The Relativistic Electron Density and Electron Correlation

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Electron density

- (indirectly) available in experiment

  (e.g.: priority research programme SPP1178 in Germany)

- structure and reactivity studies

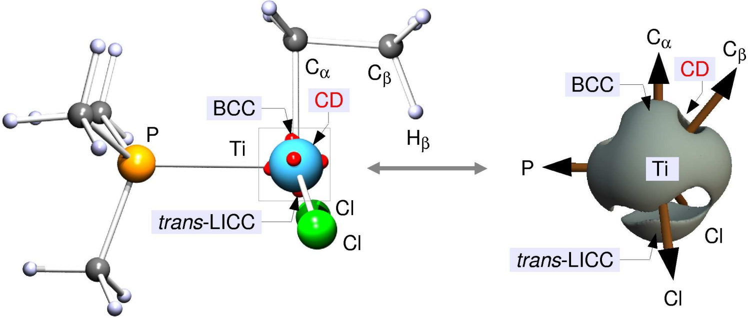
  (MO-based concepts re-formulated in terms of density;
  e.g., Woodward–Hoffmann rules)

- topological analyses

  (→ exponential growth of studies using Bader's AIM)

- spectroscopy
  (contact density in Mössbauer spectroscopy)

An example for a conceptual study by Scherer *et al.*



- Laplacian of the *experimental* electron density of $[\mathrm{EtTiCl_2(PMe_3)}]^+$
- ligand induced and bonded charge concentrations (LICCs; BCCs indicated by red spheres) and regions of pronounced charge depletion (= locally enhanced Lewis acidity) on Ti (left)
- envelope map of the negative Laplacian at the Ti center (right)

W. Scherer, G. S. McGrady, Angew. Chem. Int. Ed. *43* **2004** 1782.

How to define the electron distribution?

- Born interpretation: abs. square of wave function (1 electron only)

$$\rho(\boldsymbol{r}) = |\Psi(\boldsymbol{r})|^2$$

- Many-electron systems: integrate out all but one electronic coordinate

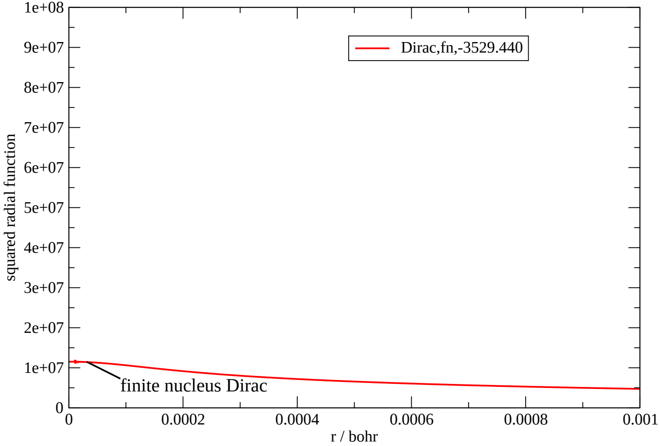
$$\rho(\boldsymbol{r}) \overset{!}{=} N \int_{-\infty}^{+\infty} \mathrm{d}^3 r_2 \cdots \int_{-\infty}^{+\infty} \mathrm{d}^3 r_{\mathrm{N}} \, |\Psi(\{\boldsymbol{r}_i\}, t)|^2$$

- ... yields sum of squared occupied (spin) orbitals for Hartree–Fock or DFT wave function

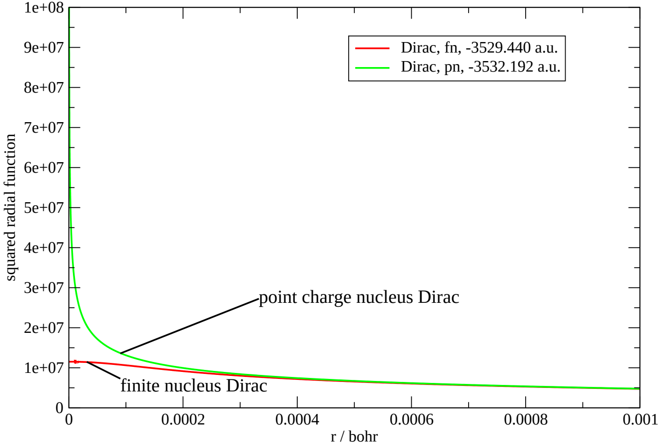
$$\rho(\boldsymbol{r}) \rightarrow \sum_{i=1}^{\mathrm{occ}} |\psi_i(\boldsymbol{r})|^2$$

- → Let us look at a simple example ...

