



Self Interaction Corrections to Density Functional Theory:

Mark R. Pederson, Physics, The University of Texas at El Paso

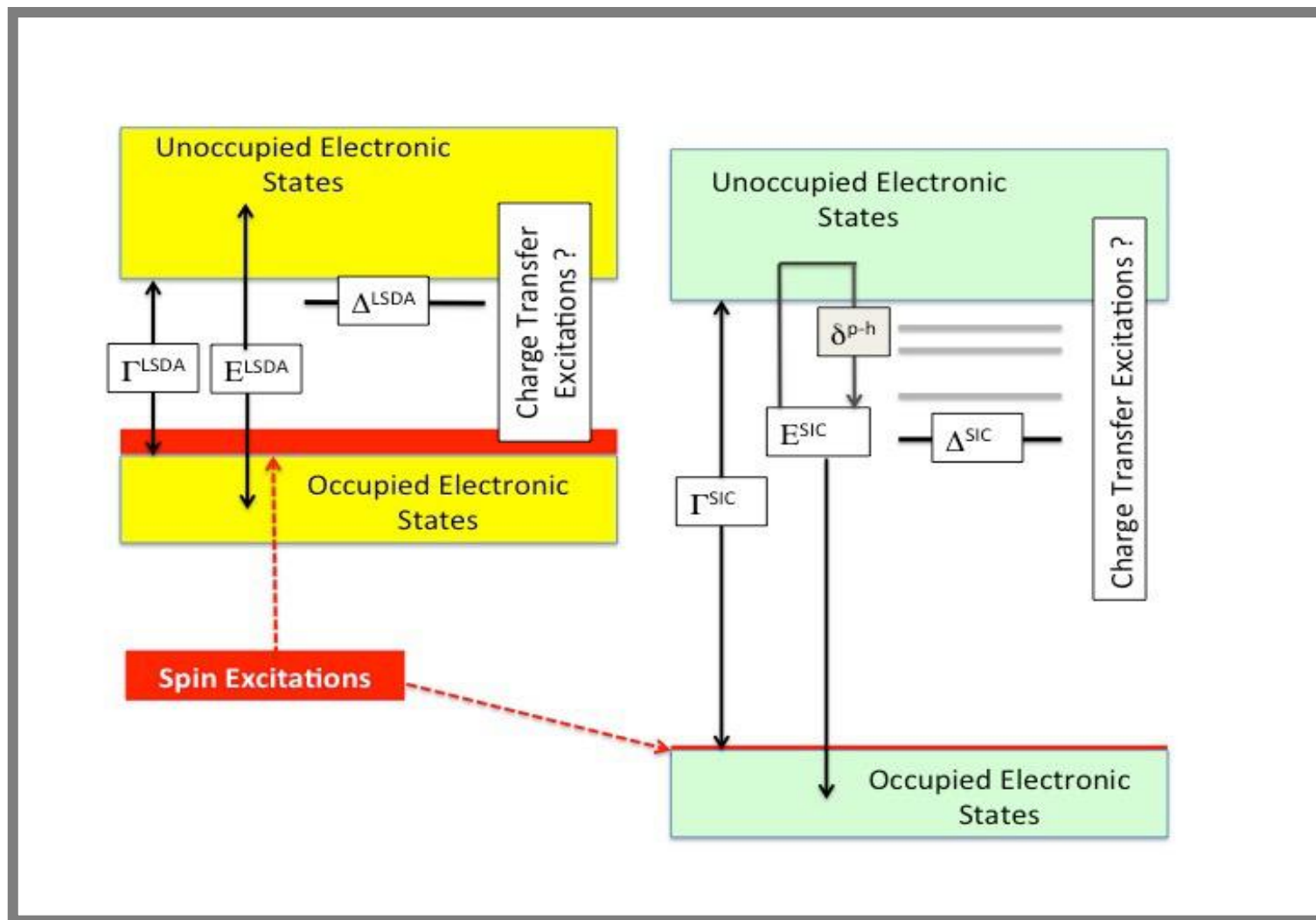
- 1981 PZSIC (Perdew & Zunger, PRB **23** 5048 (1981).
 - 1984: Localization equations
 - 2011: Road Less Followed
 - 2014: Restoration of unitary invariance
 - 2023: This chapter
- FLOSIC Post-2014 Methods
 - Drivers from molecular magnetism
 - Complex orbitals within FLOSIC?
 - Anions in solutions? OK!
 - Do solutions always exist? (Yes!)
 - Applications to f-electrons.

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Electronic and Spin Structure: DFT vs SIC-DFT



Beryllium Atom within Hartree's Approximation

$$\begin{aligned}
 E_{Hartree} &= 2\left[\langle\phi_1|-\frac{\nabla^2}{2}-\frac{4}{r}|\phi_1\rangle + \langle\phi_2|-\frac{\nabla^2}{2}-\frac{4}{r}|\phi_2\rangle\right] + \frac{1}{2} \int d^3r d^3r' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} \\
 &\quad - \frac{1}{2} \int d^3r d^3r' \frac{\phi_1^2(\vec{r})\phi_1^2(\vec{r}')}{|\vec{r}-\vec{r}'|} - \frac{1}{2} \int d^3r d^3r' \frac{\phi_2^2(\vec{r})\phi_2^2(\vec{r}')}{|\vec{r}-\vec{r}'|} \\
 \rho(\vec{r}) &= 2[\phi_1^2 + \phi_2^2]
 \end{aligned}$$

Energy is not invariant to unitary transformations

$$\begin{aligned}
 |\phi'_1\rangle &= \cos\theta|\phi_1\rangle + \sin\theta|\phi_2\rangle \\
 |\phi'_2\rangle &= -\sin\theta|\phi_1\rangle + \cos\theta|\phi_2\rangle
 \end{aligned}$$

$$d\phi'_1/d\theta = \phi'_2 \qquad d\phi'_2/d\theta = -\phi'_1$$

$$\text{if } dE/d\theta = 0, \text{ then: } \langle\phi_1|V_c(\phi_i) - V_c(\phi_2)|\phi_2\rangle = 0$$

$$V_c(\phi)(\vec{r}') = - \int d^3r \frac{\phi(\vec{r})^2}{|\vec{r}-\vec{r}'|}$$

Can we use atoms, abundant on earth to:

- Decrease or removed the need for rare-earth magnetism?
- Build Qubit arrays that are stable at room temperature?

NEWSFEED

Q MY UTEP RESOURCES FOR QUICK LINKS

UTEP Physicists Create Powerful Magnets to De-Freeze Quantum Computing

New material works at room temperature, 100 times more magnetic than iron

EL PASO, Texas (Sept. 11, 2023) — Quantum computing has the potential to revolutionize the world, allowing massive health and science computation problems to be solved exponentially faster than by classic computing. But quantum computers have a big drawback – they can only operate in subzero temperatures.

“In order to make quantum computers work, we cannot use them at room temperature,” said Ahmed El-Gendy, Ph.D., an associate professor of physics at The University of Texas at El Paso. “That means we will need to cool the computers and cool all the materials, which is very expensive.”

Now, physicists at The University of Texas at El Paso believe they have made a quantum leap in that regard. Led by El-Gendy, the team has developed a highly magnetic quantum computing material — 100 times more magnetic than pure iron — that functions at regular temperature. The material is described in the summer issue of the journal [Applied Physics Letters](#).

Magnets are used in many modern applications, including smartphones, vehicles and solid state drives — where computers’ information is stored. In quantum computers, magnets are used to enhance speed, said Ahmed, but their strong magnetic properties only work in low temperature. (Quantum computers, in fact, are currently kept at the cool temperature of -459 degrees Fahrenheit, right above absolute zero.)

Since 2019, the UTEP team has worked to create entirely new magnetic materials for quantum computing. In addition to operating in regular temperatures, the team has focused on magnets that are not made from rare Earth materials.

“All magnets are currently made from rare Earth materials, and we have a shortage of them,” El-Gendy said.



Achieved by forcing electrons onto Fe-based Ferrocene

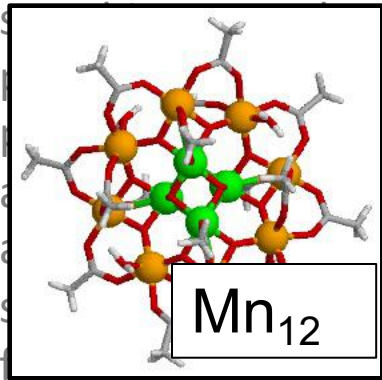
Motivation: Quantum Magnets: For Computing and In Nature (2001-2007)

Quantum computing in molecular magnets

M.N. Leuenberger and D. Loss, Nature **410**, 789-793 (2001)

University of Basel, Switzerland (1982 citations)

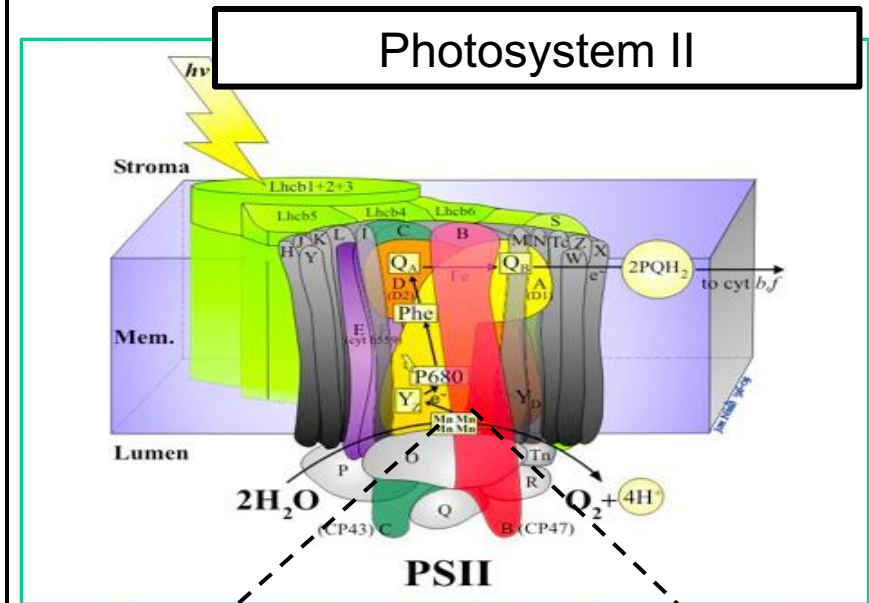
Shor and Grover demonstrated that a quantum computer can outperform any classical computer in factoring numbers and in



base by exploiting the quantum mechanics...Here we demonstrate the implementation of Grover's algorithm using molecular magnets, which consist of a **large spin**; their properties make them natural candidates for quantum computing systems. We show

theoretically **that molecular magnets can be used to build dense and efficient memory devices based on the Grover algorithm**...one

single crystal can serve as a storage unit of a dynamic random access memory device....Our proposal should be feasible using **molecular magnets Fe₈ and Mn₁₂**.



How and when did traditional quantum mechanics shift to density-functional theory?

The Achilles' heel of density-functional theory is in predicting electronic charge rearrangements.

A quick quantum trip from wavefunctions to densities

ATOM

Hydrogen Atom – One electron and one proton

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi(r, \theta, \varphi) = E\psi(r, \theta, \varphi)$$

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi}a_0^{3/2}} e^{-r/a_0}.$$

$$\text{Energy} = -13.6 Z^2/n^2 = 0.5/n^2 \text{ (atomic units)}$$

(Pauli 1926)

METAL

Free Electron Gas: Many electrons and positrons in box of volume V

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 - \cancel{\frac{e^2}{4\pi\epsilon_0 r}} \right) \psi(r, \theta, \varphi) = E\psi(r, \theta, \varphi)$$

$$\psi_k = \frac{1}{\sqrt{V}} e^{ik \cdot r}$$

$$\text{Energy} = k^2/2 \text{ (atomic units)}$$

Fill Fermi Sphere up to k_F

$$\text{Kinetic Energy} = aV^{-2/3}N^{5/3}$$

$$\text{Exchange Energy} = -bV^{-1/3}N^{4/3}$$

(Fermi 1926)

Hohenberg-Kohn-Sham 1964-1965

Energy depends on density

Note that N, the number of electrons, is the integral of the density over a box

Wigner (1934)

At low densities electrons in a positive background should form
an insulating Brillouin Zone

But what is the mechanism?

