

# Density Functional Calculations with PARAGAUSS

## Perspectives for modeling catalyst materials

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## Overview

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- Quantum Chemistry
  - Density Functional Theory
  - Numerical aspects
- Program PARAGAUSS
  - Features
  - Parallelization
- Modeling Catalyst Materials
  - Scaling of metal particles
  - Self-interaction in Kohn-Sham calculations
  - Mixed metal oxides

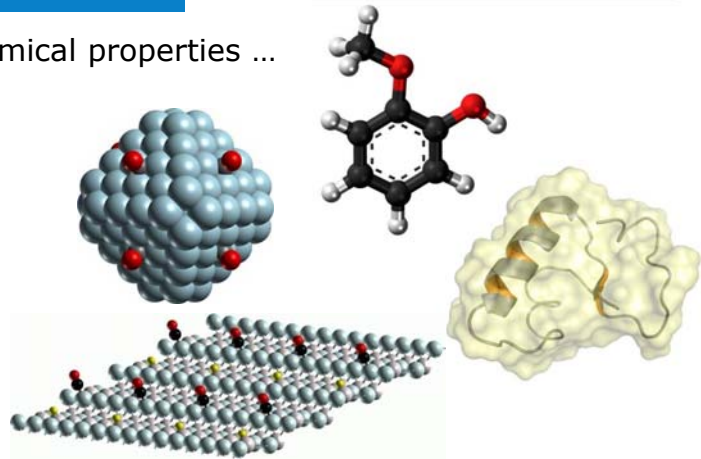
Computation of physical and chemical properties ...

- Chemical behavior, reactivity
- Spectroscopic quantities
- Materials properties

... on a microscopic scale ...

- Atoms, molecules
- Clusters, solids (crystals)
- Biomolecules, polymers

... by solving the  
Schrödinger equation  $\hat{H}\Psi = E\Psi$



Impressive progress over last decades: Nobel Prize in Chemistry 1998



Walter Kohn  
"for his development of  
density-functional theory"



John A. Pople  
"for his development of  
computational methods in  
quantum chemistry"

## Methods of Quantum Chemistry

Basis of quantum chemistry:

Many-electron Schrödinger equation  $\hat{H} \Psi(\{\mathbf{x}_i\}, \{\mathbf{R}_\alpha\}) = E \Psi(\{\mathbf{x}_i\}, \{\mathbf{R}_\alpha\})$

- Wave function  $\Psi$ , nuclear pos.  $\{\mathbf{R}_\alpha\}$   
electron space and spin coords.,  $\mathbf{x}$ ;
- Total energy as expectation value  $E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle = \int \dots \int \Psi^\dagger \hat{H} \Psi dx_1 \dots dx_N$
- High-level wave function theory approximations often far too expensive

Density Functional Theory (DFT) achieves better accuracy/cost value

Ground state energy  $E_0$  as functional of g.s. electron density  $\rho_0$ :  $E_0 = E[\rho_0]$

- Kohn-Sham formalism (KS) turns DFT into a practical tool

$$\rho(\mathbf{r}) = \sum_{\sigma i} \int |\varphi_i(\mathbf{x})|^2 d\mathbf{r} \quad \leftarrow \hat{h}\varphi_i = \varepsilon_i \varphi_i \quad \text{KS orbitals}$$

- Partitioning of total electronic energy

$$E[\rho] = T[\rho] + E_{\text{ext}}[\rho] + E_{\text{coul}}[\rho] + E_{\text{x}}[\rho] + E_{\text{corr}}[\rho]$$

- Various approx. for exchange+correlation (XC)  $E_{\text{XC}}[\rho] = E_{\text{x}}[\rho] + E_{\text{corr}}[\rho]$

- Expand KS orbitals in “basis set”  $\{\chi_a\}$  so that  $\varphi_i = \sum_a \chi_a C_{ai}$ 
  - Algebraic formulation: Matrix algebra