Sum of squared radial functions of Hg^{79+}



Sum of squared radial functions of Hg^{79+}



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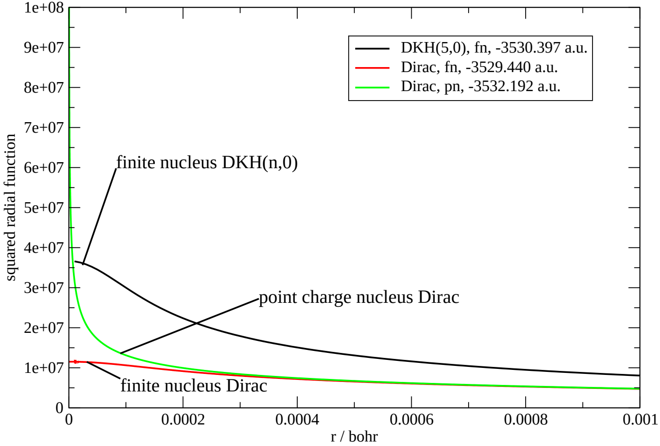

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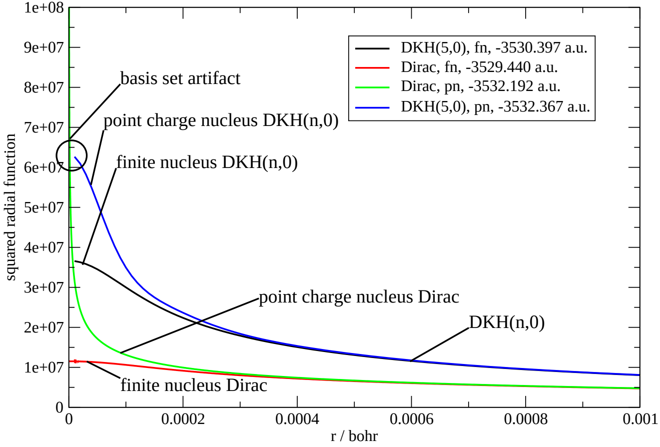

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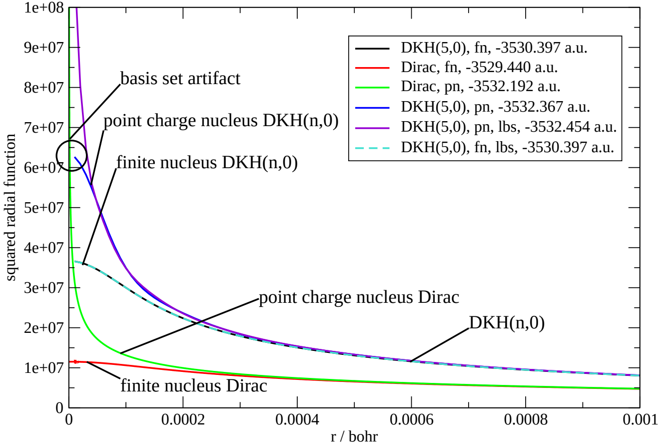

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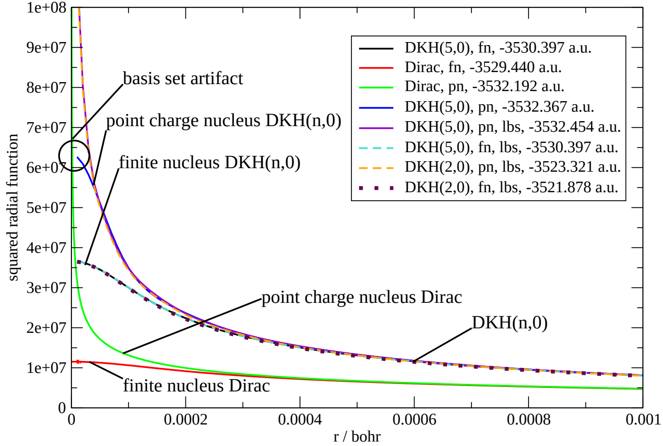
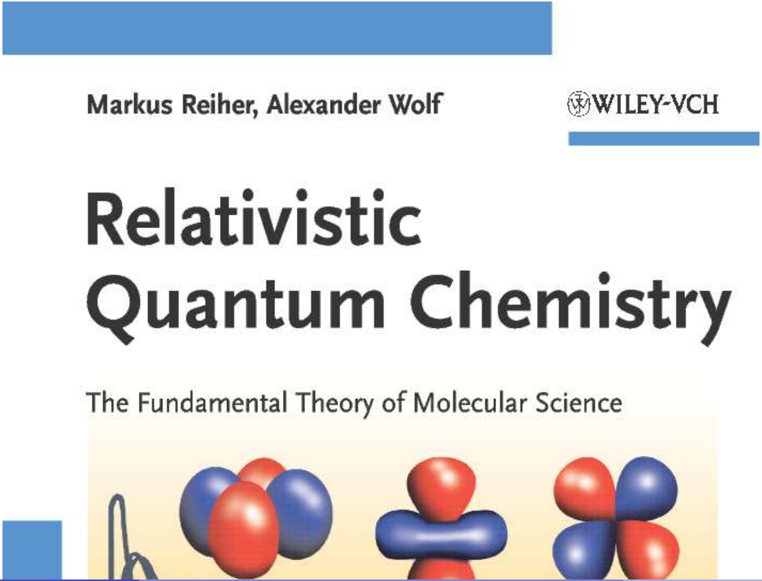