Certainly the Fermi-Model of the Free-Electron Gas does not
predict that

Is it because of exchange?

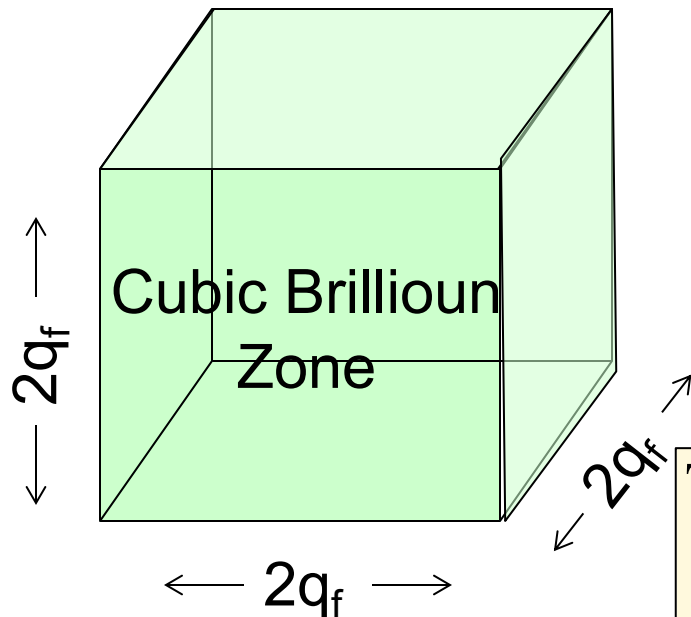
Is it because of something called “correlation”?

Wannier (1937): An insulator would fill a CUBE not a SPHERE
 Wannier liked atomic-like orbitals...as did Lowdin

$$\psi_k = \frac{1}{\sqrt{V}} e^{ik \cdot r}$$

Consider an Evenly Spaced Cubic Grid

$$A_n = (n_x, n_y, n_z)(\pi / q_f)$$



$$F_i(r) = \frac{\sum_k \psi_k(a_i) \psi_k(r)}{\sqrt{\rho(a_i)}}$$



This gives Wannier Functions (1937) of the form:

$$w(r - A_n) = \prod_x \frac{[\sin q_f(x - A_{nx})]}{\sqrt{q_f(x - A_{nx})}}$$

Question: Is it because of wave-particle duality that the original Wannier functions are Spherical Bessel Functions?

Pauling, Pople and Lennard Jones Thought Tetrahedral Orbitals were more physical

$$\psi_{2s} = \frac{e^{-r/2}}{\sqrt{32\pi}}(2-r)$$

$$\psi_{2px} = \frac{e^{-r/2}}{\sqrt{32\pi}}x$$

$$\psi_{2py} = \frac{e^{-r/2}}{\sqrt{32\pi}}y$$

$$\psi_{2pz} = \frac{e^{-r/2}}{\sqrt{32\pi}}z$$

This gives s-p hybrids of the form:

$$\varphi_{2sp} = [\psi_{2s} \pm \psi_{2px} \pm \psi_{2py} \pm \psi_{2pz}] / 2$$

SUMMARY

In the early years of quantum mechanics there was plenty of philosophizing about the use of localized vs delocalized descriptions of electronic states.

Question: How do we find how the energy depends on the density?

Answer: We ask Professor John Perdew

Which Theoretical Approximation is Qualitatively Different than all Others?

- Hartree-Fock approximation for quantum mechanical treatment of atoms and molecules.
- Multiconfiguration Self Consistent Field Approximation for quantum mechanical treatment of molecules.
- Nonrelativistic approximation to Schroedinger's equation for the electron in a hydrogen atom
- DFT approximation for quantum-mechanics of electrons in molecules and materials.
- Newton's equations for the classical treatment of planetary motion

**Atoms, molecules, solids, and surfaces: Applications of
the generalized gradient approximation for exchange and correlation**

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Generalized gradient approximation

Last two paragraphs (page 6685): Fully nonlocal alternatives to GGA's such as self interaction corrections^[39] or weighted-density approximations, [34,87,96] are considerably harder to implement especially for large systems. These fully nonlocal approximations have better asymptotic behavior of the atomic potential...In principle neither LSD or PW-GGA-II can describe the long-range part of the exchange-correlation hole.

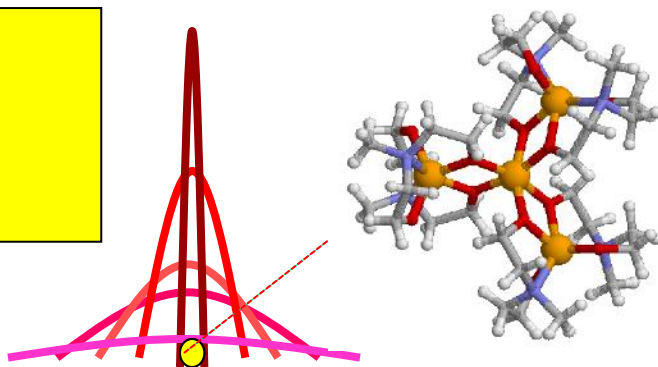
Methodology: $H\Psi=E\Psi$ (DFT+NRLMOL+SIC) ... FLOSIC

“Massively Parallel”: Pederson, Porezag, Kortus & Patton, Phys. Stat. Solidi B **217**, 197 (2000).

$$\text{Ansatz: } \Psi_{i\sigma} = \sum_{\sigma'} \Psi_{\sigma'}(\mathbf{r}) |\sigma'(\theta, \phi)\rangle$$

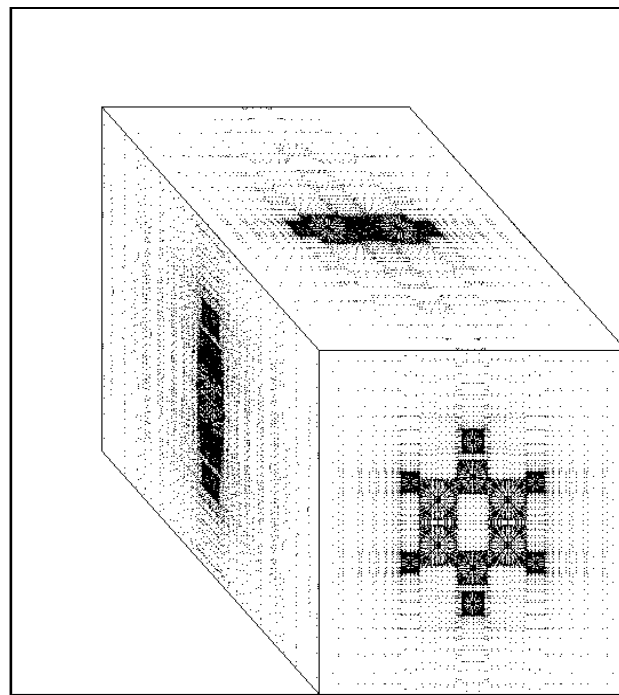
$$H \Psi_{i\sigma} = \lambda \Psi_{i\sigma}$$

$$\rho_{\sigma}(\mathbf{r}) = \sum_i |\Psi_{i\sigma}|^2$$

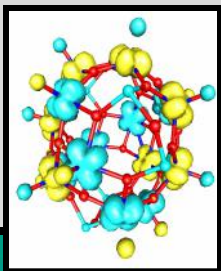


Early use of Gaussians: Lafon and Lin, PR 152, 579 1966)

Variational Mesh:
Pederson & Jackson,
PRB **41** (1990)

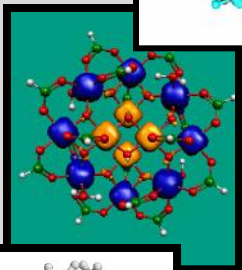


- Solve Schroedinger's equation as a function of spin orientation and total spin
 - Ferromagnetic?
 - Antiferromagnetic?
 - Most often Ferrimagnetic.
- Calculate Heisenberg Hamiltonian to obtain spin excitations.
- Determine changes in energy vs spin ordering, spin-orbit, and axes of quantization.

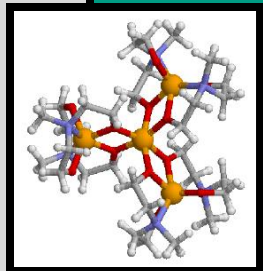


Successes within PBE-GGA for Molecular Magnets & challenges for SIC

V₁₅ -- Why are spin excitations too big?



Mn₁₂— MAE of neutral excellent but magnetism of anion depends localization of excess electron.



Fe₄ — Systematic investigation of electron transport requires correct electrode/island electronegativities.

Introducing
Fermi-Lowdin
Orbitals for

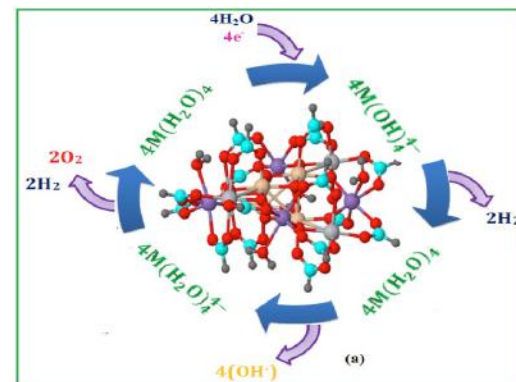
parameter free

Self Interaction
Correction

NRLMOL

Unitary Invariant

Size Extensive



A molecular magnet as a nano-laboratory?

What can we learn about DFT by Studying Delocalized Electrons and localization/delocalization transitions in Clusters?

CHEMICAL REVIEWS

REVIEW

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Challenges for Density Functional Theory

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SELF-INTERACTION ERROR



Variational Formulation of SIC-LSD (1984)

$$(H_{0\sigma} + V_{i\sigma}^{\text{SIC}})\phi_{i\sigma} = \sum_j \lambda_{ij} \phi_{j\sigma},$$

$$H_{0\sigma} = -\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) - [6\rho_{\sigma}(\mathbf{r})/\pi]^{1/3} + \int d\mathbf{r}' \rho(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1}$$

$$V_{i\sigma}^{\text{SIC}} = - \int d\mathbf{r}' \rho_{i\sigma}(\mathbf{r}) |\mathbf{r} - \mathbf{r}'|^{-1} + [6\rho_{i\sigma}(\mathbf{r})/\pi]^{1/3}.$$

$$\langle \phi_{\alpha} | V_{\alpha}^{\text{SIC}} - V_{\beta}^{\text{SIC}} | \phi_{\beta} \rangle = 0. \quad \text{Localization Equations}$$

- Localized Orbitals $\{ \phi \}$ Define Self-Interaction Correction
- Delocalized/Canonical Orbitals $\{ \psi \}$ are Kohn-Sham Orbitals
- Eigenstates of Lagrange Multiplier Matrix $\{ \lambda_{ij} \}$ define unitary transformation (**M**) between localized and KS orbital.
- Koopmans-Like Theorem for Eigenvalues.