- DFT calculations require various different numerical algorithms

- Generalized eigenvalue problem  $\mathbf{h}[\mathbf{P}]\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{e}$   $P_{ab} = \sum_i C_{ai} C_{bi}^*$

- $\mathbf{h}$  depends on  $\mathbf{C}$  : iterative solution

- Hamilton matrix  $h_{ab} = t_{ab} + v_{ab}^{\text{ext}} + v_{ab}^{\text{coul}} + v_{ab}^{\text{XC}}$  built from analytic integrals

$$t_{ab} = \frac{1}{2} \int [\nabla \chi_a(\mathbf{r})] \nabla \chi_b(\mathbf{r}) d\mathbf{r} \quad v_{ab}^{\text{ext}} = -\sum_{\alpha} Z_{\alpha} \int \frac{\chi_a(\mathbf{r}) \chi_b(\mathbf{r})}{|\mathbf{R}_{\alpha} - \mathbf{r}|} d\mathbf{r}$$

$$v_{ab}^{\text{coul}} = \frac{1}{2} \sum_{cd} P_{cd} \iint \frac{\chi_a(\mathbf{r}) \chi_b(\mathbf{r}) \chi_c(\mathbf{r}') \chi_d(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r} d\mathbf{r}' = \frac{1}{2} \sum_{cd} P_{cd} G_{abcd}$$

XC integrals computed numerically  $v_{ab}^{\text{XC}} = \int \chi_a(\mathbf{r}) \chi_b(\mathbf{r}) \frac{\partial E_{\text{XC}}[\rho(\mathbf{r})]}{\partial \rho(\mathbf{r})} d\mathbf{r}$

## Plane Wave vs. Localized Basis Sets

### Plane Wave Basis

- + FFT/PAW: Very neat approaches
- + Orthogonal basis
- + Basis set easy to improve
- Ideal for calculations solid state systems
- Repeating images for isolated systems or long-range interactions
- All-electron calculations impossible
- Advanced DFT and wave function methods very slow or not available
- Charged systems problematic
- Elaborate convergence techniques essential
- Interpretation of electronic structure often difficult

### Localized (Gaussian) Basis

- + Admit easier reduction of scaling
- + Fewer basis functions needed
- + Hierarchical models available (solvation, embedding etc.)
- Ideal for calculations on molecular systems
- Less efficient than PW for standard DFT calculations
- More memory required
- Issues when modeling extended surfaces

# ParaGauss: Highly Parallelized DFT Implementation

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PARAGAUSS



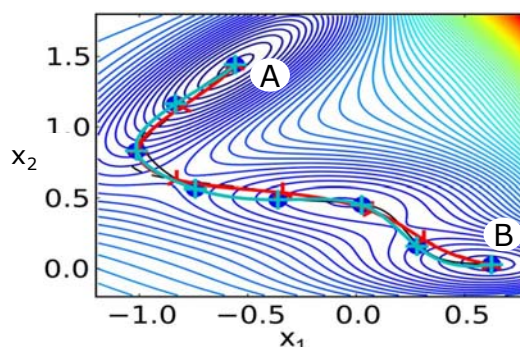
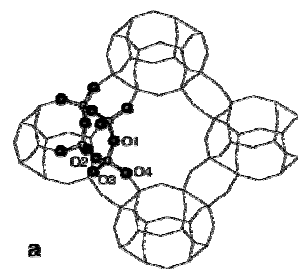
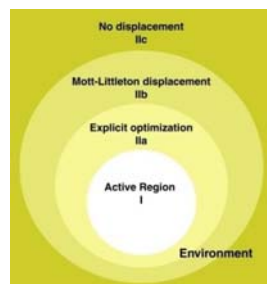
- Version 4.0, Technische Universität München, 2012  
T. Belling, T. Grauschopf, S. Krüger, F. Nörtemann, M. Staufer, M. Mayer,  
V. A. Nasluzov, U. Birkenheuer, A. Hu, A. V. Matveev, A. Shor, M. Fuchs-Rohr,  
K. M. Neyman, D. I. Ganyushin, T. Kerdcharoen, A. Woiterski, S. Majumder,  
A. B. Gordienko, M. Huix i Rotllant, R. Ramakrishnan, G. Dixit, A. Nikodem,  
T. M. Soini, M. Roderus, NR
- Started 1994 as parallel density functional package
- Continuous development,  
successful applications to a variety of chemical systems
- Recently major revisions and extensions within IGSSE-MAC initiative
- Favorable for heavy elements, large metal clusters, symmetric systems

