{r}) &= \varphi_{j,a_x}(x)\,\varphi_{j,a_y}(y)\,\varphi_{j,a_z}(z), && \text{(scaling functions)} \\
\gamma^{(1)}_{j,\mathbf{a}}(\mathbf{r}) &= \psi_{j,a_x}(x)\,\varphi_{j,a_y}(y)\,\varphi_{j,a_z}(z), && \text{with } n \text{ vanish. moments} \\
&\vdots \\
\gamma^{(4)}_{j,\mathbf{a}}(\mathbf{r}) &= \psi_{j,a_x}(x)\,\psi_{j,a_y}(y)\,\varphi_{j,a_z}(z), && \text{with } 2n \text{ vanish. moments} \\
&\vdots \\
\gamma^{(7)}_{j,\mathbf{a}}(\mathbf{r}) &= \psi_{j,a_x}(x)\,\psi_{j,a_y}(y)\,\psi_{j,a_z}(z), && \text{with } 3n \text{ vanish. moments}
\end{aligned}
$$

Anisotropic 3d-wavelets: $\zeta_{\mathbf{j},\mathbf{a}}(\mathbf{r}) = \psi_{j_x,a_x}(x)\,\psi_{j_y,a_y}(y)\,\psi_{j_z,a_z}(z)$

Anisotropic tensor product wavelets for many-particle wavefunctions

$$
\zeta_{\mathbf{j},\mathbf{a}}(\mathbf{r}) = \gamma^{(s_1)}_{j_1,\mathbf{a}_1}(\mathbf{r}_1)\,\gamma^{(s_2)}_{j_2,\mathbf{a}_2}(\mathbf{r}_2)\ldots\gamma^{(s_p)}_{j_p,\mathbf{a}_p}(\mathbf{r}_p)
$$

Multiresolution analysis of pair-correlation functions

Jastrow factor ansatz: $\mathcal{F}\,(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\,\Phi$

$$\mathcal{F}(\mathbf{x}_1, ..., \mathbf{x}_N) = \exp\left(\sum_i \mathcal{F}^{(1)}(\mathbf{x}_i) + \sum_{i<j} \mathcal{F}^{(2)}(\mathbf{x}_i, \mathbf{x}_j) \cdots \right)$$

Pair functions from local ansatz or Jastrow-perturbation theory

HJF, W. Hackbusch, H. Luo and D. Kolb, Phys. Rev. B **71**, 125115 (2005)

H. Luo, D. Kolb, HJF and W. Hackbusch, Phys. Rev. B **75**, 125111 (2007)

Integro-differential MP2 equations for pair functions

K. Szalewicz, B. Jeziorski, H. J. Monkhorst and J. G. Zabolitzky, J. Chem. Phys. **78**, 1420 (1983)

$$(\mathfrak{h}_1 + \mathfrak{h}_2 - \epsilon_a - \epsilon_b)\,\tau^{\pm}_{a,b}(\mathbf{x}_1, \mathbf{x}_2) = -Q\frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|}\,(\phi_a(\mathbf{x}_1)\phi_b(\mathbf{x}_2) \pm \phi_b(\mathbf{x}_1)\phi_a(\mathbf{x}_2))\,,$$

$$Q\tau^{\pm}_{a,b}(\mathbf{x}_1, \mathbf{x}_2) = \tau^{\pm}_{a,b}(\mathbf{x}_1, \mathbf{x}_2),$$

$$Q := (1 - p_1)(1 - p_2), \quad \text{with } p := \sum_{i=1}^{N/2} |\phi_i\rangle\langle\phi_i|$$

Similar equations have been derived for CCD

B. Jeziorski, H. J. Monkhorst, K. Szalewicz, J. G. Zabolitzky, J. Chem. Phys. **81**, 368 (1984)

Cusp conditions for best N-term approximation theory

- Asymptotic smoothness properties near cusps, i.e.

  1. $|\partial_{\mathbf{x}}^{\beta} \phi_i(\mathbf{x})| \le C_\beta |\mathbf{x} - \mathbf{A}|^{1-|\beta|}$ for $\mathbf{x} \neq \mathbf{A}$ and $|\beta| \ge 1$

     (a) HJF, W. Hackbusch and R. Schneider, ESAIM: M2AN **40**, 49 (2006)

     (b) HJF, R. Schneider and B.-W. Schulze, preprint 2007.

  2. $|\partial_{\mathbf{x}}^{\alpha} \partial_{\mathbf{y}}^{\beta} \mathcal{F}^{(2)}(\mathbf{x}, \mathbf{y})| \le c_{\alpha,\beta} |\mathbf{x} - \mathbf{y}|^{1-|\alpha|-|\beta|}$, for $\mathbf{x} \neq \mathbf{y}$ and $|\alpha| + |\beta| \ge 1$

- Kato's cusp condition

  1. T. Kato, Commun. Pure Appl. Math. **10**, 151-177 (1957).
  2. M. Hoffmann-Ostenhof and R. Seiler, Phys. Rev. A **23**, 21-23 (1981).
  3. M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, and H. Stremnitzer, Commun. Math. Phys. **163**, 185-215 (1994).
  4. S. Fournais, M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, and T. Østergaard Sørensen, Commun. Math. Phys. **255**, 183-227 (2005).