Pederson, Heaton, Lin, JCP **80**, 1972 (1984), JCP **82**, 2688 (1984), JCP **82**, 2688 (1985), JCP **84**, Pederson and Lin JCP **88**, 1807 (1988)



Five Problems with the Same Solution

1. Can the concept of Wannier functions in condensed-matter physics [3], sp^n hybridized orbitals in atomic physics, localized molecular orbitals in molecular physics [4, 5] be formulated within a universal formulation?
2. Is there a means to generalize the concept of Wannier functions, which are currently only defined in insulating systems, to metallic systems?
3. Is there a way to create a unitary transformation, generally thought of as a discrete operator represented as an $N \times N$ matrix, that explicitly depends continuously on the one particle density matrix?
4. Is there a way to start with a set of Kohn-Sham orbitals and define a quasi-classical "electronic geometry" that is, in some way, the reciprocal lattice of the Kohn-Sham orbitals?
5. How does one re-formulate the self-interaction correction [8] to the density-functional approximation in a manner that assures the resulting energy is both size consistent and unitarily invariant?

How do we make an NxN unitary transformation depend on spin density?

A Fermi Orbital is normalized and captures all the density at its position and determines the exact exchange energy.

$$E_{\sigma}^x = -\frac{1}{2} \int d\vec{a} \int d\vec{r} \frac{|\sum_{\alpha} \psi_{\alpha\sigma}^*(\vec{r}) \psi_{\alpha\sigma}(\vec{a})|^2}{|\vec{r} - \vec{a}|} = -\frac{1}{2} \int d\vec{a} \rho(\vec{a}) \int d\vec{r} \frac{|\sum_{\alpha} \psi_{\alpha\sigma}^*(\vec{r}) \psi_{\alpha\sigma}(\vec{a})|^2}{\rho(\vec{a}) |\vec{r} - \vec{a}|} \quad (4)$$

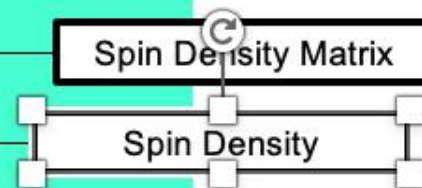
$$E_{\sigma}^x = -\frac{1}{2} \int d\vec{a} \rho(\vec{a}) \int d\vec{r} \left[\frac{\rho(\vec{r}, \vec{a})}{\sqrt{\rho(\vec{a})}} \right] \left[\frac{\rho(\vec{a}, \vec{r})}{\sqrt{\rho(\vec{a})}} \right] \frac{1}{|\vec{r} - \vec{a}|} = -\frac{1}{2} \int d\vec{a} \rho(\vec{a}) \int d\vec{r} \frac{|F_{\vec{a}}(\vec{r})|^2}{|\vec{r} - \vec{a}|} \quad (5)$$

Given a set of KS of orbitals and Electronic "Positions":

$\{\psi_1, \psi_2, \psi_3, \dots, \psi_N\}$ and $\{a_1, a_2, a_3, \dots, a_N\}$

Luken
1984

$$F_i(r) = \frac{\sum_{\alpha} \psi_{\alpha}(a_i) \psi_{\alpha}(r)}{\sqrt{\rho(a_i)}}$$



Lowdin-Orthogonalize. The Unitary Transformation between localized and Canonical Orbitals depends explicitly on density matrix!

MR Pederson thanks Richard Heaton for Mentioning this Possibility in August 1986

The Fermi Exchange Hole Provides the Exchange Energy Density per Electron for each Spin

$$E_x = \int \rho(a) d^3 a \int d^3 r \frac{\sum_{\alpha\beta} \psi_{\alpha}(r) \psi_{\alpha}(a) \psi_{\beta}(r) \psi_{\beta}(a)}{\sqrt{\rho(a)} \sqrt{\rho(a)} |r - a|}$$

In other terminology, this kernel is often written as $n_x(\mathbf{r}, \mathbf{r}')$

Communication: Self-interaction correction with unitary invariance in density functional theory

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(Received 7 February 2014; accepted 14 March 2014; published online 26 March 2014)

Improves HOMO level alignments relative to experiment

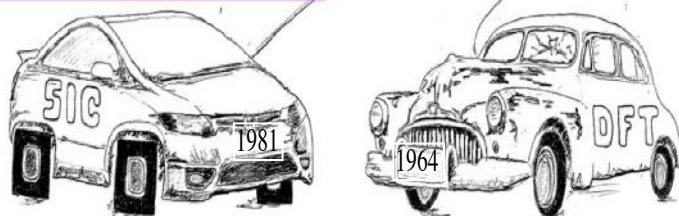
$$F_{i\sigma}(\mathbf{r}) = \frac{\sum_{\alpha} \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) \psi_{\alpha\sigma}(\mathbf{r})}{\sqrt{\sum_{\alpha} |\psi_{\alpha\sigma}(\mathbf{a}_{i\sigma})|^2}} = \frac{\rho_{\sigma}(\mathbf{a}_{i\sigma}, \mathbf{r})}{\sqrt{\rho_{\sigma}(\mathbf{a}_{i\sigma})}} \equiv \sum_{\alpha} T_{i\alpha}^{\sigma} \psi_{\alpha\sigma}(\mathbf{r}).$$

$$[H^{DFT} + V_i^{SIC}] \varphi_i(r) = \sum_j \lambda_j \varphi_j(r) \quad (1)$$

$$\langle \varphi_i | V_i^{SIC} - V_j^{SIC} | \varphi_i \rangle = 0 \quad (2)$$

$$H^{DFT} \psi_{\alpha}(r) = \epsilon_{\alpha} \psi_{\alpha}(r) \quad (3)$$

$$\rho(r) = 2 \sum_i |\varphi_i(r)|^2 = 2 \sum_{\alpha} |\psi_{\alpha}(r)|^2 \quad (4)$$



MCMAHUS 2014

1. For a trial set of KS orbitals $\{\psi_{\alpha\sigma}\}$ find N_{σ} centroids $\{\mathbf{a}_{1\sigma}, \mathbf{a}_{2\sigma}, \dots, \mathbf{a}_{N_{\sigma}\sigma}\}$ which provide a set of N_{σ} normalized linearly independent, but not orthogonal FO $\{F_{1\sigma}, F_{2\sigma} \dots F_{N_{\sigma}\sigma}\}$ which, from Eq. (4), will always lie in the space spanned by the KS orbitals.
2. Use Löwdin's method of symmetric orthonormalization^{31,38} to construct a set of localized orthonormal orbitals $\{\phi_{1\sigma}, \phi_{2\sigma}, \dots, \phi_{N_{\sigma}\sigma}\}$ and construct the SIC-DFT energy of Eq. (1) from the set of FOs. This set is a unitary transformation on the KS orbitals.
3. Minimize the SIC-DFT energy as a function of the KS orbitals and the classical centroids of the FOs.

Original Self-Interaction Correction Was Not Unitarily Invariant

Communication: Self-interaction correction with unitary invariance in density functional theory

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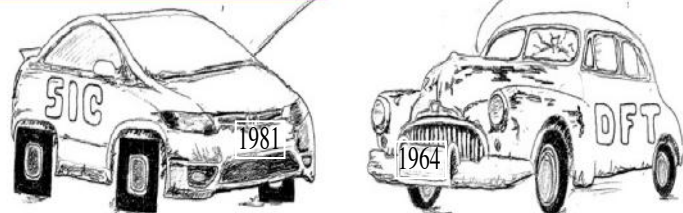
Improves HOMO level alignments relative to experiment

Systematic Improvement for π -bonded systems

$$[H^{DFT} + V_i^{SIC}] \varphi_i(r) = \sum_j \lambda_j \varphi_j(r) \quad (1)$$

$$\langle \varphi_i | V_i^{SIC} - V_j^{SIC} | \varphi_i \rangle = 0 \quad (2)$$

$$H^{DFT} \psi_\alpha(r) = \varepsilon_\alpha \psi_\alpha(r) \quad (3)$$



$$\rho(r) = 2 \sum_i |\varphi_i(r)|^2 = 2 \sum_\alpha |\psi_\alpha(r)|^2 \quad (4)$$

McMANUS 2014

Mol.	LSD (PW92)	GGA (PBE)	SIC- LSD	FSIC- LSD	Expt.
N ₂	11.58	10.49	10.89	9.80	9.84
O ₂	7.62	6.30	5.77	4.80	5.12
CO	12.94	11.65	12.02	11.00	11.32
CO ₂	20.57	18.16	18.29	16.88	17.00
C ₂ H ₂	19.93	18.01	19.81	18.93	17.52
LiF	6.75	6.01	6.17	5.61	6.03
H ₂	4.91	4.51	4.97	4.97	4.77
Li ₂	1.03	1.06	1.04	1.02	1.06
CH ₄	20.06	18.24	20.25	20.23	18.21
NH ₃	14.56	13.05	14.21	14.24	12.88
H ₂ O	11.64	10.27	10.68	10.71	10.10
MAE	1.62	0.41	0.94	0.62	

Original Self-Interaction Correction Was Not Unitarily Invariant

Fermi orbital derivatives in self-interaction corrected density functional theory: Applications to closed shell atoms

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Optimizing the Electronic Geometry / Reciprocal Lattice

$$\frac{dE^{SIC}}{da_m} = \sum_k \{ \langle \frac{d\phi_k}{da_m} | V_k^{SIC} | \phi_k \rangle + \langle \phi_k | V_k^{SIC} | \frac{d\phi_k}{da_m} \rangle \},$$

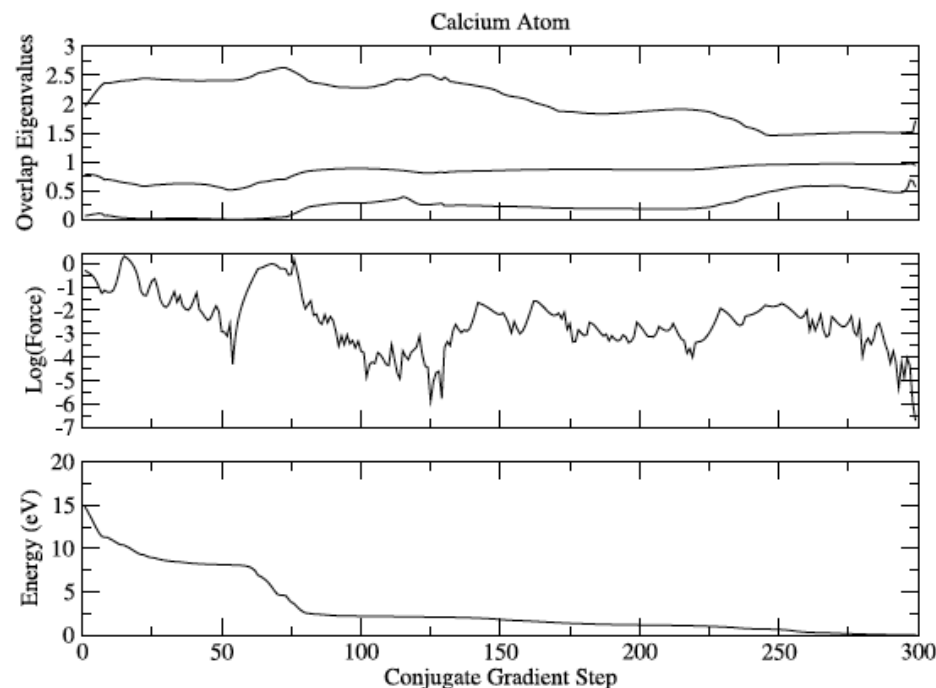
$$\begin{aligned} \frac{dE^{SIC}}{da_m} &= \sum_{kl} \{ \langle \frac{d\phi_k}{da_m} | \phi_l \rangle \langle \phi_l | V_k^{SIC} | \phi_k \rangle \\ &\quad + \langle \phi_k | V_k^{SIC} | \phi_l \rangle \langle \phi_l | \frac{d\phi_k}{da_m} \rangle \}, \end{aligned}$$

$$\frac{dE^{SIC}}{da_m} = \sum_{kl} \epsilon_{kl}^k \{ \langle \frac{d\phi_k}{da_m} | \phi_l \rangle + \langle \phi_l | \frac{d\phi_k}{da_m} \rangle \},$$

$$\begin{aligned} \frac{dE^{SIC}}{da_m} &= \sum_{kl} \epsilon_{kl}^k \{ \langle \frac{d\phi_k}{da_m} | \phi_l \rangle + \langle \phi_l | \frac{d\phi_k}{da_m} \rangle \\ &\quad + \langle \frac{d\phi_l}{da_m} | \phi_k \rangle - \langle \frac{d\phi_l}{da_m} | \phi_k \rangle \}, \end{aligned}$$

$$\frac{dE^{SIC}}{da_m} = \sum'_{kl} \epsilon_{kl}^k \{ \langle \frac{d\phi_k}{da_m} | \phi_l \rangle - \langle \frac{d\phi_l}{da_m} | \phi_k \rangle \}$$

$$\equiv \sum'_{kl} \epsilon_{kl}^k \Delta_{lk,m},$$



Works well IF an initial geometry can be guessed Is it possible always?