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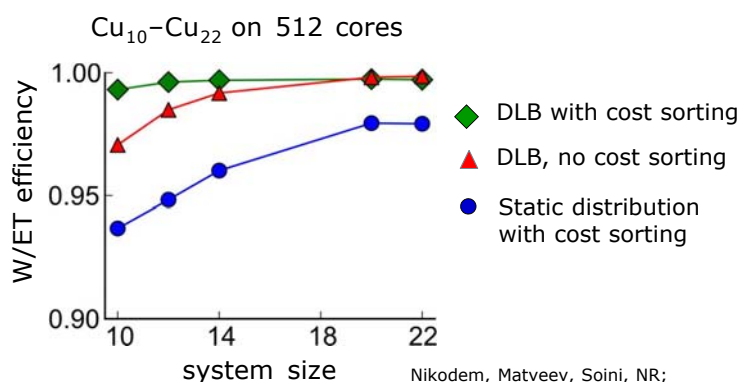
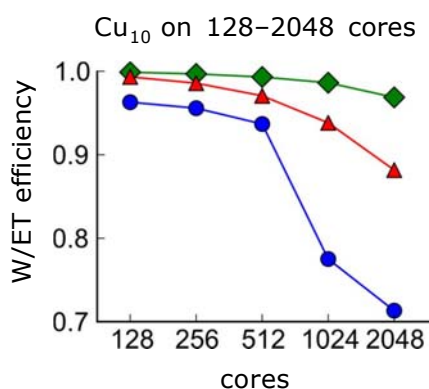
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- Use of **group representation theory** to block matrices  
Exploit spatial symmetry: 74 point groups & double groups
- Hybrid density functionals
- DFT+U self interaction corrections
- Scalar relativistic method (DKH)
- 1<sup>st</sup> and 2<sup>nd</sup> order energy gradients also for scalar relativistics
- Spin-orbit interaction
- Solvation via PCM, RISM
- Embedding in cryst. Environment: EPE, covEPE
- Linear response TDDFT for spectra
- High performance parallelization
- PARATOOLS suite for exploring potential energy surfaces



## Parallelization Approaches

- Originally **master-slave** concept (1994)
- **Dynamic load balancing** (DLB, 2012)
  - **Self-management**: Processes do computation and load balancing
  - Initial tasks equally distributed
  - Idle process **steals part of tasks** from randomly chosen other process
  - DLB highly efficient, scales favorably with system size

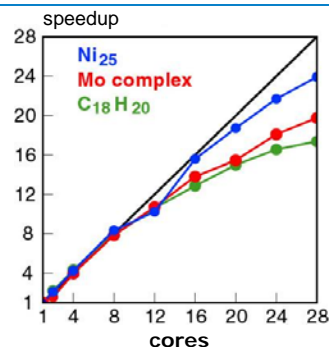


Nikodem, Matveev, Soini, NR;  
*Int J Quantum Chem* 114 (2014)

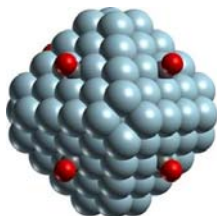
- Master-Slave (1999)
  - Specific algorithms for various tasks
  - Efficient already for very small problems