- Sobolev spaces with mixed partial derivatives

  1. H. Yserentant, Numer. Math. **98**, 731-759 (2004); ibid. **101**, 381-389 (2005).
  2. M. Griebel and J. Hamaekers ESAIM: M2AN **41**, 215-248 (2007).

RPA Jastrow factor for a homogeneous electron gas

Fourier representation: $\widehat{\mathcal{F}}(k) = \frac{1}{2\rho S_F}\left[1 - \left(1 + \frac{4\rho\widehat{v}S_F^2}{k^2}\right)^{\frac{1}{2}}\right]$

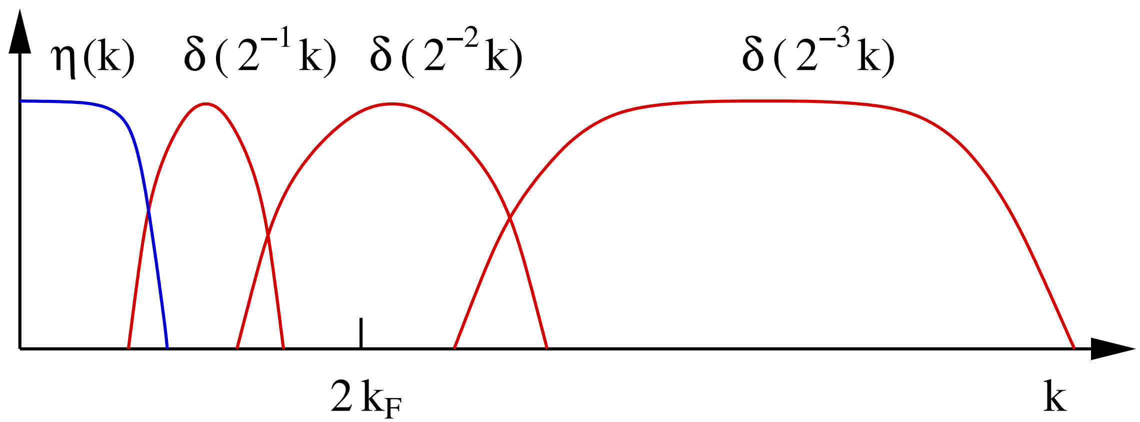
Static structure factor: $S_F(k) = \begin{cases} \frac{3}{4}\frac{k}{k_F} - \frac{1}{16}\left(\frac{k}{k_F}\right)^3, & k < 2k_F \\ 1, & k \geq 2k_F \end{cases}$

- Exact description of long-range correlations in metals.
- Accurate correlation energies in variational Monte Carlo calculations.
- Discontinuity of $\widehat{\mathcal{F}}''(k)$ at $k = 2k_F$.

Payley-Littlewood decompostion

Partition of unity: $1 = \eta(k) + \sum_{j=1}^{\infty} \delta(2^{-j}k)$

$$\eta(k) = \begin{cases} 1, & k < \epsilon < 2k_F \\ 0, & k \geq \epsilon \end{cases}, \delta(k) := \eta(k) - \eta(2k)$$



$$S_0\mathcal{F}(r) := \frac{1}{(2\pi)^3}\int d^3k\, e^{i\mathbf{kr}}\eta(k)\hat{\mathcal{F}}(k), \quad \Delta_j\mathcal{F}(r) := \frac{1}{(2\pi)^3}\int d^3k\, e^{i\mathbf{kr}}\delta(2^{-j}k)\hat{\mathcal{F}}(k)$$

$$\mathcal{F}(r) = S_0\mathcal{F}(r) + \sum_{j=0}^{\infty} \Delta_j\mathcal{F}(r)$$

Long-range correlations

Asymptotic expansion: $S_0\mathcal{F}(r) \sim \frac{\tilde{a}_0}{r} + \sum_{j=0}^{\infty} \tilde{a}_{2j+1} r^{-2j-2}$

"Asymptotic smoothness property" at large inter-electron distances

$$\left|\partial_{\mathbf{r}_1}^{\alpha}\partial_{\mathbf{r}_2}^{\beta} S_0\mathcal{F}(|\mathbf{r}_1-\mathbf{r}_2|)\right| \leq C_{\alpha,\beta}\,(1+|\mathbf{r}_1-\mathbf{r}_2|)^{-(1+|\alpha|+|\beta|)}$$