- Electron density in quantum theory
  - **Definition of electron density**
  - Approximate Hamiltonian operators
  - Electron density distributions for various Hamiltonian operators
- Calculation of electron density distributions
  - Effects from approximate Hamiltonian operators
  - A difficult case: contact densities
  - Electron density in conceptual theories

For all details on the theory see:



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WILEY-VCH

Relativistic Quantum Chemistry

The Fundamental Theory of Molecular Science

Electron density is an observable → Operator can be assigned

- Density operator defined as

$$\hat{\rho}_{\boldsymbol{r}} = \sum_{i=1}^{N} \delta^{(3)}(\boldsymbol{r} - \boldsymbol{r}_i)$$

(compare to classical expression for set of point charges)

- Expectation value yields particle density

$$\rho(\boldsymbol{r}) \quad \overset{!}{=} \quad \langle \Psi(\{\boldsymbol{r}_i\}, t) | \hat{\rho}_{\boldsymbol{r}} | \Psi(\{\boldsymbol{r}_i\}, t) \rangle$$

$$= \int_{-\infty}^{+\infty} \mathrm{d}^3 r_1 \int_{-\infty}^{+\infty} \mathrm{d}^3 r_2 \cdots \int_{-\infty}^{+\infty} \mathrm{d}^3 r_{\mathrm{N}} \; \Psi^*(\{\boldsymbol{r}_i\}, t) \; \rho_{\boldsymbol{r}} \; \Psi(\{\boldsymbol{r}_i\}, t)$$

- *Charge* density:

$$\rho_c(\boldsymbol{r}) = -e \; \rho(\boldsymbol{r})$$

Continuity equation

- *The continuity equation is the fundamental equation relating electron and current density*

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \boldsymbol{j} = 0$$

→ Can be used to define these quantities !

- Deduction of continuity equation from expectation value of density operator uniquely defines electron distribution of an N-electron system in any QM (model) theory.
- Note: the continuity equation also follows from Heisenberg equation of motion for the density operator

Consider change of electron density with time

- Apply the Ehrenfest theorem

$$\frac{\mathrm{d}\langle\Psi|\hat{O}|\Psi\rangle}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}\langle\Psi|[\hat{H},\hat{O}]|\Psi\rangle + \left\langle\Psi\left|\frac{\partial\hat{O}}{\partial t}\right|\Psi\right\rangle$$

- Insert density operator

$$\underbrace{\frac{\mathrm{d}\left\langle\Psi(\{\boldsymbol{r}_i\},t)\middle|\rho_{\boldsymbol{r}}\middle|\Psi(\{\boldsymbol{r}_i\},t)\right\rangle}{\mathrm{d}t}}_{\frac{\partial\rho(\boldsymbol{r},t)}{\partial t}} = \underbrace{\frac{\mathrm{i}}{\hbar}\left\langle\Psi(\{\boldsymbol{r}_i\},t)\middle|[\hat{H},\hat{\rho}_{\boldsymbol{r}}]\middle|\Psi(\{\boldsymbol{r}_i\},t)\right\rangle}_{-\nabla\cdot\boldsymbol{j}}$$

(2nd term on r.h.s. vanishes as density operator does not depend on t)

- Choice of Hamiltonian $\hat{H}$ and wave function Ψ determine the current density $\boldsymbol{j}$

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Dirac–Coulomb–Breit (DCB) operator

- *'Fully' relativistic Hamiltonian for M nuclei and N electrons:*

$$\hat{H}_{\mathrm{DCB}} = \sum_{I=1}^{M} \frac{\boldsymbol{p}_I^2}{2m_I} + \sum_{i=1}^{N} \hat{h}_{\mathrm{D}}(i) + \sum_{I=1}^{M} \sum_{J=I+1}^{M} \frac{Z_I Z_J e^2}{|\boldsymbol{R}_I - \boldsymbol{R}_J|} + \sum_{i=1}^{N} \sum_{j=i+1}^{N} g(i,j)$$

(for the sake of brevity, leave the mathematical obstacles aside)