sp^3 Hybrids: A subclass of Fermi-Lowdin Orbital Sets

$$\psi_{2s} = \frac{e^{-r/2}}{\sqrt{32\pi}}(2-r)$$

$$\psi_{2px} = \frac{e^{-r/2}}{\sqrt{32\pi}}x$$

$$\psi_{2py} = \frac{e^{-r/2}}{\sqrt{32\pi}}y$$

$$\psi_{2pz} = \frac{e^{-r/2}}{\sqrt{32\pi}}z$$

Find Tetrahedron with Vertices such that:

$$\psi_{2s} = \psi_{2px} = \psi_{2py} = \psi_{2pz}$$
$$|x| = |y| = |z| = 2 - r$$

$$F_i(r) = \frac{\sum_{\alpha} \psi_{\alpha}(a_i) \psi_{\alpha}(r)}{\sqrt{\rho(a_i)}}$$

This gives s-p hybrids of the form:

$$\varphi_{2sp} = [\psi_{2s} \pm \psi_{2px} \pm \psi_{2py} \pm \psi_{2pz}] / 2$$

Edminston-Ruedenberg, Boys, McWeeny, SIC-LSD Orbitals are Subclasses of Fermi-Lowdin Orbital Sets for Molecular Systems (Example: N₂)

$$F_i(r) = \frac{\sum_{\alpha} \psi_{\alpha}(a_i) \psi_{\alpha}(r)}{\sqrt{\rho(a_i)}}$$

ER: Maximize Self Coulomb Repulsion

Boys/McWeeny/Vanderbilt: Minimize $\langle r^2 \rangle$

SIC-LSD: Minimize SIC Energy (Pederson/Kluepfel)

Lowdin Orbitals: Agrees with atom-centered FO

NOT COMPLEX BUT
SYMMETRY PRESERVING

This gives three doubly occupied banana bonds:

$$\varphi_n = \frac{1}{\sqrt{3}} \left[\psi_{2\sigma_g} - \sqrt{3} \left\{ \cos\left(\frac{2n\pi}{3}\right) \psi_{2\pi_x} + \sin\left(\frac{2n\pi}{3}\right) \psi_{2\pi_y} \right\} \right]$$

$$n = -1, 0, +1$$

and two doubly occupied lone-pair orbitals :

$$\varphi_{2sa/2sb} = \frac{1}{\sqrt{2}} [\psi_{3\sigma_g} \pm \psi_{2\sigma_u}]$$

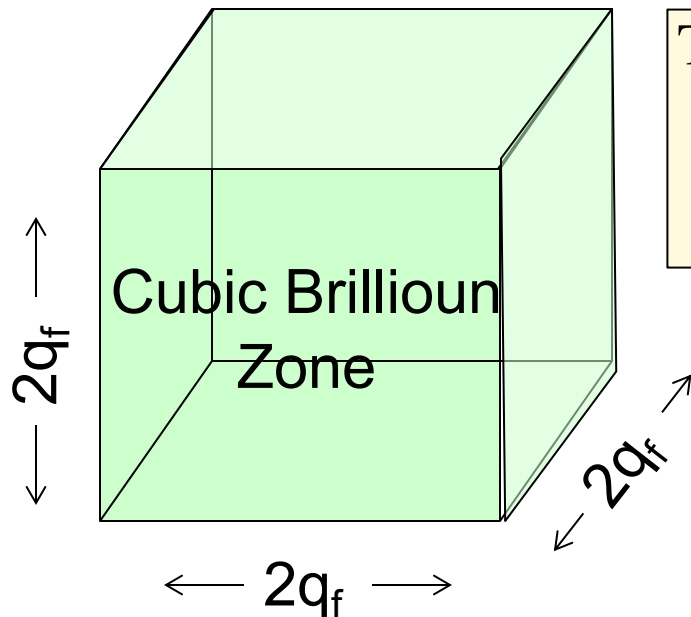
$$\psi_k = \frac{1}{\sqrt{V}} e^{ik \cdot r}$$

Consider an Evenly Spaced Cubic Grid

$$A_n = (n_x, n_y, n_z)(\pi / q_f)$$

This gives Wannier Functions (1937) of the form:

$$w(r - A_n) = \prod_x \frac{[\sin q_f(x - A_{nx})]}{\sqrt{q_f}(x - A_{nx})}$$



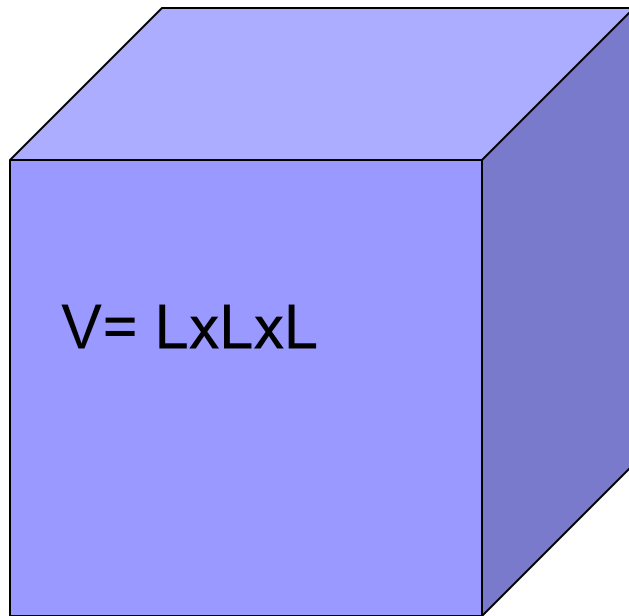
$$F_i(r) = \frac{\sum_k \psi_k(a_i) \psi_k(r)}{\sqrt{\rho(a_i)}}$$

Fermi
Orbital

The square of the “Fermi Orbital” is the Fermi Exchange Hole, integrated over all space is the exchange energy of a single determinant.

Applications of SIC to the Uniform Electron Gas

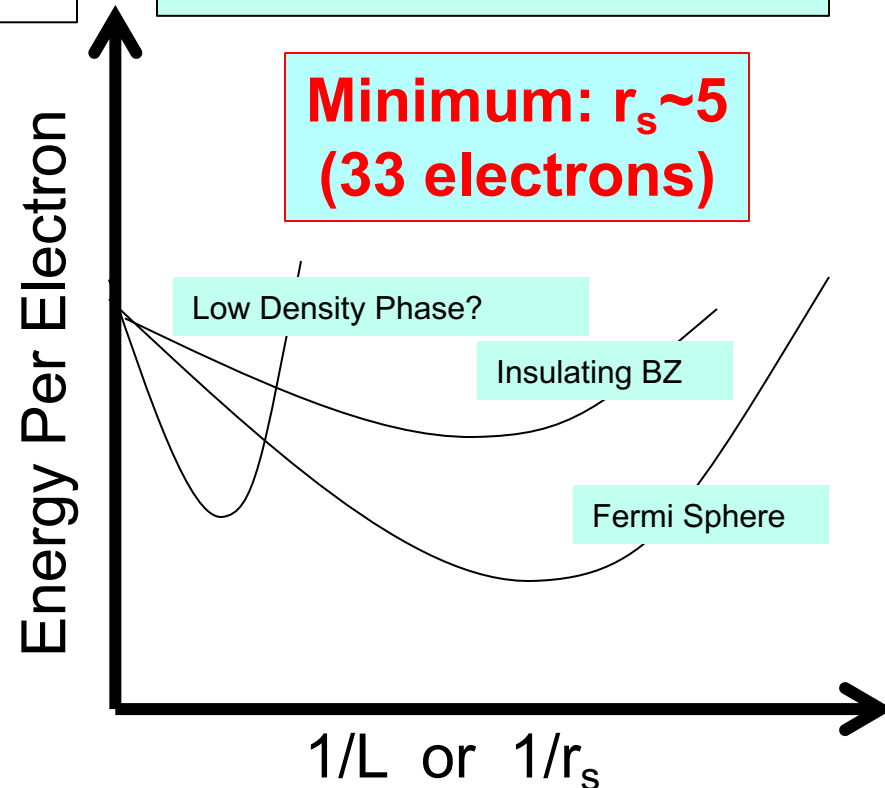
- Put electrons into finite box
- Choose some set of plane wave states.
- All sets lead to uniform density.
- Extrapolate to infinite number of electrons.



Real Space

Curvature and slope at $1/L=0$ depends on:

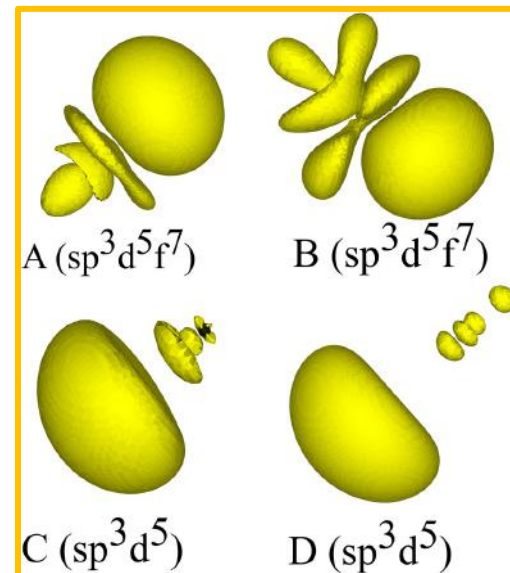
- Number of electrons
- Fermi surface shape.
- Level of correlation.
- **Orbitals used for SIC**



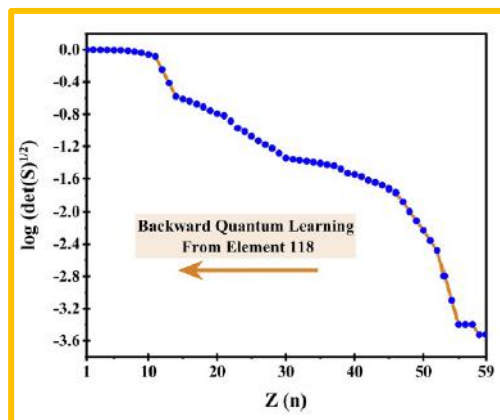
Rather than start at Z=1 and work our way up, lets start with Oganesson (Z=118) and work downward.

