Reactivity Descriptors from Density Functional Theory: Application in Organic and Inorganic Chemistry

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Recent applications of Conceptual DFT in discussing the electronic structure/reactivity of Group 14-compounds.

Importance of Group 14 elements: C, Si, Ge, Sn, Pb...

Issues - Divalent compounds ↔ Spin properties

- Lewis Acidity/Basicity of Silylenes, Germynes, ...

- Evolution of electronegativity - hardness through the group: anomalous behaviour?
Outline

1. Introduction: Conceptual vs. Computational DFT

2. Spin-Polarised Conceptual DFT Study of Carbenes, Silylenes, Germylenes and Stannylenes.

3. Lewis Acid-Base Properties of Silylenes and Germylenes

4. Properties of Group 14 XY$_3$ Functional Groups

5. General Conclusions
1. Introduction: Conceptual vs. Computational DFT

Density Functional Theory (Hohenberg/Kohn)

\[ \rho(r) \] determines \( v(r) \)

Position and charge of the nuclei

Since \( \int \rho(r) \, dr = N \)

\[ \rho(r) \] determines \( H_{\text{op}} \rightarrow \Psi \)

All atomic and molecular properties
Looking for the optimal $\rho$ \[ \frac{\delta E}{\delta \rho(r)} = 0 \] with \[ \int \rho(r) dr = N \]

Lagrangian Multiplier $\mu \quad \mu = \nu(r) + \frac{\delta F}{\delta \rho(r)}$

**Practical implementation:**

- Kohn-Sham equations
- Nature of the Exchange Correlation Potential

**Computational DFT (Parr)**
Chemical Concepts from DFT

Chemical reaction involves perturbation of a system in \( \nu \) and/or \( N \)

Consider

\[ E = E[N, \nu] \]

\[
\begin{align*}
\mathrm{d}E &= \left( \frac{\partial E}{\partial N} \right)_{\nu(r)} \, \mathrm{d}N + \int \left( \frac{\delta E}{\delta \nu(r)} \right)_N \, \delta \nu(r) \, \mathrm{d}r \\
\end{align*}
\]

As \( E = E[\rho] \)

\[
\mathrm{d}E = \int \left( \frac{\delta E}{\delta \rho(r)} \right)_\nu \, \delta \rho(r) \, \mathrm{d}r \\
\text{with} \quad \left( \frac{\delta E}{\delta \rho(r)} \right)_\nu = \mu
\]

Lagrangian Multiplier

\[
\begin{align*}
\mathrm{d}E_\nu &= \mu \int \delta \rho(r) \, \mathrm{d}r = \mu \, \mathrm{d}N \\
\mu &= \left( \frac{\partial E}{\partial N} \right)_\nu
\end{align*}
\]
Identification of \( \mu = \left( \frac{\partial E}{\partial N} \right)_v \) = Negative of the electronegativity: \( -\chi \)


Interesting chemical quantities: response functions

Considering \( E = E[N,v] \)

\[
\left( \frac{\partial^{m+n} E}{\partial^n N \delta^m v(r)} \right)
\]

Conceptual DFT


+ theoretical justification for a number of principles:

» Electronegativity equalization principle (Sanderson)

» Hard and Soft Acids and Bases Principle (Pearson)

» Maximum Hardness Principle (Pearson)
\[ E = E[N, \nu] \]

- Electron chemical potential
  \[ \left( \frac{\partial E}{\partial N} \right)_\nu = \mu = -\chi \]
- Electron density
  \[ \left( \frac{\partial E}{\partial \nu(r)} \right)_N = \rho(r) \]
- Chemical hardness
  \[ \left( \frac{\partial^2 E}{\partial N^2} \right)_\nu = \eta \]
- Fukui function
  \[ \frac{\delta \mu}{\delta \nu(r)} \bigg|_N = \left( \frac{\partial \rho(r)}{\partial N} \right)_\nu = f(r) \]
- Linear response function
  \[ \frac{\delta \rho(r)}{\delta \nu(r')} \bigg|_N = \omega(r, r') \]

Softness
\[ S = \frac{1}{\eta} \]

\[ s(r) = \left( \frac{\partial \rho(r)}{\partial \mu} \right)_\nu = Sf(r) \]

Local softness
Local hardness
**Electrophilicity**: 