Short-range correlations

Short-range Jastrow factor: $\mathcal{F}_s(r) = \sum_{j=n}^{\infty} \Delta_j \mathcal{F}(r)$

Symbol of ΨDO: $\partial_{\mathbf{k}}^{\alpha}\hat{\mathcal{F}}_s(k) \leq C_{\alpha}\,(1+k)^{-4-|\alpha|} \Longrightarrow \hat{\mathcal{F}}_s \in S^{-4}$

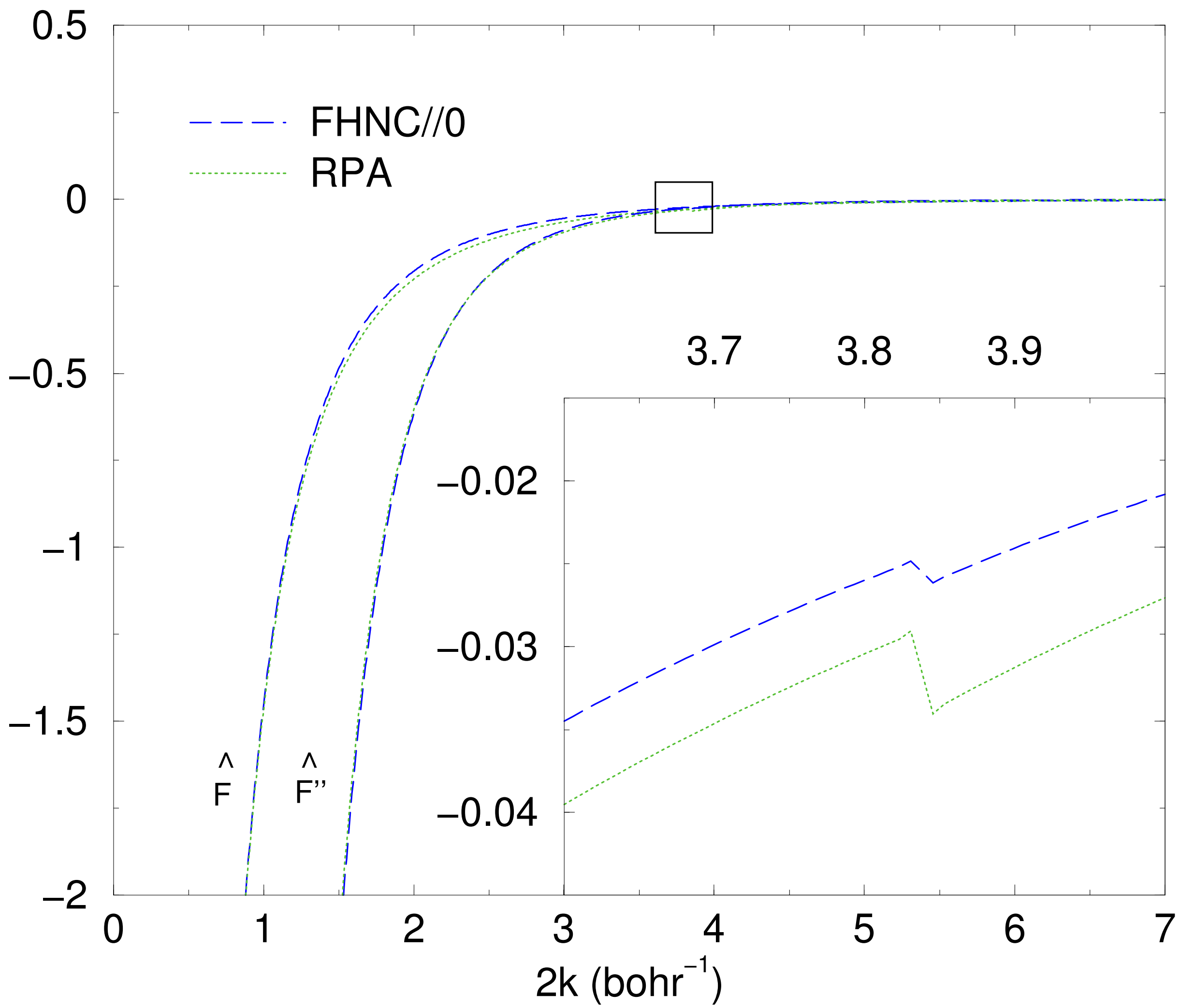
Asymptotic smoothness property:

$$\partial_{\mathbf{r}_1}^{\alpha}\partial_{\mathbf{r}_2}^{\beta}\mathcal{F}_s(|\mathbf{r}_1-\mathbf{r}_2|) \leq C_{\alpha,\beta}|\mathbf{r}_1-\mathbf{r}_2|^{1-|\alpha|-|\beta|-N}$$

for any $N \in \mathbb{N}$ mit $|\alpha|+|\beta|+N > 1$

Discontinuity of second derivatives

$$\Delta_j \mathcal{F}(r) \sim o\left(\frac{1}{r^2}\right) \text{ for } 2k_F \in \operatorname{supp} \delta(2^{-j}k)$$