- 'Fully relativistic' single-electron Hamiltonian

$$\hat{h}_{\mathrm{D}}(i) = c\boldsymbol{\alpha}_i \cdot \left(\hat{\boldsymbol{p}}_i + \frac{e}{c}\boldsymbol{A}\right) + (\boldsymbol{\beta}_i - 1)m_e c^2 - e\phi - \sum_{I=1}^{M} \frac{Z_I e^2}{|\hat{\boldsymbol{r}}_i - \boldsymbol{R}_I|}$$

- Dirac matrices $\boldsymbol{\alpha}_i = (\alpha_x, \alpha_y, \alpha_z)$ and β

$$\alpha_x = \begin{pmatrix} \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} & \sigma_x \\ \sigma_x & \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} \end{pmatrix}, \quad \alpha_y = \begin{pmatrix} \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} & \sigma_y \\ \sigma_y & \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} \end{pmatrix}, \quad \alpha_z = \begin{pmatrix} \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} & \sigma_z \\ \sigma_z & \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

which are built from the Pauli spin matrices $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Electron–electron interaction

- Is actually the reason why DCB is approximate; first-quantized
- Coulomb–Breit operator (Gaussian units)

$$g(i,j) = \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}\left[1 - \frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{2} - \frac{(\boldsymbol{\alpha}_i \cdot (\boldsymbol{r}_i - \boldsymbol{r}_j))(\boldsymbol{\alpha}_j \cdot (\boldsymbol{r}_i - \boldsymbol{r}_j))}{2|\boldsymbol{r}_i - \boldsymbol{r}_j|^2}\right]$$

→ Includes Coulomb and magnetic interactions

→ Derives from classical Darwin energy

→ Considers retardation effects on transmission of interaction

- Gaunt interaction is first approximation to Coulomb–Breit operator

$$g(i,j) = \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}\left[1 - \boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j\right]$$

(neglects retardation; includes instantaneous magnetic interaction)

Douglas–Kroll–Hess theory (DKH)

- Unitary transformation U block-diagonalizes the Dirac Hamiltonian

$$h_{bd} = U h_{\mathrm{D}} U^{\dagger} = \begin{pmatrix} h_+ & \begin{smallmatrix} 0 & 0 \\ 0 & 0 \end{smallmatrix} \\ \begin{smallmatrix} 0 & 0 \\ 0 & 0 \end{smallmatrix} & h_- \end{pmatrix}$$

  - h_+ : operator for electronic states
  - h_- : operator for positronic states

- Also, wave function is transformed: $\tilde{\psi} = U\psi \rightarrow \tilde{\psi}^L$
- Then, any property requires transformation of operator

$$\left\langle \Psi | \hat{O} | \Psi \right\rangle = \left\langle U\Psi | U\hat{O}U^{\dagger} | U\Psi \right\rangle = \left\langle \tilde{\Psi}^L | \tilde{O}^{\mathrm{LL}} | \tilde{\Psi}^{\mathrm{L}} \right\rangle$$

- Hence, squared DKH orbitals do not yield the density !
- Technical detail: U is constructed as product of infinitely many unitary transformations, $U = U_\infty \cdots U_3 U_2 U_1 U_0$ each Taylor-expanded in terms of an anti-hermitian operator
- Yields order-by-order approximation for orbitals and operators

Regular approximations

- Relate small and large components by energy-dependent X-operator (derivable!)

$$\psi_i^S = \underbrace{\frac{c\boldsymbol{\sigma}\cdot\boldsymbol{p}}{\varepsilon_i - V + 2m_ec^2}}_{X(\varepsilon_i)}\psi_i^L = \frac{c\boldsymbol{\sigma}\cdot\boldsymbol{p}}{2m_ec^2 - V}\sum_{k=0}^{\infty}\left(\frac{\varepsilon_i}{V-2m_ec^2}\right)^k\psi_i^L$$

- Truncation yields n-th oder regular approximation (nORA)

$$\hat{h}_{\mathrm{KORA}} = V + (\boldsymbol{\sigma}\cdot\boldsymbol{p})\frac{c^2}{2m_ec^2-V}\left[\sum_{k=0}^{n}\left(\frac{\varepsilon_i}{V-2m_ec^2}\right)^k\right](\boldsymbol{\sigma}\cdot\boldsymbol{p})$$

- Zeroth-order regular approximation (ZORA):

$$\hat{h}_{\mathrm{ZORA}} = \boldsymbol{\sigma}\cdot\boldsymbol{p}\frac{c^2}{2m_ec^2-V}\boldsymbol{\sigma}\cdot\boldsymbol{p} + V$$

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Electron density from single Slater determinant of 4-spinors