Energy change to second order due to change in $N$ (Constant $\nu$): 

$$\Delta E \approx \mu \Delta N + \frac{1}{2} \eta \Delta N$$

Electrophilic ligand immersed in idealised free electron sea of zero chemical potential ($T=0$)

Saturation point of electron inflow for the ligand

$$\frac{\Delta E}{\Delta N} = 0$$

$$\Delta N_{\text{max}} = -\frac{\mu}{\eta}$$

Stabilisation energy:

$$\Delta E = -\frac{\mu^2}{2\eta}$$

**Electrophilicity index**

$$\omega \equiv \frac{\mu^2}{2\eta}$$

Spin-polarised systems:

\[ \rho_\alpha(r) \neq \rho_\beta(r) \]

\[ \rho = \rho_\alpha(r) + \rho_\beta(r) \quad N = \int \rho(r) dr \]

\[ \rho_s = \rho_\alpha(r) - \rho_\beta(r) \quad N_s = \int \rho_s(r) dr \]

\[ E = E[N, N_s, \nu] \]

Spin potential

\[ \left( \frac{\partial E}{\partial N_s} \right)_{N, \nu} = \mu_s \]

Spin hardness

\[ \left( \frac{\partial^2 E}{\partial N_s^2} \right)_{N, \nu} = \eta_{ss} \]

Generalised Fukui functions

\[ \left( \frac{\partial \rho_s(r)}{\partial N_s} \right)_{N_s, \nu} = f_{ss}(r) \]

\[ \left( \frac{\partial \rho_s(r)}{\partial N} \right)_{N_s, \nu} = f_{sN}(r) \]

\[ \left( \frac{\partial \rho(r)}{\partial N} \right)_{N_s, \nu} = f_{NN}(r) \]
Energy change to second order due to change in $N_s$ (Constant N, $v$):

$$\Delta E \approx \mu_s \Delta N_s + \frac{1}{2} \eta_{ss} \Delta N_s^2$$

Ligand immersed in idealised free “spin” sea:

Saturation point of spin inflow:

$$\frac{\Delta E}{\Delta N_s} = 0$$

Energy difference
Energy difference:

$$\Delta E = -\frac{\mu_s^2}{2\eta_{ss}}$$

**Spin-philicity index**

$$\omega_s^+ \equiv \frac{(\mu_s^+)^2}{2\eta_{ss}}$$

**Spin-donicity index**

$$\omega_s^- \equiv \frac{(\mu_s^-)^2}{2\eta_{ss}}$$

*Relevant to two neighbouring spin states.


Plot of the energy of $E$ vs. $N_s$ at constant $N, \nu$

(singlet ground state)

Spin potential $\mu_s$

Numerical values for Acrylonitril
(CH$_2$=CH-C\(\equiv\)N)

Spin hardness $\eta_{ss}$

\[ \eta_{0-2}^0 = -0.046 \]
\[ \eta_{2-4}^0 = -0.055 \]
\[ \eta_{4-6}^0 = -0.037 \]


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2. Spin-Polarised Conceptual DFT Study of Carbenes, Silylenes, Germylenes and Stannylenes.

Systems studied (B3LYP/6-31G*) :

- $X = C, Si, Ge, Sn$

\[
\begin{align*}
\text{R} & \quad \text{H} & \quad X: \\
\text{R} & \quad \text{R} & \quad X: \\
\text{R} & \quad \text{R} & \quad X: \\
\text{R} & \quad \text{R} & \quad X: \\
\text{R} & \quad \text{R} & \quad X: \\
\end{align*}
\]

(R = H, Li, BeH, CH$_3$, NH$_2$, OH, F, Na, MgH, AlH$_2$, SiH$_3$, PH$_2$, SH, Cl)

(R = NH$_2$, OH, F, SH, Cl)

(R = NH$_2$, R$_2$ = OH, SH ; R$_1$ = OH, R$_2$ = SH)