Best N-Term Approximation for Anisotropic Wavelet Bases

Nonlinear submanifold Σ_N of linear vector space spanned by $\{\zeta_i : i \in \Lambda\}$

$$\Sigma_N := \left\{ \sum_{i \in \Delta} c_i \zeta_i : \Delta \subset \Lambda, \#\Delta \leq N \right\}$$

Approximation error for $f \in H^1(\Omega)$: $\sigma_N(f) := \inf_{f_N \in \Sigma_N} \|f - f_N\|_{H^1}$

Convergence rate: $\sigma_N(f) \sim N^{-\alpha}$ for $f \in \mathcal{B}_q^\alpha(\Omega)$ (approximation space)

Norm equivalences for tensor product Besov spaces

$$\| f \|_{\mathcal{B}_q^\alpha(\Omega)}^q = \sum_{\mathbf{j}} 2^{\max\{j_i\} q} \left(\sum_{\mathbf{a}} \left| \langle \zeta_{\mathbf{j},\mathbf{a}} | f \rangle \right|^q \right) \quad \text{with } \frac{1}{q} = \alpha + \frac{1}{2}$$

(i) $\psi_{j,a} \in B_q^\beta(L_q)$ for some $\beta > 3\alpha$

(ii) $\psi_{j,a}$ has p vanishing moments with $p > 3\alpha + 1$.

Application to pair-correlation functions

HJF, W. Hackbusch and R. Schneider, ESAIM: M2AN **41**, 261 (2007)

Pair functions with inter-electron and electron-nuclear cusps.

Assumption 1. *The two-particle correlation function* $\mathcal{F}^{(2)}$ *belongs to* $C^\infty(\mathbb{R}^3 \times \mathbb{R}^3 \setminus D)$, *with* $D := \{(\mathbf{x},\mathbf{y}) \in \mathbb{R}^3 \times \mathbb{R}^3 : \mathbf{x} = \mathbf{y}\}$.

Furthermore it satisfies the asymptotic smoothness property

$$|\partial_{\mathbf{x}}^{\alpha}\partial_{\mathbf{y}}^{\beta}\mathcal{F}^{(2)}(\mathbf{x},\mathbf{y})| \leq c_{\alpha,\beta}\,|\mathbf{x}-\mathbf{y}|^{1-|\alpha|-|\beta|} \quad , \ \text{for } \mathbf{x} \neq \mathbf{y} \text{ and } |\alpha|+|\beta| \geq 1,$$

in any bounded neighbourhood $\Omega \times \Omega \subset \mathbb{R}^3 \times \mathbb{R}^3$.

Lemma 1. *Suppose* $\mathcal{F}^{(2)}$ *satisfies Assumption 1. Then* $\mathcal{F}$ *belongs to* $\mathcal{B}_q^{\alpha}(H^1(\Omega \times \Omega))$ *for* $\alpha < \frac{1}{2}$ *and* $\frac{1}{q} = \alpha + \frac{1}{2}$.

Assumption 2. *The two-particle correlation function* $\mathcal{F}^{(2)}$ *belongs to* $C^\infty(\mathbb{R}^3 \times \mathbb{R}^3 \setminus (D \cup N))$, *with* $D := \{(\mathbf{x},\mathbf{y}) \in \mathbb{R}^3 \times \mathbb{R}^3 : \mathbf{x} = \mathbf{y}\}$ *and* $N := \{(\mathbf{x},\mathbf{y}) \in \mathbb{R}^3 \times \mathbb{R}^3 : \mathbf{x} = \mathbf{A} \vee \mathbf{y} = \mathbf{A}\}$.

Furthermore it satisfies the generalized asymptotic smoothness property

$$
\begin{aligned}
|\partial^\alpha_{\mathbf{x}} \partial^\beta_{\mathbf{y}} \mathcal{F}^{(2)}(\mathbf{x},\mathbf{y})| \;\leq\; & c_{\alpha,\beta} \sup_{\alpha_1,\beta_1} \left(\delta_{|\alpha_1|} + |\mathbf{x}-\mathbf{A}|^{1-|\alpha_1|}\right) \left(\delta_{|\beta_1|} + |\mathbf{y}-\mathbf{A}|^{1-|\beta_1|}\right) \\
& \times \left(\delta_{(|\alpha_2|+|\beta_2|)} + |\mathbf{x}-\mathbf{y}|^{1-|\alpha|_2-|\beta|_2}\right),
\end{aligned}
$$

for $(\mathbf{x},\mathbf{y}) \notin D \cup N$, $|\alpha| + |\beta| > 1$ *and* $\alpha_1 + \alpha_2 = \alpha$, $\beta_1 + \beta_2 = \beta$, *in a bounded neighbourhood* $\Omega \times \Omega \subset \mathbb{R}^3 \times \mathbb{R}^3$ *of the nucleus* $\mathbf{A}$.