- Insert Slater determinant (SD) Θ into expectation value (+ apply Slater–Condon rules)

$$\begin{aligned}\rho^{\mathrm{SD}}_{\mathrm{DCB}}(\boldsymbol{r}) &= \langle\Theta(\{\boldsymbol{r}_j\})\,|\rho_{\boldsymbol{r}}|\,\Theta(\{\boldsymbol{r}_j\})\rangle \\ &= \sum_{i=1}^{N}\left\langle\psi_i(\boldsymbol{r}_i)\left|\delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}_i)\right|\psi_i(\boldsymbol{r}_i)\right\rangle_{\boldsymbol{r}_i}\end{aligned}$$

- One-electron integrals then yield fully relativistic density

$$\rho^{\mathrm{SD}}_{\mathrm{DCB}}(\boldsymbol{r}) = \sum_{i=1}^{N}\psi_i^{\dagger}(\boldsymbol{r})\cdot\psi_i(\boldsymbol{r})$$

Current density for the Dirac–Coulomb–Breit operator

- Use continuity equation

$$\frac{\partial \left\langle \Psi \middle| \rho_{\boldsymbol{r}} \middle| \Psi \right\rangle}{\partial t} = \frac{\mathrm{i}}{\hbar} \left\langle \Psi \middle| \left[\sum_{i=1}^{N} c\boldsymbol{\alpha}_i \cdot \boldsymbol{p}_i, \rho_{\boldsymbol{r}} \right] \middle| \Psi \right\rangle$$

$$= -\boldsymbol{\nabla} \cdot cN \left\langle \Psi \middle| \boldsymbol{\alpha}_1 \delta^{(3)}(\boldsymbol{r} - \boldsymbol{r}_1) \middle| \Psi \right\rangle$$

- Hence, DCB current density $\boldsymbol{j}_{\mathrm{DCB}} \overset{!}{=} cN \left\langle \Psi \middle| \boldsymbol{\alpha}_1 \delta^{(3)}(\boldsymbol{r} - \boldsymbol{r}_1) \middle| \Psi \right\rangle$ now only depends on choice of *four-component* many-electron wave function Ψ

- For a single Slater determinant, the relativistic current density reads

$$\boldsymbol{j}_{\mathrm{DCB}}^{\mathrm{SD}}(\boldsymbol{r}) = c \sum_{i=1}^{N} \psi_i^{\dagger}(\boldsymbol{r}) \cdot \boldsymbol{\alpha} \cdot \psi_i(\boldsymbol{r})$$

Two-component approaches

- For DKH, density operator must be transformed !

$$\frac{\partial}{\partial t}\left\langle \underbrace{\boldsymbol{U}\Psi}_{\tilde{\Psi}} \left| U \rho_{\boldsymbol{r}} \boldsymbol{U}^{\dagger} \right| \boldsymbol{U}\Psi \right\rangle = -\nabla \cdot cN \left\langle \boldsymbol{U}\Psi \left| U^{(1)} \boldsymbol{\alpha}_1 \delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}_1) U^{(1)\dagger} \right| \boldsymbol{U}\Psi \right\rangle$$

- DKH electron and current densities for one Slater determinant:

$$\rho^{\text{SD}}_{\text{DKH}}(\boldsymbol{r}) = \sum_{i=1}^{N} \left\langle \tilde{\psi}_i \left| U^{(i)} \delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}_i) U^{(i)\dagger} \right| \tilde{\psi}_i \right\rangle$$

$$\boldsymbol{j}^{\text{SD}}_{\text{DKH}}(\boldsymbol{r}) = c \sum_{i=1}^{N} \left\langle \tilde{\psi}_i \left| U^{(i)} \boldsymbol{\alpha}_i \delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}_i) U^{(i)\dagger} \right| \tilde{\psi}_i \right\rangle$$

Electron density in the non-relativistic framework

- Insert Schrödinger Hamiltonian into continuity equation:

$$\frac{\partial \left\langle \Psi \middle| \rho_{\boldsymbol{r}} \middle| \Psi \right\rangle}{\mathrm{d}t} = -\nabla \cdot \frac{N\hbar}{2m_e \mathrm{i}} \left[\langle \Psi^* \nabla_1 \Psi \rangle - \langle (\nabla_1 \Psi) \Psi^* \rangle \right]$$

- For single Slater determinant, electron and current densities are

$$\begin{aligned} \rho^{\mathrm{SD}}_{\mathrm{NR}}(\boldsymbol{r}) &= \sum_{i=1}^{N} \psi_i^*(\boldsymbol{r}) \psi_i(\boldsymbol{r}) \\ \boldsymbol{j}^{\mathrm{SD}}_{\mathrm{NR}}(\boldsymbol{r}) &= \frac{\hbar}{2m_e \mathrm{i}} \sum_{i=1}^{N} \left[\psi_i^*(\boldsymbol{r}) \nabla \psi_i(\boldsymbol{r}) - (\nabla \psi_i(\boldsymbol{r})) \psi_i^*(\boldsymbol{r}) \right] \end{aligned}$$