- Kao *et al* [JCP **247** 164107 (2017)] showed that the FOD-radius is predicted reasonably well by choosing a radius, that maximizes the value of the orbital amplitude.
- If we know which M spherical-harmonics for a given principal quantum number are present we can find M points that maximize the value of the determinant of spherical harmonics. $M=N^2$ for rare-gases (N =principal quantum number)
- For a closed shell, such as Rn or Og, this means we find the 16 points that maximize the value of the Slater Determinant on a sphere of unit radius.








$$\underline{W} = \begin{bmatrix} Y_{00}(\hat{a}_1) & Y_{1,-1}(\hat{a}_1) & Y_{1,0}(\hat{a}_1) & Y_{1,1}(\hat{a}_1) & \cdots & Y_{n-1,-n+1}(\hat{a}_1) & \cdots & Y_{n-1,n-1}(\hat{a}_1) \\ Y_{00}(\hat{a}_2) & Y_{1,-1}(\hat{a}_2) & Y_{1,0}(\hat{a}_2) & Y_{1,1}(\hat{a}_2) & \cdots & Y_{n-1,-n+1}(\hat{a}_2) & \cdots & Y_{n-1,n-1}(\hat{a}_2) \\ \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \cdots & \vdots \\ Y_{00}(\hat{a}_{n^2}) & Y_{1,-1}(\hat{a}_{n^2}) & Y_{1,0}(\hat{a}_{n^2}) & Y_{1,1}(\hat{a}_{n^2}) & \cdots & Y_{n-1,-n+1}(\hat{a}_{n^2}) & \cdots & Y_{n-1,n-1}(\hat{a}_{n^2}) \end{bmatrix}_{n^2 \times n^2}.$$



Universal and
permutable spdf
hybrids?



Downward quantum learning from element 118: Automated generation of Fermi-Löwdin orbitals for all atoms

Mark R. Pederson,^{1,a}  Alexander I. Johnson,¹  Kushantha P. K. Withanage,¹ Sherab Dolma,¹ 
Gustavo Bravo Flores,¹  Zahra Hooshmand,¹  Kusal Khandal,¹ Peter O. Lasode,¹ Tunna Baruah,¹ 
and Koblar A. Jackson² 

$$\underline{S}_{ij} = \langle F_i | F_j \rangle = \frac{\sum_{\alpha} \psi_{\alpha}(\mathbf{a}_i) \psi_{\alpha}(\mathbf{a}_j)}{\sqrt{\rho(\mathbf{a}_i) \rho(\mathbf{a}_j)}} = \frac{\sum_{\alpha} W_{\alpha i} W_{\alpha j}}{\sqrt{\rho(\mathbf{a}_i) \rho(\mathbf{a}_j)}},$$

$$\sqrt{\rho(\mathbf{a}_i)} \underline{S}_{ij} \sqrt{\rho(\mathbf{a}_j)} = \sum_{\alpha} W_{\alpha i} W_{\alpha j},$$

$$\sum_{pq} \sqrt{\rho(\mathbf{a}_p)} \delta_{ip} \underline{S}_{pq} \delta_{qj} \sqrt{\rho(\mathbf{a}_j)} = \sum_{\alpha} W_{\alpha i} W_{\alpha j}.$$

$$\underline{P} \times \underline{S} \times \underline{P}^T = \underline{W} \times \underline{W}^T,$$

$$\det(\underline{P})^2 \det(\underline{S}) = \det(\underline{W})^2.$$

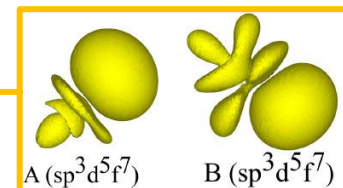
A solution exists if a HF Slater
Determinant is non-zero somewhere!

- An N-electron solution provides at least one solution for the N-1, N-2, N-3, ..., 1 electron problem.
- An N-electron solution may spawn up to $2^N - 1$ solutions for systems with fewer electrons.
- Should the FLOSIC FODs be instead defined by points in $3N$ -dimensional space that maximizes the KS SD?
 - Faster?
 - Less over-bound?
 - Less noded?

Table of Starting Points for Closed Shell Noble Gas Atoms Z=2 to 118

TABLE I. Reasonable starting FODs and radii for noble gas atoms. Based on Linnett-like structures for inverting FOD-positions for opposite spins,³⁰ the highest symmetry for the spin-densities in the Ne and Ar is T_d , while the symmetry of the density can be O_h . Similarly, the highest symmetry for the spin-density of Kr–Og is C_{3v} , while the symmetry for the spin-density can be D_{3d} . A variety of lower point group symmetries that would be compatible with incomplete shells of angular momenta are possible in other ions. Illustrations for a member from families A, B, C, and D are provided in Fig. 2.

Config.	a_x	a_y	a_z	Sym	N _{equiv}	R_{Og}	R_{Rn}	R_{Xe}	R_{Kr}	R_{Ar}	R_{Ne}	R_{He}
s	0.0000	0.0000	0.0000	N/A	1	0.0000	0.000	0.00	0.00	0.00	0.00	0.00
sp	0.5774	0.5774	0.5774	T_d	4	0.0356	0.074	0.12	0.19	0.44		
spd	1.0000	−0.0000	−0.0000	T_d	6	0.1012	0.18	0.33				
spd	−0.4083	−0.4083	0.8165	C_{3v}	3	0.1012	0.18	0.33				
spdf (A)	−0.5774	−0.5774	0.5774	T_d	4	0.2808	0.43					
spdf (B)	−0.8789	−0.3373	−0.3373	T_d	12	0.2808	0.43					
spdf	−0.8704	−0.3482	−0.3482	T_d	12	0.6138						
spdf	−0.5774	−0.5774	0.5774	T_d	4	0.6138						
spd (C)	1.0000	−0.0000	−0.0000	T_d	6	0.9045	1.00	0.85	0.60			
spd (D)	0.4082	0.4082	−0.8165	C_{3v}	3	0.9045	1.00	0.85	0.60			
sp	−0.5774	0.5774	0.5774	T_d	4	2.4656	2.47	2.28	1.92	1.68	1.07	



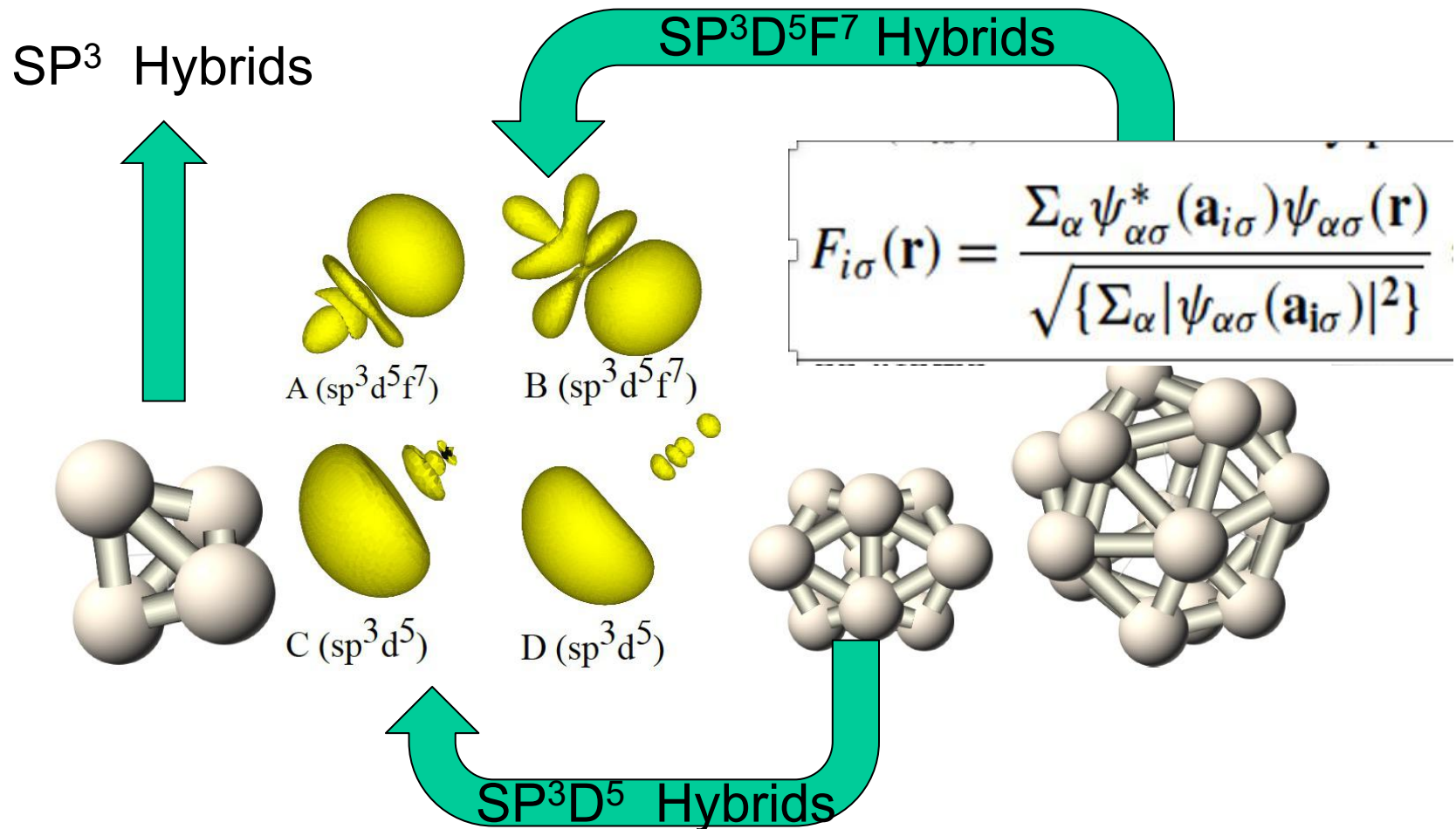
He	1
Ne	1-4
Ar	1-4-4
Kr	1-4-9-4
Xe	1-4-9-9-4
Rn	1-4-9-16-9-4
Og	1-4-9-16-16-9-4

Atom	LDA	FLOSIC	Expt.	Atom	LDA	FLOSIC	Expt.
Ar	10.38	16.71	15.76	Ne	13.54	24.35	21.56
Cl	8.30	14.16	12.97	F	10.34	20.20	17.42
S	6.24	11.91	10.36	O	7.40	16.39	13.62
P	6.34	10.95	10.49	N	8.39	15.76	14.53
Si	4.65	8.89	8.15	C	6.11	12.46	11.26
Al	3.05	6.98	5.98	B	4.10	9.36	8.30
Mg	4.78	8.49	7.65	Be	5.59	10.84	9.32
Na	3.11	6.46	5.14	Li	3.17	6.92	5.39
Rn	7.98	11.90	10.75	Og	7.44	11.20	8.9
At	6.68	10.52	9.22	Ts	5.99	9.89	7.70
Po	5.35	9.19	8.42	Lv	4.95	8.67	8.64
Bi	5.40	8.70	7.29	Mc	5.11	8.42	5.68
Pb	4.18	7.35	7.42	Fl	3.96	7.25	8.53
Tl	2.96	6.10	6.11	Nh	2.83	6.07	7.31

From N-electron calculation:

- Remove “HOMO FOD”
- Remove matching KS-Orbital
- Perform (N-1)-electron calculation.

Fermi-Lowdin Orbitals in Rare-Gas Atoms and their Reciprocal Lattice



Each Set of Orbitals is Defined by Reciprocal Polyhedra



Self-interaction Correction for Solvated Anions



M.R. Pederson, Kushantha K. P. Withanage, Yoh Yamamoto, Priyanka B. Shukla,
Alexander I. Johnson, Zahra Hooshmand Gharehbagh, Karl Johnson,
Rajendra R. Zope, Tunna Baruah, Juan E. Peralta, Der-you Kao, and Koblar A. Jackson.