- QMC Jastrow factors: $\mathcal{F}^{(2)}(\mathbf{x},\mathbf{y}) = \sum_{l,m,n} c_{lmn} |\mathbf{x}-\mathbf{y}|^l |\mathbf{x}-\mathbf{A}|^m |\mathbf{y}-\mathbf{A}|^n$

Lemma 2. *Suppose* $\mathcal{F}^{(2)}$ *satisfies Assumption 2. Then* $\mathcal{F}$ *belongs to* $\mathcal{B}^\alpha_q(H^1(\Omega \times \Omega))$ *for* $\alpha < \frac{1}{2}$ *and* $\frac{1}{q} = \alpha + \frac{1}{2}$.

Best N-term approximation versus GTO bases

Best N-term approximation

- Wavelet approximation of pair-correlation functions:
  - $\| \mathcal{F}^{(2)} - \mathcal{F}_N^{(2)} \|_{H^1} \leq CN^{-\frac{1}{2}+\epsilon}$ for any $\epsilon > 0$
  - $O(N^{-1+\epsilon})$ convergence of the energy.

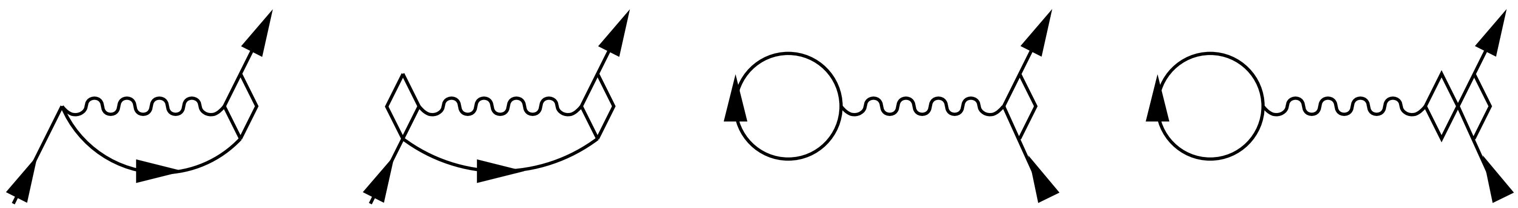
GTO VXZ $(X = 2, 3, 4, \ldots)$ **bases**:

A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A.K. Wilson, Chem. Phys. Lett. **286**, 243 (1998)

- Post HF methods (CISD, CCSD, etc.)
  - $O(X^{-3})$ convergence of the energy with $O(X^6)$ degrees of freedom.
  - $O(N^{-\frac{1}{2}})$ convergence of the energy.

Computation of two-electron integrals in JPT

Basic two-electron integrals for first-order pair-correlation function



$\mathbf{r}_2 \longrightarrow \mathbf{r}_1$	$\frac{1}{2}\rho(\mathbf{r}_1,\mathbf{r}_2)$			r_{12}^{-1}	
α ◊	$\gamma_\alpha(\mathbf{r})$	M	α ◊◊ β	$\gamma_\alpha(\mathbf{r})\,\gamma_\beta(\mathbf{r})$	$O(M \log M)$

- Diagram 2 provides additional sparsity due to vanishing moments.
- Best N-term approximation yields $N \sim O(M \log M)$ (sparse grids).
- Adaptive methods scale “almost” linear with respect to N.

A. Cohen, W. Dahmen and R.A. DeVore, Math. Comp. **70**, 27 (2001)

Density-fitting scheme using tensor product approximation

S.R. Chinnamsetty, M. Espig, B.N. Khoromskij, W. Hackbusch, HJF, J. Chem. Phys. **127**, 084110 (2007)

$$\int d^3x d^3y\, \eta_\alpha(\mathbf{x}) \frac{1}{|\,\mathbf{x}-\mathbf{y}\,|} \eta_\beta(\mathbf{y}) \quad \text{with } \eta(\mathbf{x}) = \begin{cases} \phi_i(\mathbf{x})\phi_j(\mathbf{x}) \\ \phi_i(\mathbf{x})\phi_j(\mathbf{x})\gamma_\alpha(\mathbf{x}) \\ \phi_i(\mathbf{x})\phi_j(\mathbf{x})\gamma_\alpha(\mathbf{x})\gamma_\beta(\mathbf{x}). \end{cases}$$

Best separable rank κ approximation

$$\eta(\mathbf{x}) \approx \sum_{k=1}^{\kappa} \eta_k^{(1)}(x_1)\, \eta_k^{(2)}(x_2)\, \eta_k^{(3)}(x_3)$$

Newton algorithm (M. Espig) for least-squares problem in $L^2(\mathbb{R}^3)$

$$\sigma_\kappa(f) := \inf_{\eta_k^{(i)} \in L^2(\mathbb{R})} \left\| \eta(\mathbf{x}) - \sum_{k=1}^{\kappa} \eta_k^{(1)}(x_1)\, \eta_k^{(2)}(x_2)\, \eta_k^{(3)}(x_3) \right\|_{L^2(\mathbb{R}^3)}$$

Computational complexity: Assumption $\kappa \ll K$

(1) Initial orthogonalization step: $O(n_l K^2)$ (QR decomposition).