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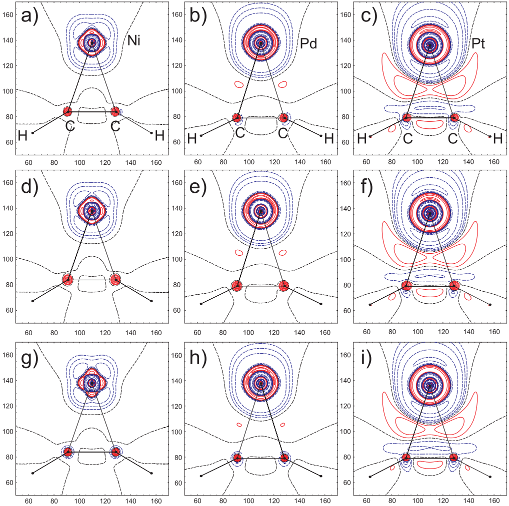
DCB, DKH, ZORA-SO for acetylene Ni, Pd, Pt complexes



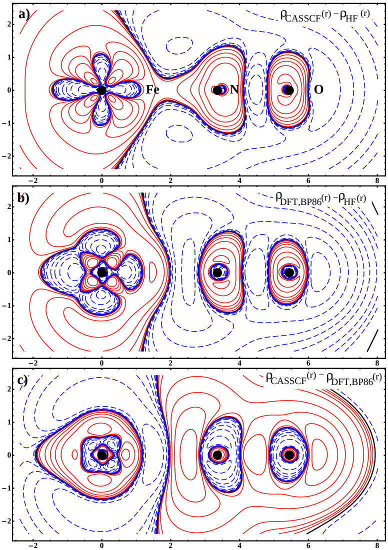
- **Difference electron densities**
  - $\rho_{\text{4comp}}(\boldsymbol{r}) - \rho_{\text{nonrel}}(\boldsymbol{r})$: panels a, b and c
  - $\rho_{\text{ZORA}}(\boldsymbol{r}) - \rho_{\text{nonrel}}(\boldsymbol{r})$: panels d,e and f
  - $\rho_{\text{DKH10}}(\boldsymbol{r}) - \rho_{\text{nonrel}}(\boldsymbol{r})$: panels g, h and i
- Relativistic effects most pronounced for Pt
- Scalar-relativistic DKH covers most relativistic effects

G. Eickerling, R. Mastalerz, V. Herz, H.-J. Himmel, W. Scherer, M. Reiher, J. Chem. Theory Comput. *3* **2007** 2182

Significance of electron correlation effects ?

- Quite many studies on small, light molecules.
- Early one on H_2 by Bader and Chandra:
  - Hartree–Fock (HF) overestimates density in central bonding region.
  - Density around nuclei is underestimated by Hartree–Fock.
- Other studies comparing CI and HF come to similar conclusions: → density shifted from bonding region towards nuclei when considering electron-correlation effects

Correlation effects for TM complexes — $Fe(NO)^{2+}$ example



- **Difference densities**
  (HF≡ no correlation)
- Around Fe atom, correlation density exhibits four minima
- Minima are surrounded by four maxima

  → electron density is shifted from bonding region to atomic nuclei

S. Fux, M. Reiher, Structure & Bonding (2011), in press.

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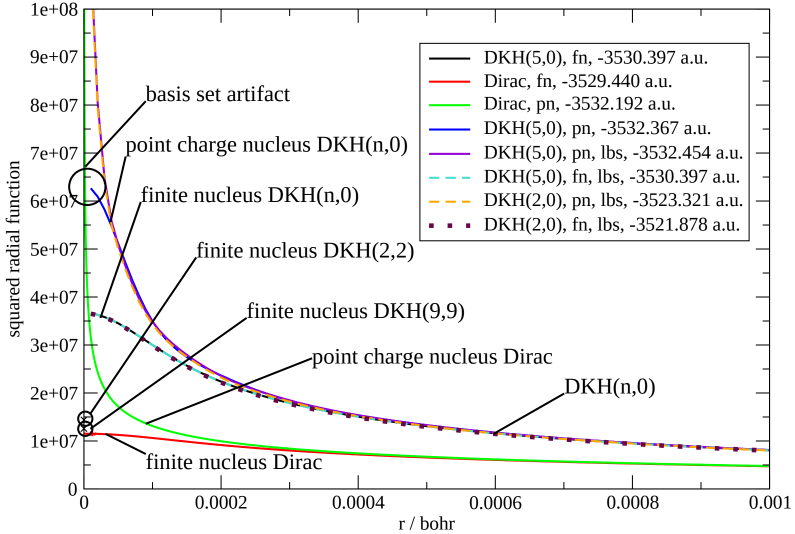
DKH density at the atomic nucleus