Issues

- singlet - triplet gap
- spin philicity vs. spin donicity
Vertical Singlet-Triplet Energy difference: the Spin Potential

\[ E = E[N_s, N, \nu] \]

constant: \[ E_T \approx E_S + \left( \frac{\partial E}{\partial N_s} \right)^{(S)}_{N, \nu} \Delta N_s + \frac{1}{2} \left( \frac{\partial^2 E}{\partial N_s^2} \right)^{(S)}_{N, \nu} \Delta N_s^2 \]

\[ \mu_s^{(S)+} \]

\[ \eta_{ss}^{(S)} = \frac{\mu_s^{(T)-} - \mu_s^{(S)+}}{2} \]

\[ \Delta N_s = N_s^{(T)} - N_s^{(S)} = 2 \]

\[ E_T - E_S \approx 2\mu_s^{(S)+} + \frac{1}{2} \left( \frac{\mu_s^{(T)-} - \mu_s^{(S)+}}{2} \right)^{(S)}_{N, \nu} 4 = \mu_s^{(S)+} + \mu_s^{(T)-} \]
Computation of these properties

\[ \mu^{(S)+}_s = \left( \frac{\partial E}{\partial N_s} \right)^{(S)+}_{N,v} \equiv \frac{(\varepsilon_L^\alpha(S) - \varepsilon_H^\beta(S))}{2} \]

\[ \mu^{(T)-}_s = \left( \frac{\partial E}{\partial N_s} \right)^{(T)-}_{N,v} \equiv \frac{(\varepsilon_H^\alpha(T) - \varepsilon_L^\beta(T))}{2} \]
Koopman's type spin potentials

Singlet-Triplet gap
Spin hardness

- $\eta_{ss} \left(= \eta_{0-2}^0 \right)$
- $XH_2$

<table>
<thead>
<tr>
<th>X</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-1.69 (T)</td>
<td>-1.05 (S)</td>
<td>-0.92 (S)</td>
</tr>
</tbody>
</table>

For a constant $\mu_s$, $\Delta E_{ST} \approx \frac{1}{2} \eta_{ss} (\Delta N_s)^2$

Increasing (less negative) $\eta_{ss}$ with increasing atomic number of central atom → increases singlet-triplet gap

$Z \uparrow$ → Increasing spin hardness → favouring singlet
cfr. Decreasing hardness → increasing polarizability

→ Combined effect of $\mu_{ss}$, $\eta_{ss}$ → spin philicity, spin donicity?
Singlet ground state

Triplet state

\[ \Delta E_v \]

Spin-philicity index

\[ \omega^+_s = \frac{(\mu_{s}^{(S)+})^2}{2\eta_{ss}} \]

Energy changes in the direction of increasing multiphilicity

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Also good correlation for the germylenes and stannylenes:
Singlet state

\[ \Delta E_v \]

Triplet ground state

\[ \omega_s^- = \frac{\left(\mu_s^{(T)}-\right)^2}{2\eta_{ss}} \]

Spin-donicity index

Energy change in the direction of decreasing multiplicity
• Spin potentials can be used to approximate singlet-triplet gaps

• Spin hardness : increases with increasing Z, favouring singlet

• Spin philicity and donicity can predict the singlet-triplet gaps to a good accuracy

3. Hard and Soft Acids and Bases Interactions of Silylenes and Germynes

Silylenes
Germynes

\[ \rightarrow \text{Electrophilic properties} \]

Interaction with Lewis bases:
\[ \text{NH}_3, \text{PH}_3, \text{AsH}_3 \]

\[ \rightarrow \text{Nucleophilic properties} \]

Interaction with Lewis acids:
\[ \text{BH}_3, \text{AlH}_3 \]

? Relationship via Conceptual DFT
Silylenes

Conceptual DFT approach on a system in which a single atom may have both electrophilic and nucleophilic properties (ambiphilic character)

Reactivity vs. nucleophiles (Lewis bases): NH₃, PH₃, AsH₃: decreasing η
electrophiles (Lewis acids): BH₃, AlH₃: decreasing η

→ Interpretation via HSAB (singlet cases)

→ Analogies with germynylenes: trends in Periodic Table

→ Relationship with stability?
3.1. Electrophilic properties

Electrostatic potential (local hardness)

\[
\begin{align*}
\text{XYSi} + \text{NH}_3 \rightarrow \text{XYSiNH}_3 \\
\text{XYGe} + \text{NH}_3 \rightarrow \text{XYGeNH}_3
\end{align*}
\]

Correlation evolution:

\( \text{NH}_3 > \text{PH}_3 > \text{AsH}_3 \)
Electrophilicity index:

- Increasing electrophilicity (global and locally at Si atom) → higher interaction energy

- Correlation less favourable with softer bases (PH$_3$, AsH$_3$) → Charge controlled reactions; cf. good correlation with “hard descriptor” V

- Complexation most favourable with the harder silylene as compared to germylene
3.2. Nucleophilic properties

\[ \text{XYSi} + \text{BH}_3 \rightarrow \text{XYSiBH}_3 \]

\[ \text{XYSi} + \text{AlH}_3 \rightarrow \text{XYSiAH}_3 \]

Electrostatic potential
A small group of (stable) disubstituted silylenes effectively behaves both as Lewis acids and Lewis bases: ambiphilic character.