(2) Newton algorithm: $O(\kappa K r_{max} + \kappa^3)$ with memory $O(\kappa r_{max})$.

Tensor product quadrature for Coulomb potential

$$\int \gamma_{j,\mathbf{a}}^{(\mathbf{p})}(\mathbf{x}) \frac{1}{|\mathbf{x}-\mathbf{y}|} \gamma_{j,\mathbf{b}}^{(\mathbf{q})}(\mathbf{y})\, d\mathbf{x} d\mathbf{y} = \frac{2^{-2j+1}}{\sqrt{\pi}} \int_0^\infty \mathcal{I}^{(\mathbf{p},\mathbf{q})}(t, \mathbf{a}-\mathbf{b}) dt$$

$$\mathcal{I}^{(\mathbf{p},\mathbf{q})}(t,\mathbf{a}) = G^{(p_1,q_1)}(a_1,t)\, G^{(p_2,q_2)}(a_2,t)\, G^{(p_3,q_3)}(a_3,t)$$

$$G^{(p,q)}(a,t) = \int\int \psi^{(p)}(x-a)\, e^{-(x-y)^2 t^2}\, \psi^{(q)}(y)\, dx dy$$

$$\psi_{j,a}^{(0)}(x) := \varphi_{j,a}(x),\ \psi_{j,a}^{(1)}(x) := \psi_{j,a}(x)$$

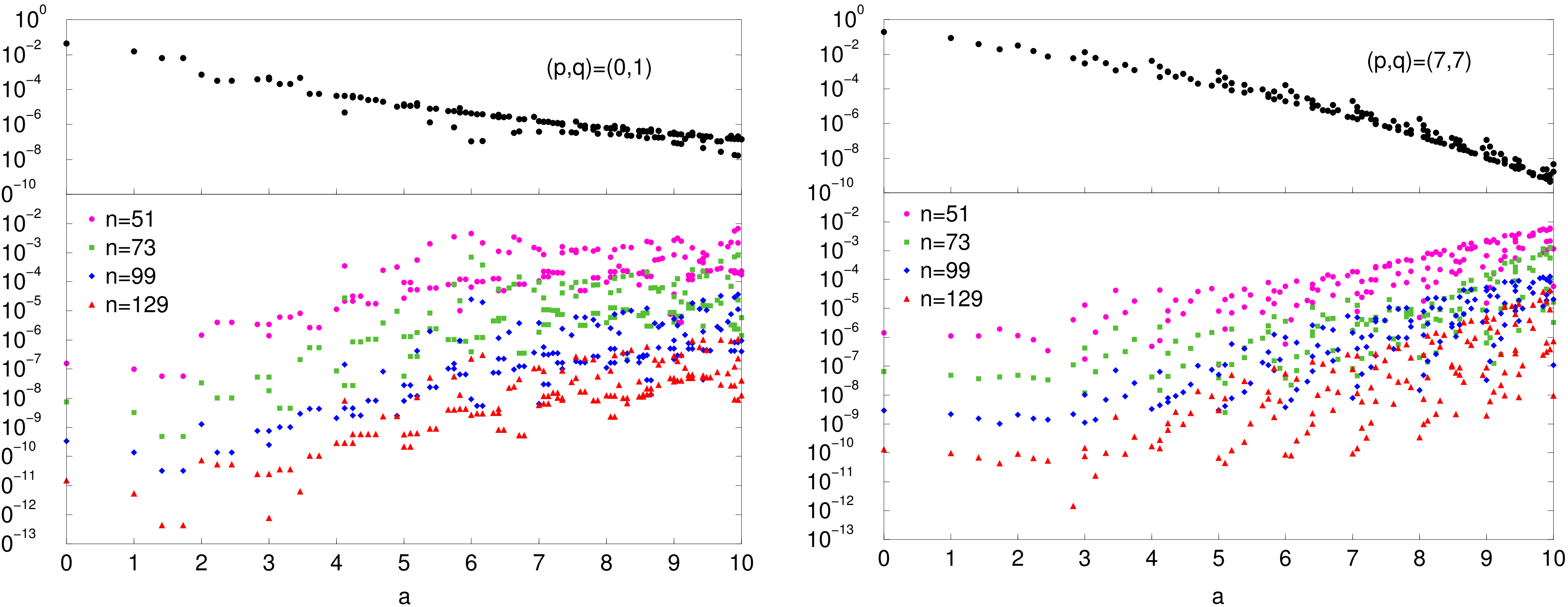
Exponential quadrature rule with uniformly bounded integration error