R. Mastalerz, R. Lindh, M. Reiher, Chem. Phys. Lett. *465* **2008** 157

Short-range behavior of radial atomic spinors

$$\begin{pmatrix} V_i(r) + mc^2 - \epsilon_i & c\hbar\left[-\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa_i}{r}\right] \\ c\hbar\left[\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa_i}{r}\right] & V_i(r) - mc^2 - \epsilon_i \end{pmatrix} \begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix} = \begin{pmatrix} X_i^P(r) \\ X_i^Q(r) \end{pmatrix}$$

expand the radial functions

$$P_i(r) = r^{\alpha_i} \sum_{k=0}^{\infty} a_k^{(i)} r^k \quad ; \quad Q_i(r) = r^{\alpha_i} \sum_{k=0}^{\infty} b_k^{(i)} r^k$$

insert and evaluate short-range deq. yields exponent

$$\alpha = \begin{cases} \sqrt{\kappa_i^2 - Z^2/c^2} & \text{point-like nuclei} \\ |\kappa_i| & \text{finite-sized nuclei} \end{cases}$$

→ yields short-range behavior of radial functions with $|\kappa_i| = 1$

$$\lim_{r\to 0} \rho_i^L(r) = \lim_{r\to 0} \frac{P_i^2(r)}{r^2} = \lim_{r\to 0} \left(\frac{r^{2\alpha} a_0^{(i)} 2}{r^2} + \ldots \right) = \begin{cases} \lim\limits_{r\to 0} r^{2\alpha-2} a_0^2 \quad (\alpha < 1) & \text{singular} \\ a_0^2 & \text{finite} \end{cases}$$

Basis sets for Fe compounds

- electron density for finite-nucleus external potential can be approximated by Gaussians
- extensive study of basis set development for Fe:
  - R. Mastalerz, P.-O. Widmark, B. O. Roos, R. Lindh, M. Reiher, J. Chem. Phys. *133* **2010** 144111
- DKH(2,2) CASSCF contact density of Fe $\rho(\boldsymbol{r}_{\mathrm{Fe}})$ in bohr^{-3}

basis set	$\rho(\boldsymbol{r}_{\mathrm{Fe}})$FeH	$\rho(\boldsymbol{r}_{\mathrm{Fe}})FeF_3$	$\rho(\boldsymbol{r}_{\mathrm{Fe}})FeO_2$	$\rho(\boldsymbol{r}_{\mathrm{Fe}})$FeO	$\rho(\boldsymbol{r}_{\mathrm{Fe}})$FeC
(29s/14p/11d)	15369.471	15369.548	15369.989	15369.317	15369.654
$[7s/6p/5d]$	15369.631	15370.471	15370.595	15369.619	15370.074
$[8s/7p/6d]$	15369.646	15370.300	15370.678	15369.706	15370.100
$[9s/8p/7d]$	15369.660	15370.372	15370.722	15369.774	15370.246
		$\Delta\rho$(**Fe**F)$_3$	$\Delta\rho$(**Fe**O$_2$)	$\Delta\rho$(**Fe**O)	$\Delta\rho$(**Fe**C)
(29s/14p/11d)	—	0.076	0.518	−0.155	0.183
$[7s/6p/5d]$	—	0.840	0.963	−0.012	0.443
$[8s/7p/6d]$	—	0.655	1.033	0.060	0.455
$[9s/8p/7d]$	—	0.712	1.062	0.114	0.586

Role of electronic structure model

- DKH(2,2) contact density $\rho(\boldsymbol{r}_{\mathrm{Fe}})$ (in bohr^{-3}) for the Fe^{3+} $^6S(d^5)$ and Fe^{2+} $^7S(d^5s^1)$ states
- large primitive basis set $(28s/10p/7d)$ was used in these calculations
- for the DFT calculations an ultrafine radial grid was used

	UHF	ROHF	ACPF	B3LYP
$^6S(d^5)$	15365.562	15365.619	15365.806	15421.728
$^7S(d^5s^1)$	15375.095	15375.190	15375.599	15432.144
$\Delta\rho(\boldsymbol{r}_{\mathrm{Fe}})$	9.533	9.571	9.794	10.416
	M06	PBE	PBE0	BLYP
$^6S(d^5)$	15509.353	15417.218	15403.938	15449.778
$^7S(d^5s^1)$	15519.789	15427.801	15414.330	15460.336
$\Delta\rho(\boldsymbol{r}_{\mathrm{Fe}})$	10.436	10.583	10.392	10.558