Role of the substituents in REACTIVITY and STABILITY

$\text{Si} \quad R', R''$

Electrophile

Nucleophile

$R, R' = \text{NH}_2, \text{OH}, \text{SH}$

- $R, R''$ donating electrons into empty 3p-orbital $\rightarrow$ electrophilicity $\downarrow$
  $\rightarrow$ Increasing nucleophilicity

- $R, R''$ not donating electrons into empty 3p-orbital $\rightarrow$ electrophilic system

Relation with stability: $\pi$ donating groups $\rightarrow$ stabilization $\uparrow$

$\downarrow$ nucleophilicity $\uparrow$

$\downarrow$ electrophilicity $\downarrow$
$R^2 = 0.97$

4. Properties of Group 14 \( \text{XY}_3 \) Functional Groups

4.1. Introduction

Electronegativity variation of Group 14 elements:

<table>
<thead>
<tr>
<th>Electronegativity Method</th>
<th>C</th>
<th>Pb</th>
<th>Ge</th>
<th>Sn</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pauling</td>
<td>&gt;</td>
<td>&gt;</td>
<td>&gt;</td>
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<td>Sanderson</td>
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<td>Allred-Rochow</td>
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<td>Allen</td>
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<tr>
<td>Mulliken</td>
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<tr>
<td>Mulliken-Jaffe</td>
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<tr>
<td>Gordy</td>
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</tbody>
</table>

Irregularities (absence in Group 17-Halogens)

Relativistic effects?

- \( \text{XY}_3 \) functional groups
  - \( X : \text{C, Si, Ge, Sn, Pb, Uuq (eka-Pb)} \)
  - \( Y : \text{F, Cl, Br, I, At, H, CH}_3 \)
4.2. Computational methods

Geometry optimisation of H-XY₃

\[
\chi = -\left( \frac{\partial E}{\partial N} \right)_v \approx \frac{I + A}{2}, \quad \eta = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)_v \approx \frac{I - A}{2}, \quad \omega = \frac{\chi^2}{2\eta}
\]

Three levels of theory:

- NR : BP86/QZ4P
- SR : BP86 + Scalar ZORA/QZ4P
- SO : BP86 + ZORA/QZ4P

(ADF)
4.3. Ionisation energies & electron affinities

Atomic NR and SR values for these quantities:
reasonable correlation with experimental values for the lighter elements

Heavy elements clearly need the inclusion of spin-orbit coupling

Order for X seldom transferred to XY₃
4.4. Electronegativity

- Importance of relativistic effects for heavier elements
- \( XY_3 \) with \( Y = H \) or \( CH_3 \) : electronegativity ordering : \( C > Uuq > Pb > Sn > Ge > Si \)

\[
\text{Y is a halogen : Uuq > Pb > Sn > Ge > C > Si}
\]

- Passing from an atom to a functional group can dramatically change the electronegativity sequences!
- In all cases \( Ge > Si \) as opposed to free atom cases : important when discussing electronegativity scales.
4.5. Hardness

- At the highest level: C > Uuq > Pb > Si > Ge > Sn in agreement with experiment
- Opposed to the halogens: F > Cl > Br > I > At: monotonous decrease
- Functional groups: all three methods following the ordering:
  C > Si > Ge > Sn > Pb > Uuq
- Calculations confirm that Group 14 shows less monotonicity in its behaviour as compared to Group 17


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5. Conclusions

Conceptual DFT $\leftrightarrow$ Properties of Group 14 elements

Interpretation

- Singlet-triplet gaps of divalent compounds
- Electrophilic/Nucleophilic character and stability of divalent compounds
- Remarkable evolution of electronegativity and hardness at atomic and functional group level
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