$$\left| \int_0^\infty \mathcal{I}^{(\mathbf{p},\mathbf{q})}(t,\mathbf{a}) dt - h \sum_{m=-M}^{M} e^{mh} \mathcal{I}^{(\mathbf{p},\mathbf{q})}(e^{mh}, \mathbf{a}) \right| \lesssim e^{-\alpha\sqrt{M}}$$

with $\alpha = 2\sqrt{\pi\delta}$ ($\alpha = \sqrt{2\pi\delta}$) for any $\delta < \frac{\pi}{4}$ and $h = \sqrt{\frac{\pi\delta}{M}}$ ($h = \sqrt{\frac{2\pi\delta}{M}}$)

S. Schwinger, Diploma thesis MPI Leipzig 05

Biorthogonal wavelet basis (6 vanishing moments)



Fast computation of Coulomb integrals via tensor products

$$\int\int \eta_\alpha(\mathbf{x}) \frac{1}{|\,\mathbf{x}-\mathbf{y}\,|} \eta_\beta(\mathbf{y})\, d\mathbf{x}d\mathbf{y} \approx \sum_j 2^{-2j} {\sum_{\mathbf{p},\mathbf{q}}}' \sum_{m=-M}^{M} \omega_m \prod_{i=1}^{3} L^{(i)}_{j,p_i,q_i}(t_m)$$

$$L^{(i)}_{j,p_i,q_i}(t_m) = \sum_{a_i,b_i} \langle \eta^{(i)}_\alpha | \tilde{\psi}^{(p_i)}_{j,a_i+b_i} \rangle \langle \tilde{\psi}^{(q_i)}_{j,b_i} | \eta^{(i)}_\beta \rangle \, G^{(p_i,q_i)}(a_i, t_m)$$

Alternative approach: Intermediate compression step

$$\begin{aligned}
\int \frac{1}{|\,\mathbf{x}-\mathbf{y}\,|} \eta_\beta(\mathbf{y}) d\mathbf{y} \;&\approx\; \sum_{j=j_0}^{j_{max}} \sum_{k=1}^{\kappa_{j,\beta}} v^{(1)}_{k,j,\beta}(x_1)\, v^{(2)}_{k,j,\beta}(x_2)\, v^{(3)}_{k,j,\beta}(x_3) \\
&\approx\; \sum_{k=1}^{\kappa_\beta} w^{(1)}_{k,\beta}(x_1)\, w^{(2)}_{k,\beta}(x_2)\, w^{(3)}_{k,\beta}(x_3)
\end{aligned}$$

Assembling of two-electron integrals

$$\int\int \eta_\alpha(\mathbf{x}) \frac{1}{|\,\mathbf{x}-\mathbf{y}\,|} \eta_\beta(\mathbf{y}) d\mathbf{x}d\mathbf{y} = \sum_{k=1}^{\kappa_\alpha} \sum_{l=1}^{\kappa_\beta} \langle \eta^{(1)}_{k,\alpha} | w^{(1)}_{l,\beta} \rangle \langle \eta^{(2)}_{k,\alpha} | w^{(2)}_{l,\beta} \rangle \langle \eta^{(3)}_{k,\alpha} | w^{(3)}_{l,\beta} \rangle$$

Error in HF energy (mhartree) for best separable approximations of the electron density (κ) and Hartree potential (κ').

	κ	$E^a_\kappa - E_{GTO}$	L^2_ρ	κ'	$E^c_{\kappa'} - E_{GTO}$	$L^2_{V_H}$
CH_4	20	-0.57	$8.1 \cdot 10^{-5}$	10	-39.50	$6.2 \cdot 10^{-4}$
				15	-1.40	$1.3 \cdot 10^{-4}$
				20	-0.63	$5.3 \cdot 10^{-5}$
	35	-0.09	$1.9 \cdot 10^{-5}$	10	-39.07	$6.2 \cdot 10^{-4}$
				15	-0.93	$1.3 \cdot 10^{-4}$
				20	-0.16	$3.9 \cdot 10^{-5}$
C_2H_2	35	-2.41	$2.1 \cdot 10^{-4}$	30	-10.00	$1.8 \cdot 10^{-4}$
				40	-0.84	$6.4 \cdot 10^{-5}$
	40	-0.95	$1.8 \cdot 10^{-4}$	30	-4.35	$1.7 \cdot 10^{-4}$
				40	0.97	$5.3 \cdot 10^{-5}$
	50	-0.50	$1.3 \cdot 10^{-4}$			
C_2H_6	30	-11.14	$3.0 \cdot 10^{-4}$	30	-9.57	$4.5 \cdot 10^{-5}$
	40	-0.68	$1.2 \cdot 10^{-4}$	40	-0.98	$1.6 \cdot 10^{-5}$
				50	-0.95	$7.5 \cdot 10^{-6}$
				60	-0.58	$3.3 \cdot 10^{-6}$