300–700 basis functions, GGA

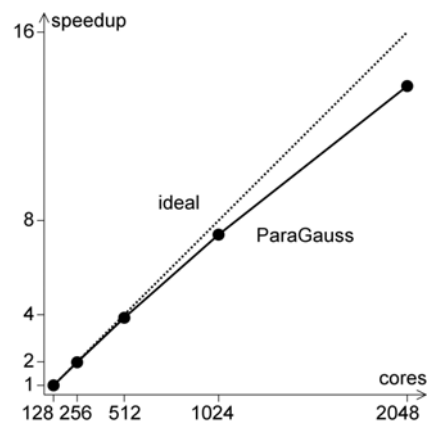
Belling, Grauschopf, Krüger, Mayer, Nörtemann, Staufer, Zenger, NR  
in High Performance Scientific and Engineering Computing,  
Bungartz, Durst, Zenger (eds.) Springer 1999



- DLB (2012)
  - General algorithm for most tasks
  - PARAGAUSS:
    - Hybrid DFT calculation Pt<sub>140</sub>(CO)<sub>8</sub>
    - 2 × 10<sup>14</sup>  $G_{abcd}$  integrals, 2 × 10<sup>10</sup> batches
  - Efficiency > 93% for up to 2048 cores



Nikodem, Matveev, Soini, NR;  
*Int J Quantum Chem* 114 (2014)

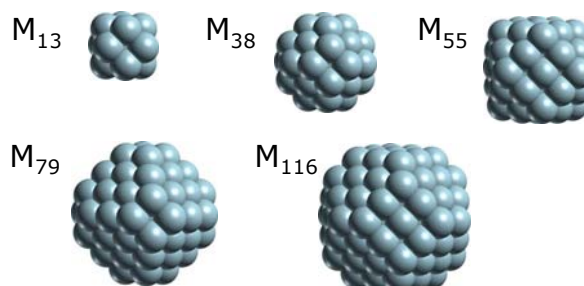


## Modelling Catalyst Materials

- Many properties  $X(n)$  scale with surface/volume ratio  $S/V \sim R^2/R^3 = 1/R \sim n^{-1/3}$  or average atomic coordination number

$$X(n) = X_\infty + k_X n^{-1/3}$$

- Binding energies
- Bond-lengths
- Electronic properties
- Adsorption energies

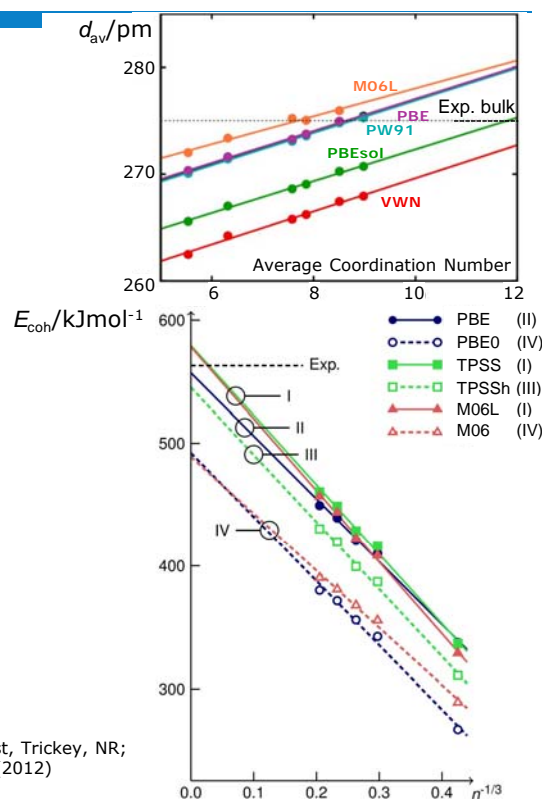


- Extrapolation: finite systems  $\rightarrow$  bulk or surface
  - Bulk or surface modelling
  - Physically motivated test set: Assessment of DFT methods for large metallic species

# Transition Metal Clusters

- Average bond-lengths  $d_{av}$ 
  - $Pd_n$   $n = 13, 38, 55, 79, 147$  local XC functionals
  - PBEsol bulk limit most accurate due to parametrization on solids