R. Mastalerz, P.-O. Widmark, B. O. Roos, R. Lindh, M. Reiher,
J. Chem. Phys. *133* **2010** 144111

Role of DKH orders

- Fe^{3+} $^6S(d^5)$ and Fe^{2+} $^7S(d^5s^1)$ from unrestricted Hartree–Fock
- large primitive basis set: $(28s/10p/7d)$

	$\rho(\boldsymbol{r}_{\mathrm{Fe}})$ Fe^{3+} $[^6S(d^5)]$	$\rho(\boldsymbol{r}_{\mathrm{Fe}})$ Fe^{2+} $[^7S(d^5s^1)]$	$\Delta\rho(\boldsymbol{r}_{\mathrm{Fe}})$
DKH(2,2)	15365.562	15375.095	9.533
DKH(3,3)	15021.145	15030.465	9.320
DKH(4,4)	15087.450	15096.810	9.361
DKH(5,5)	15075.658	15085.011	9.354
DKH(6,6)	15077.805	15087.160	9.355
DKH(7,7)	15077.428	15086.782	9.355
DKH(8,8)	15077.491	15086.846	9.355

- Arbitrary-order scalar-relativistic DKH Hamiltonian and property code implemented in MOLCAS:

M. Reiher, A. Wolf, J. Chem. Phys. *121* **2004** 10945;
A. Wolf, M. Reiher, J. Chem. Phys. *124* **2006** 064103

Work in progress: Dirac–Coulomb contact density calculations

- example: closed-shell Hg atom and HgF_2 molecule
- uncontracted basis sets based on Dyall's TZ basis + 2s1p

method	$\rho(\mathbf{Hg})$	$\rho(\mathbf{Hg}F_2)$	$\Delta\rho$
CCSD(T)	2363990.738	2363842.247	148.491
HF	2363929.120	2363801.198	127.922
B3LYP	2370863.147	2370757.273	105.874
BLYP	2373687.688	2373591.810	95.878
PBE	2372713.575	2372614.830	98.745
PBE0	2370507.827	2370396.753	111.074

S. Knecht, S. Fux, R. van Meer, T. Saue, L. Visscher, M. Reiher, *Theor. Chem. Acc.*, **2010** to be submitted

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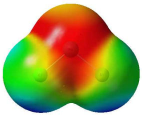
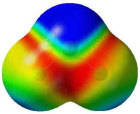
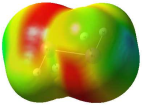
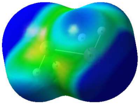
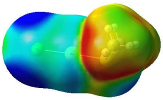
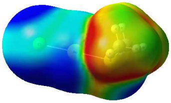
Reactivity descriptors in conceptual DFT

symbol	descriptor	energy derivative
μ	chemical potential	$\left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})}$
$\rho(\boldsymbol{r})$	electron density	$\left(\frac{\delta E}{\delta v(\boldsymbol{r})}\right)_N$
$\chi(\boldsymbol{r},\boldsymbol{r}')$	linear response function	$\left(\frac{\delta^2 E}{\delta v(\boldsymbol{r})\delta v(\boldsymbol{r}')}\right)_N = \left(\frac{\delta \rho(\boldsymbol{r})}{\delta v(\boldsymbol{r})}\right)_N$
η	chemical hardness	$\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathbf{r})} = \left(\frac{\partial \mu}{\partial N}\right)_{v(\mathbf{r})}$
S	chemical softness	$\frac{1}{\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{v(\mathbf{r})}$
$f(\boldsymbol{r})$	Fukui function	$\left(\frac{\delta \partial E}{\delta v(\boldsymbol{r})\partial N}\right) = \left(\frac{\partial \rho(\boldsymbol{r})}{\partial N}\right)_{v(\mathbf{r})}$

Fukui function $f^{-}(r)$ for 3 heavy-element molecules

	relativistic	non−relativistic
$PbCl_2$	a) 	b) 
Bi_2H_2	c) 	d) 
$(CH_3)_2SAuCl$	e) 	f) 

- Relativistic effects most pronounced for $PbCl_2$ and Bi_2H_4
  → changes chemical interpretation
- $(CH_3)_2SAuCl$: comparatively small relativistic effects

N. Sablon, R. Mastalerz, F. De Proft, P. Geerlings, M. Reiher, Theor. Chem. Acc. *127* **2010** 195

Summary and Conclusion

- foundations of electron density in relativistic theory
- numerical effects on the calculated density
  - peculiarities of approximate relativistic methods
  - 'relativistic effects' on density and descriptors of conceptual DFT
  - accurate calculation of contact densities (and isomer shifts)

Review of some of the material presented:
S. Fux, M. Reiher, Structure & Bonding (2011), in press.

General presentation:

M. Reiher, A. Wolf, *Relativistic Quantum Chemistry*, Wiley-VCH, 2009.

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