To appear in J. Chem Physics
Accepted 20 September 2023



Anions in DFT

- Anions are not bound in DFA calculations due to self-interaction error.
e.g.: $\text{OH}^- \rightarrow$ Positive HOMO (+2.75 eV)
- Interaction of anions with other molecules become unphysical

H_2O : LUMO = -0.62 eV

OH^- : HOMO = +2.75 eV

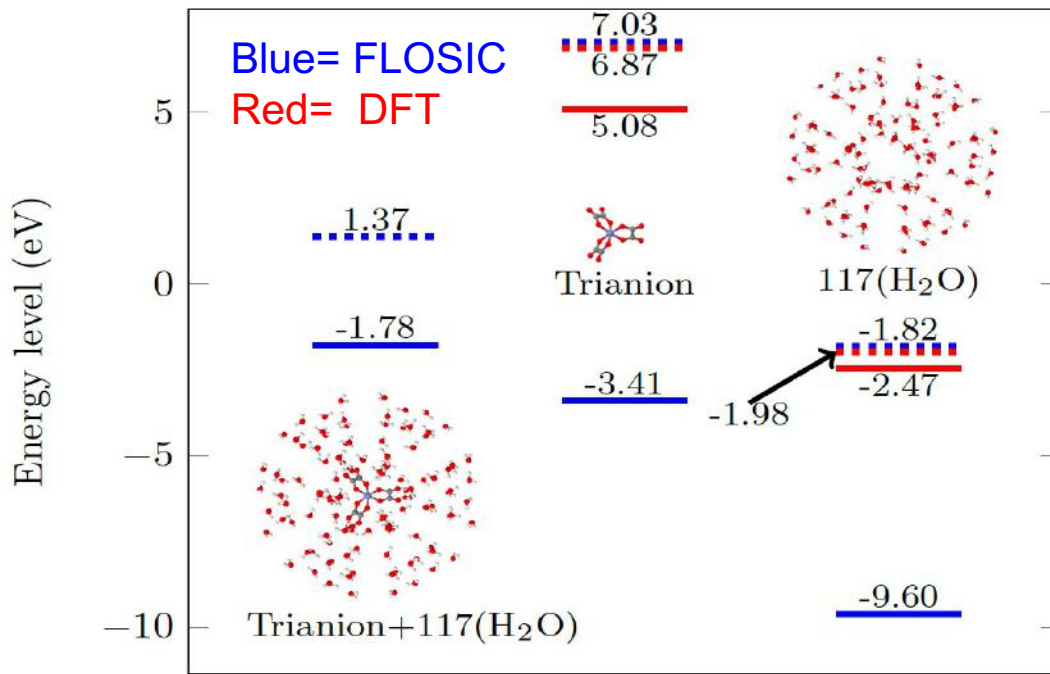


But interactions with anions can be found in nature and we need to model them !

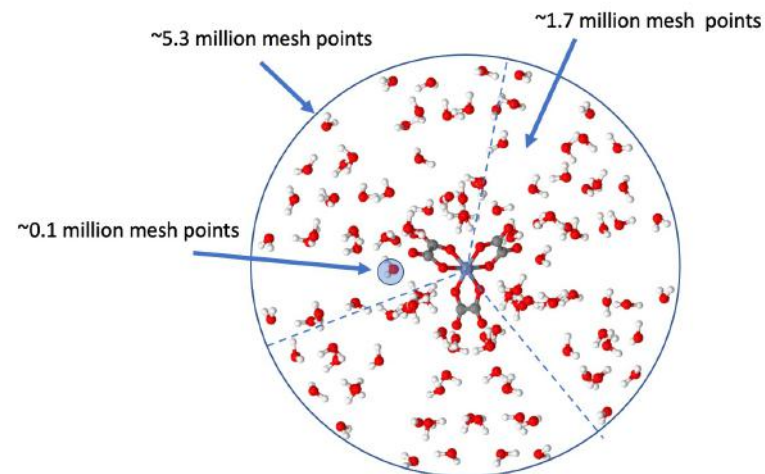
Tri-anion+117(H₂O): FLOSIC

Pederson et al., To be submitted (2023)

Homo (solid) and LUMO (dotted)



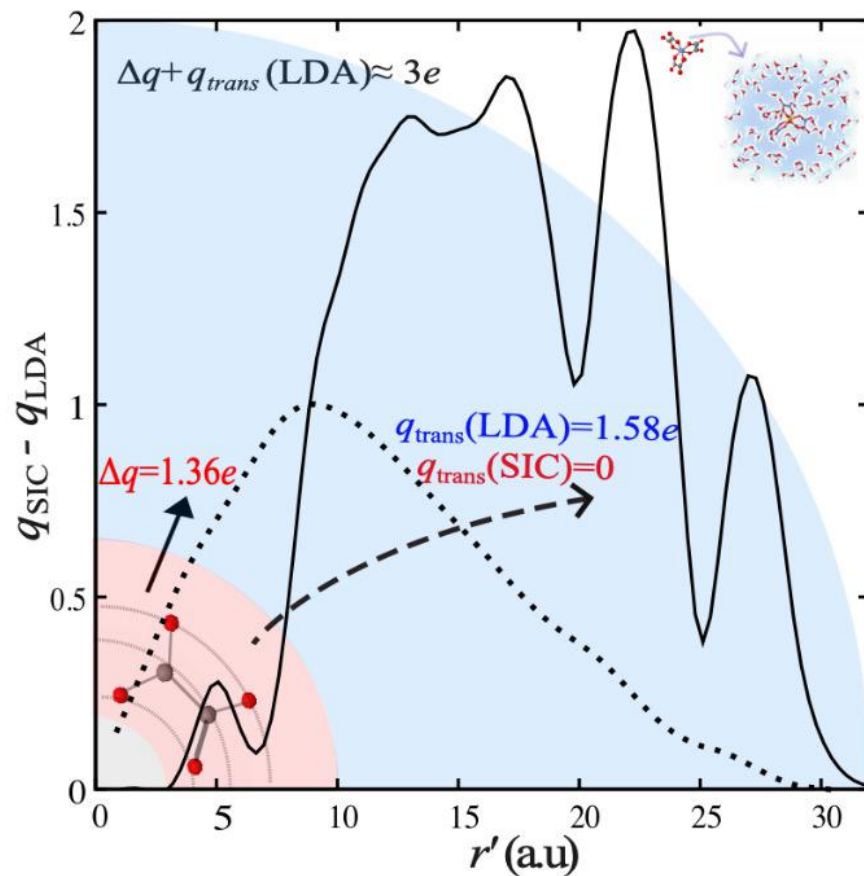
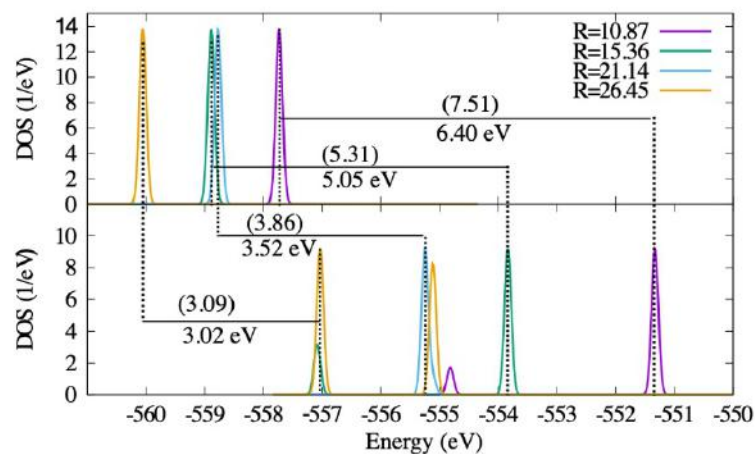
Achieving DFT-efficiency
requires rewriting codes



- FLOSIC predicts bound HOMOs for isolated Trianion and Trianion+117(H₂O).
- HOMO of Trianion+117(H₂O) is lower than LUMO of water
 - No charge transfer from Trianion to water

Factor of 125 increase
in efficiency due to
sparsity of FLOSIC
formulation.

Oxygen 1s x-ray core-level spectra to determine charge of trianion



Distance of Water Droplet Center

System	DFA	$\lambda(HOMO)$	$\lambda(LUMO)$	$\lambda(Cr_{1s})$
H ₂ O	LDA	-0.269	-0.025	
H ₂ O	GGA	-0.264	-0.025	
H ₂ O	Hybrid	-0.431	0.055	
H ₂ O	FLOSIC	-0.542	-0.014	
(H ₂ O) ₁₁₇	FLOSIC	-0.353	-0.067	
(H ₂ O) ₁₁₇	LDA	-0.091	-0.073	
Cr(C ₂ O ₄) ₃ ⁻³	LDA	+0.187	+0.253	-213.573
Cr(C ₂ O ₄) ₃ ⁻³	FLOSIC	-0.125	0.258	-219.921
Cr(C ₂ O ₄) ₃ (H ₂ O) ₃ ^{-1.4}	LDA	-0.073	-0.073	
Cr(C ₂ O ₄) ₃ (H ₂ O) ₃ ⁻³	LDA	+0.157	+0.228	-213.602
Cr(C ₂ O ₄) ₃ (H ₂ O) ₃ ⁻³	Hybrid	-0.032	0.316	-215.981
Cr(C ₂ O ₄) ₃ (H ₂ O) ₃ ⁻³	FLOSIC	-0.136	0.236	-219.896
Cr(C ₂ O ₄) ₃ ⁻³ (H ₂ O) ₁₁₇	Hybrid	0.055	0.119	
Cr(C ₂ O ₄) ₃ ⁻³ (H ₂ O) ₁₁₇	FLOSIC	-0.066	0.051	-219.924
CrCl ₃	LDA	-0.234	-0.205	-213.995
CrCl ₃	Δ_{SCF}^{LDA}			-218.642
CrCl ₃	Δ_{SCF}^{GGA}			-219.173
CrCl ₃	$\Delta_{SCF}^{HF}(LDA)$			-219.672
CrCl ₃	$\Delta_{SCF}^{HF}(GGA)$			-219.712
CrCl ₃	FLOSIC	-0.497	-0.250	-220.333
Cr(1s)	NIST-Vapor			-220.310
CrCl ₃	Expt			-220.494

Complex ?

In absence of gap or spin-orbit, FLOSIC always finds real localized orbitals.

We must not throw out unitary invariance.

Complex Local Orbitals in PZ-Zunger with Localization Equations can't be worse so it must be better!



Communication: Self-interaction correction with unitary invariance in density functional theory, M.R. Pederson, A. Ruzsinszky and J. P. Perdew, J. Chem. Phys. **140**, 121103 (2014).

Effect of Complex Optimal Orbitals on Atomization Energies with the Perdew-Zunger Self-Interaction Correction to DFT, S. Lehtola, E.O. Jonsson and H. Jonsson, J. Chem. Theory Computer **12** 4296-4306 (2016) [Plus much earlier]

SIC and FLOSIC: Can/Must/Should energy-minimizing local orbitals be complex?

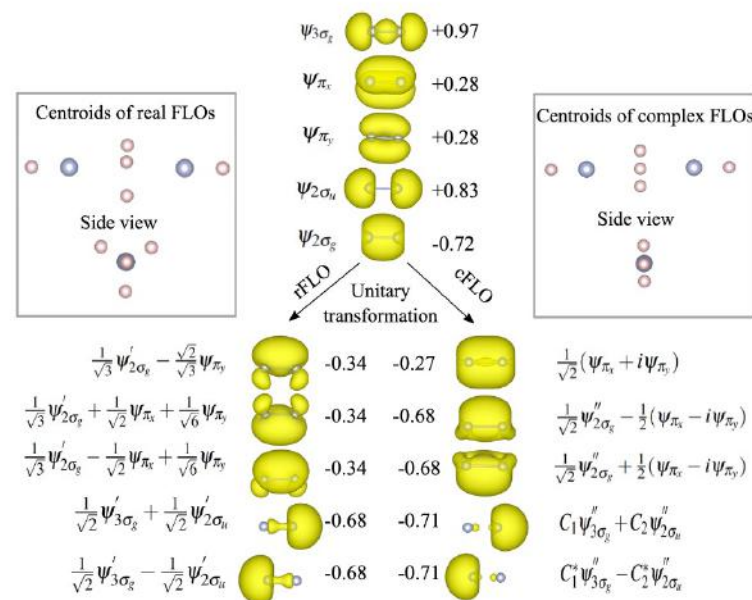


Pederson, Heaton Lin, JCP 1984: For N_2 , at equilibrium, complex π_u -orbitals provide exchange-correlation energy density with full cylindrical symmetry.