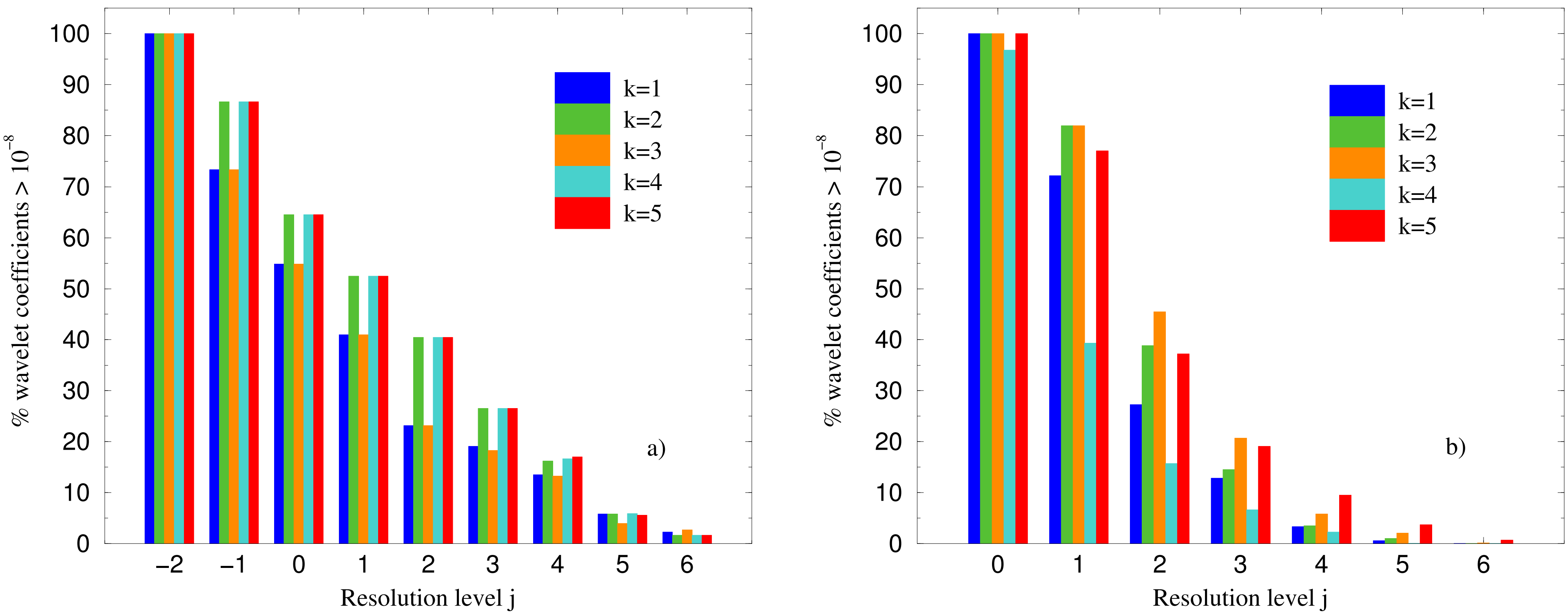
[a] HF energy with best separable rank κ approximation of electron density.

[c] HF energy with subsequent compression of the Hartree potential to rank κ'.

Wavelet compression of univariate components

J. M. Ford and E. Tyrtyshnikov, SIAM J. Sci. Comput. **25**, 961 (2003)

$$\eta_k^{(i)}(x_i) \approx \sum_a \eta_{k,0,l_0,a}^{(i)} \psi_{l_0,a}^{(0)}(x_i) + \sum_{j=l_0}^{l-1} \sum_a \eta_{k,1,j,a}^{(i)} \psi_{j,a}^{(1)}(x_i)$$



Wavelet compression using Daubechies wavelets $(p = 5)$

a) Electron density of C_2H_6 at rank $\kappa = 5$.

b) Hartree potential of C_2H_6 at rank $\kappa' = 5$.

Conclusions and outlook

- Wavelet based multiresolution analysis of electron correlations

  1. Approximation of pair-correlation **functions**.

  2. Adaptive treatment of electron correlations.

  3. Convergence in energy $O(N^{-1+\epsilon})$ versus $O(N^{-1/2})$ (GTO basis).

  4. Computation of two-electron integrals with $O(N)$ complexity.

- Future work

  1. Wavelet implementation of JPT2 method. (Honjun Luo's talk)

  2. Tensor product approximation of electron correlations.