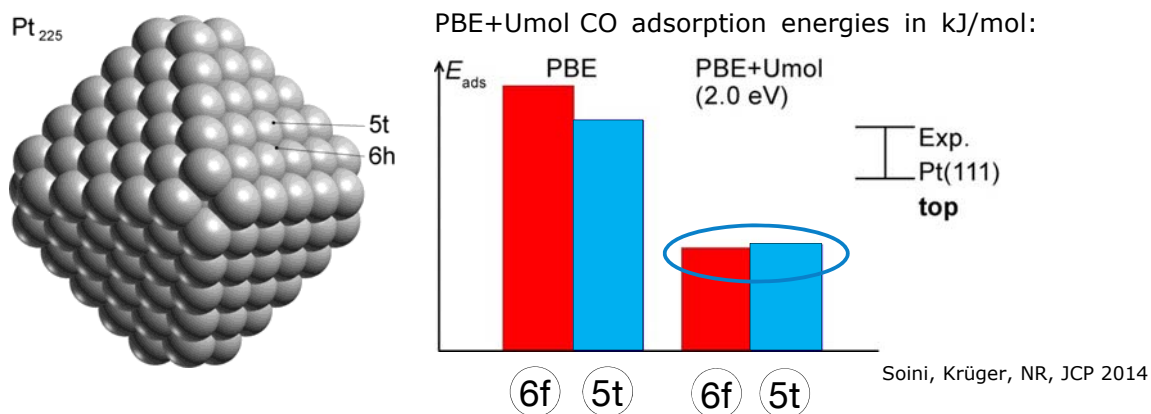
- Cohesive energies  $E_{coh}$ 
  - $Pt_n$   $n = 13, 38, 55, 79, 116$  local vs. hybrid DFT methods
  - Semi-local approximation PBE best
  - Hybrid functional TPSSh: comparable overall accuracy
  - Hybrid DFT problematic for metals but essential for certain situations



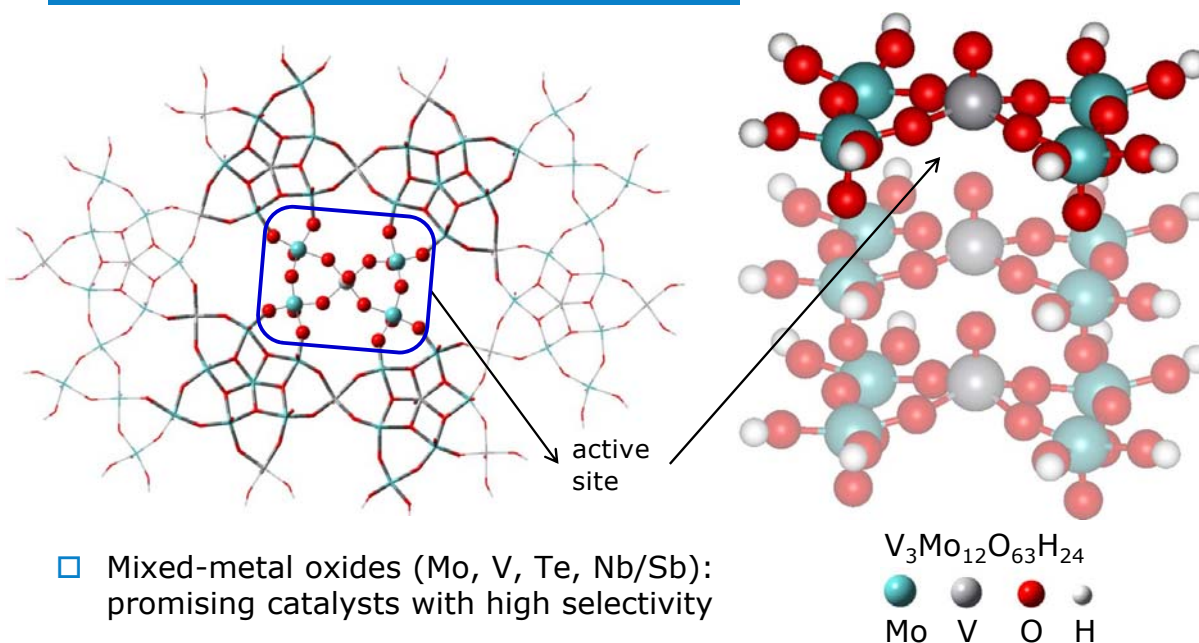
Koitz, Soini, Genest, Trickey, NR;  
*J Chem Phys* 137 (2012)