Kluepfel, Kluepfel, Jonsson PRB 84 050501R (2011): Complex orbitals are important in all systems for energy minimization.

Complex Fermi–Löwdin orbital self interaction correction, **K. Withanage**, K.A. Jackson, M.R. Pederson, **Communication**, J. Chem. Phys. **156** 221103 (2022).

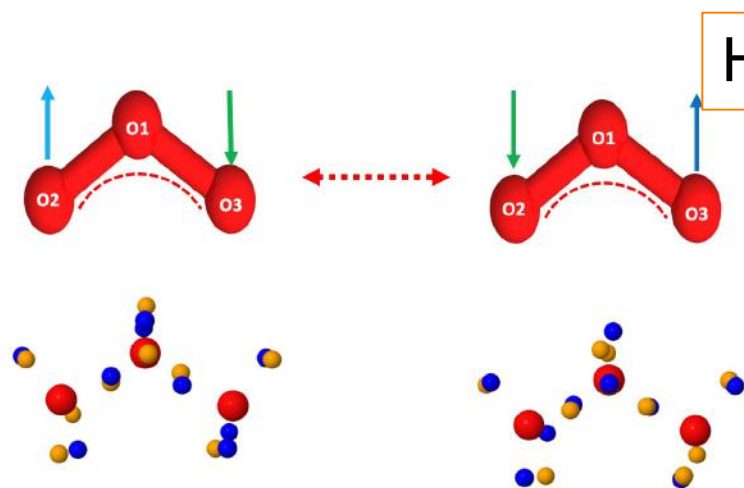
- cFLOs in atoms are more spherical.
- cFLOs in dimers, with PW91, do not necessarily choose cylindrical symmetry.
- **cFLOs are NOT primary cause for spin-symmetry breaking in stretched bond limits. Other mechanism needed.**
- Self-exchange correlation drives choice of cFLOs.



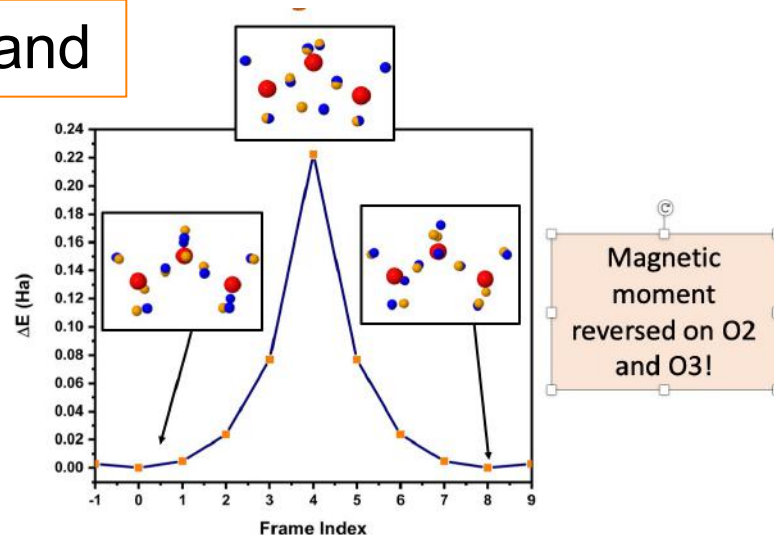
Are broken symmetry methods allowed/needed for Ozone?

DFA: Yes/No

FLOSIC: Yes/Yes



Hooshmand



Singlet-Triplet Splitting (PBE-GGA)

EXPT (Arnold)	1.18 eV
GGA-PBE:	1.10 eV

Goddard Biradical	0.93 eV
FLOSIC BiRadical	0.70 eV
CASSCF (Tsuneda)	0.90 eV

Xantheas and Miliordos
(CASSCF 2014)
18 percent bi-radical

Hooshmand and Pederson
(FOD-CI 2022)
34 percent bi-radical

Two degenerate determinants needed to exactly represent H_2 molecule at infinite separation. **BUT INFINITE CHOICES!**

See early discussion by Gunnarsson, Harris, Jones (1977)

MARK PEDERSON'S
EXPLANATION

$$\Psi = \frac{1}{\sqrt{2}} [\sigma_g^\uparrow \sigma_g^\downarrow - \sigma_u^\uparrow \sigma_u^\downarrow] \quad \text{HYDROGEN IN THE STRETCHED BOND LIMIT}$$

$$\sigma_g = \frac{1}{\sqrt{2}} [\phi_A + \phi_B]$$

$$\Psi = \frac{1}{2\sqrt{2}} [(\phi_A^\uparrow + \phi_B^\uparrow)(\phi_A^\downarrow + \phi_B^\downarrow) - (\phi_A^\uparrow - \phi_B^\uparrow)(\phi_A^\downarrow - \phi_B^\downarrow)]$$

$$= \frac{1}{2\sqrt{2}} [\phi_A^\uparrow \phi_A^\downarrow + \phi_B^\uparrow \phi_A^\downarrow + \phi_A^\uparrow \phi_B^\downarrow + \phi_B^\uparrow \phi_B^\downarrow - \phi_A^\uparrow \phi_A^\downarrow + \phi_B^\uparrow \phi_A^\downarrow + \phi_A^\uparrow \phi_B^\downarrow - \phi_B^\uparrow \phi_B^\downarrow]$$

symmetry breaking terms survive

ionic terms cancel one another

$$\Psi = \frac{1}{\sqrt{2}} [\sigma_g^\uparrow \sigma_g^\downarrow - \sigma_u^\uparrow \sigma_u^\downarrow] = \frac{1}{\sqrt{2}} [\phi_B^\uparrow \phi_A^\downarrow + \phi_A^\uparrow \phi_B^\downarrow]$$

off diagonal "correlation energy" is large and negative

off diagonal "correlation energy" is \neq ZERO!

The total energy of Ψ is the same in both cases. The negative correlation energy for the symmetrized case cancels the ionic (coulomb) and exchange, $\phi_B^\uparrow \phi_A^\downarrow$ & $\phi_A^\uparrow \phi_B^\downarrow$ have the same energy & represent the correct stretched bond limit. Broken symmetry solutions have exact same "energy since off diagonal correlation energy" is ZERO!

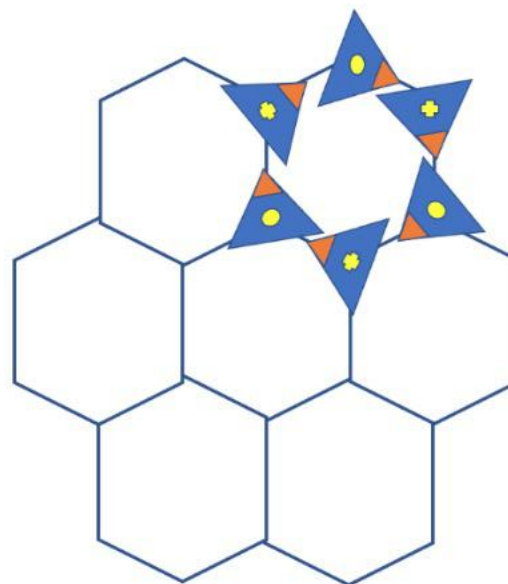
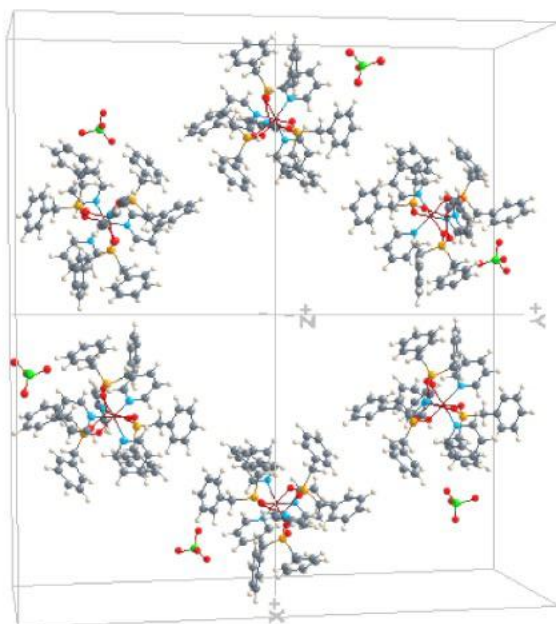
NB: Ordering important! Pair terms represent antisymmetric SDs!

Restoring Symmetry and Enhancing Exchange in Anisotropic Hexagonal Quantum-Magnet Arrays

Mark R. Pederson and Zahra Hooshmand¹ and Shuanglong Liu and Hai-Ping Cheng²

¹*Department of Physics, University of Texas at El Paso, TX 79968, USA*

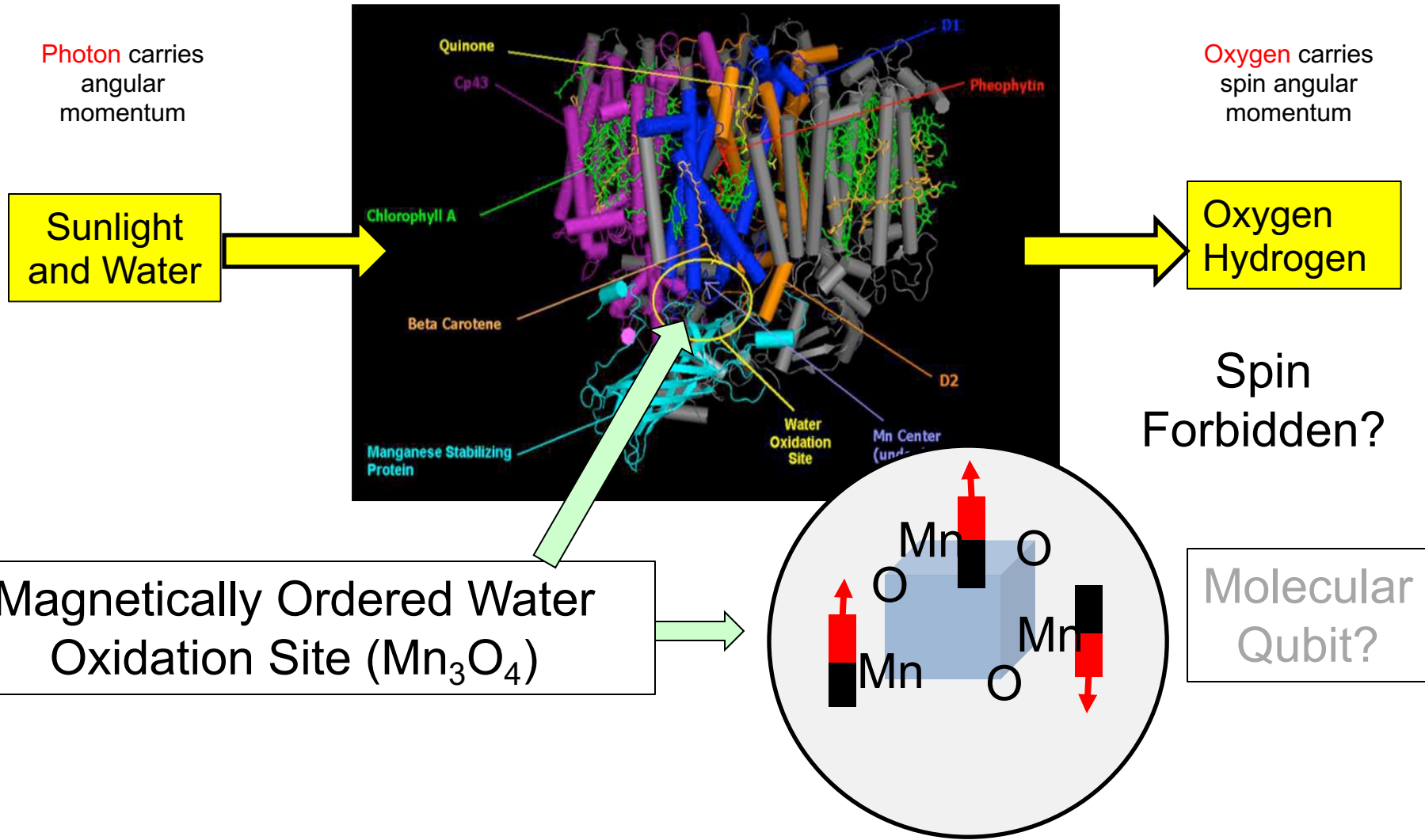
²*Department of Physics, University of Florida, Gainesville FL 32612, USA*



FLOSIC at Five: Challenges, Simplifications and Complexities

Mark R. Pederson

Pondering Photocatalytic Water Oxidation

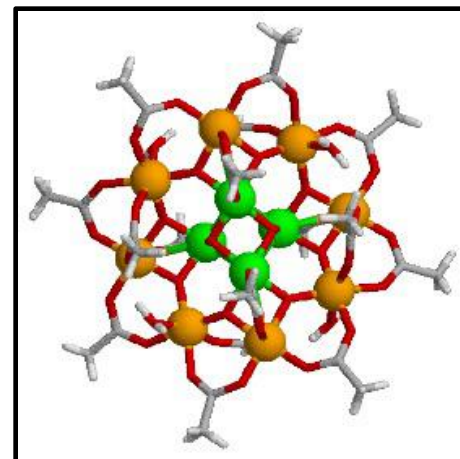
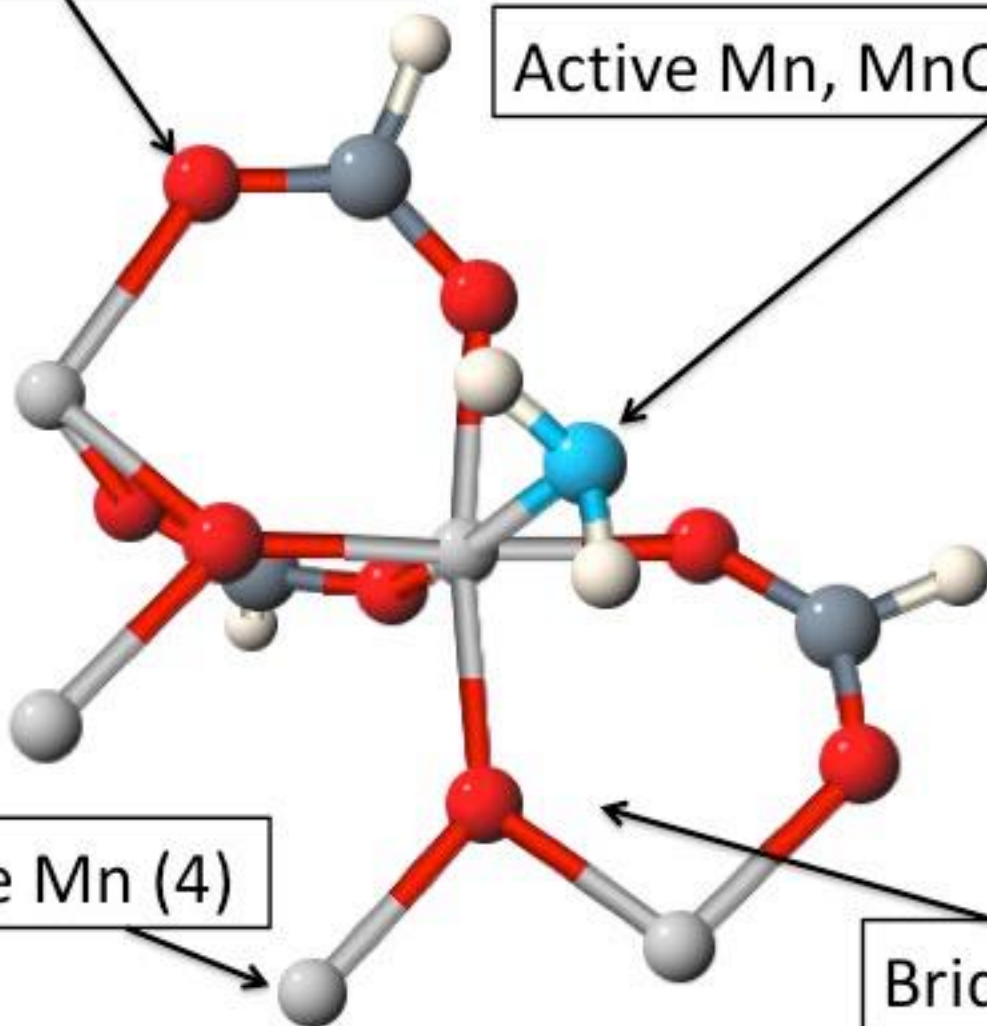


Formate Groups (3)

Active Mn, MnO Bond and HOH

Passive Mn (4)

Bridge Oxygens (2)



FLOSI FOR UNDERSTAND WATER SPLITTING

J. Batool, T.Hahn and M.R. Pederson, Magnetic Signatures of Hydroxyl- and Water- Terminated Neutral and Tetra-Anionic Mn₁₂-Acetate, J.Comput. Chem. **40** 2301 (2019).

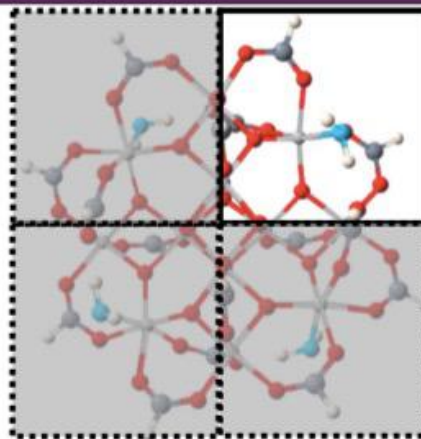
Expt: Mn₁₂-Acetate (Christou, *et al.*)

- Molecule exists in three anionic states.
- Believed to decompose as tetra-anion.

Park, *et al.*: Can magnetic signals from Mn₁₂-Acetate be used to determine charge states?

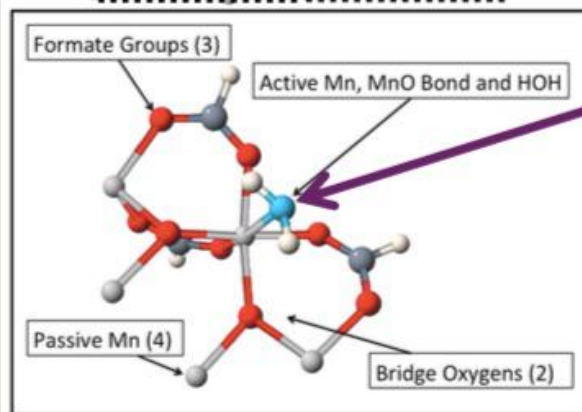
Batool, *et al.*: Can magnetic signals be used to chemical modifications of terminating ligands?

- Known to exist as in neutral, anionic, di-anionic, and tri-anionic charges states (in dielectric media).
- Believed to decompose as tetra-anion.



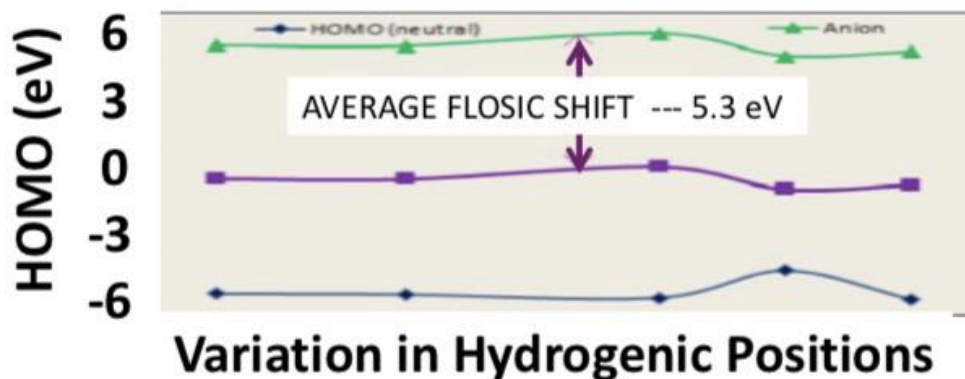
J Batool & M Pederson , To appear in PIEAS

What if **four** H₂O's are replaced by **four** electronically equivalent OH⁻ radicals?



Room for exactly four extra electrons? And stability.

SIC Shifts of Ligands found in Mn_{12} -Acetate Molecule (J. Batool and M. Pederson)



Position of protons do not change Fermi Level.

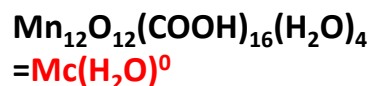
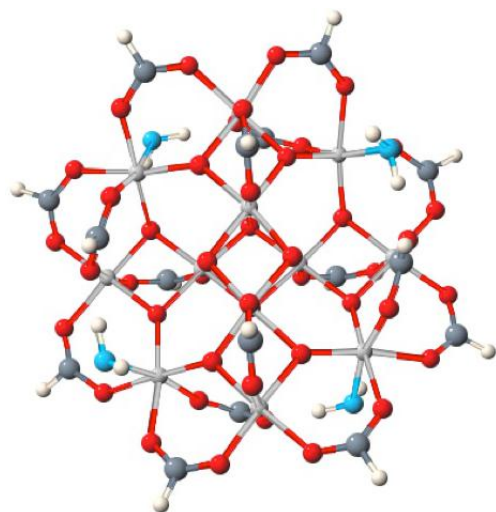
Inclusion of FLOSIC leads to tetra-anion that is near a stability/instability transition.

TABLE II: SIC-induced stabilization of HOMO levels, for fragments found in the $\text{Mn}_{12}\text{O}_{12}(\text{COOR})_{16}(\text{H}_2\text{O})_4$ are presented. The size of these shifts strongly support the total-energy calculations which show the tetra-anion to be as stable than the neutral molecule.

Fragment	CH_4	H_2O	H_2	H^-	OH^{-1}	O^{2-}	MnO_2
$\Delta\lambda^{FLOSIC}(\text{eV})$	-6.5	-7.4	-6.5	-4.5	-6.45	-5.1	-7.6

- Single Point FLOSIC – Now only 10 time slower than GGA
- Constraint for Single-Point FLOSIC needed.

Magnetic Reorientation Energy of Mn₁₂-Acetate vs Electron addition and proton removal



4 cubane $\text{Mn}^{4+} S=3/2$

4 passive crown $\text{Mn}^{3+} S=4$

# of electrons	$\text{Mc}(\text{H}_2\text{O})^{-4} \xrightarrow{4e^-} \text{Mc}(\text{H}_2\text{O})^0 = \text{Mc}(\text{OH})^{-4} \xrightarrow{2\text{H}_2} \text{Mc}(\text{OH})^0 \xrightarrow{4e^-}$			
electronic configuration	$[\text{Ar}]3d^5$	$[\text{Ar}]3d^4$	$[\text{Ar}]3d^4$	$[\text{Ar}]3d^3$
4 active crown Mn	$\text{Mn}^{2+} S=5/2$	$\text{Mn}^{3+} S=4$	$\text{Mn}^{3+} S=4$	$\text{Mn}^{4+} S=3/2$
magnetic anisotropy energy	27K	55K	10K	35K

Magnetism strongly depends on charge and proton positions