Adsorption site preference of CO on Pt(111):

- Experimental: Top position
- GGA, semi-local XC functional: hollow position preferred
- Self-interaction affects CO  $2\pi^*$  orbital  
→ corrected with empirical self-interaction correction **DFT+Umol**
- DFT+Umol yields **correct site preference** but underestimates  $E_{\text{ads}}$

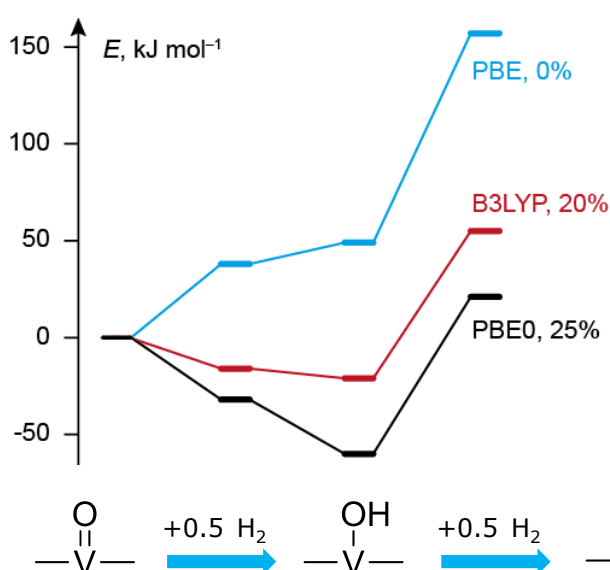


## Mixed Metal Oxides



- Mixed-metal oxides (Mo, V, Te, Nb/Sb): promising catalysts with high selectivity
- Mo-V-O systems as example
  - Unique structures
  - Large unit cell model computationally demanding





- GGA (PBE) qualitatively different from hybrid DFT (PBE0, B3LYP)
- Reduction steps endothermic in PBE, exothermic in PBE0
- GGA calculations questionable due to self-interaction error
- Results of hybrid methods vary with fraction of exact exchange (PBE0 vs. B3LYP)

Hydrogenation energies of vanadyl groups in a Mo-V mixed-metal oxide model cluster

Zhao, Chiu, Genest, NR; *Comp Theor Chem* (2014)  
<http://dx.doi.org/10.1016/j.comptc.2014.06.016>

## Summary and Outlook

- Methodological progress
  - Dynamic load balancing: General algorithm for highly parallel quantum chemistry
  - Parallel exact exchange implementation in ParaGauss for favorably scaling hybrid DFT calculations for large applications
  - Efficient self interaction correction DFT+U<sub>mol</sub>
- New applications accessible in catalysis: Mixed metal oxides
  - Efficient hybrid DFT for electron localization in mixed oxidation state compounds
- Further development
  - Sparse, parallel data structures
  - Efficient memory management, caching
  - Algorithmic improvements: Linear scaling, convergence acceleration

- ParaGauss team TUM  
Sven Krüger, Alexei Matveev, Astrid Nikodem,  
Martin Roderus, Thomas Soini
- Applications team TUM  
Cheng-chau Chiu, Alexander Genest,  
Ralph Koitz, Thomas Soini
- Munich Centre of Advanced Computing, MAC  
Hans-Joachim Bungartz, Michael Gerndt
- KONWIHR  
Christoph Zenger, Michael Griebel
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Leibniz-Rechenzentrum München

## □ Thank you

