Dogmatic and Pragmatic Spirits in Time-Dependent Density Functional Theory

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Acknowledgments

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- Ms. Ester Livshits (PhD student, Jerusalem)
- Dr. Helen Eisenberg (Postdoc, Jerusalem)
- Tamar Gershon (PhD student, Jerusalem)
- Professor Leeor Kronik (Weizmann)
- Professor Daniel Neuhauser (UCLA)
- Professor Anna Krylov (USC)

Funding
- Israel Science Foundation (ISF)
- US-Israel Binational Science Foundation (BSF)
- FAME network of excellence
Self repulsion in “usual” DFT

Self repulsion

- An electron is repelled not only by other electrons, but also by itself
- Good at the short range (emulates correlation)
- But much too much at long range

Unphysical behavior

- Static polarizability
- Stability of anions
- Charge quantization in decoupled systems
- Charge transfer excitations
- Rydberg excitations
What is self-repulsion?

Take a charge \( q_1 \) at \( \mathbf{r}_1 \) and bring another charge \( q_2 \) from infinity to \( \mathbf{r}_2 \).

The energy for this is:

\[
E_2 = \frac{q_1 q_2}{r_{12}} \quad r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|.
\]

Next, bring another charge \( q_3 \) from infinity to \( \mathbf{r}_3 \):

\[
E_3 = \frac{q_1 q_3}{r_{13}} + \frac{q_2 q_3}{r_{23}}.
\]

The total energy is a sum over pairs:

\[
E = \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}}.
\]

For continuous charge dist:

\[
E = \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' \quad (n(\mathbf{r}) \text{ density of charge})
\]

But this includes self interaction - analogous to the \( i = j \) terms

In Hartree-Fock theory we have:

\[
\rho(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N_{\text{occ}}} \phi_i(\mathbf{r}) \phi_i(\mathbf{r}') \quad n(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r})
\]

The 2-electron repulsion is:

\[
E_{ee} = \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' - \frac{1}{2} \int \frac{|\rho(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' \\
\text{Direct or Hatree} \quad \text{Exchange}
\]

So in HF theory self-repulsion is automatically removed.
Consequence of self-repulsion

Physically correct: charge should usually be quantized
O$_2$ sticking on Al(111)

- LSDA/GGA: no barrier
- Scheffler et al:
  - Electron to O$_2$ too early
  - O$_2^-$ is strongly attracted
  - Introduced “spin rules”
  - Lowering the spin on the triplet O$_2$ was forbidden
  - This is a strange ad hoc mechanism

O$_2$+Al$_5$: the emergence of a barrier
Density Functional Theory

\[ \hat{T} = -\frac{1}{2} \sum_j \nabla_j^2 \quad \hat{U} = \frac{1}{2} \sum_{j \neq j'} \frac{1}{r_{jj'}} \]

\( \psi_{gs} = \) Unique gs WF of electrons having gs density \( n(r) \)

\( \psi_0 = \) Unique gs WF of non-int Fermions having gs density \( n(r) \)

\[ E = \langle \psi_{gs} | \hat{T} + \hat{V} + \hat{U} | \psi_{gs} \rangle = \langle \psi_0 | \hat{T} + \hat{V} + \hat{U} | \psi_0 \rangle + E_C[n] \]

\[ \langle \psi_{gs} | \hat{V} | \psi_{gs} \rangle = \int v(r) n(r) d^3r = \langle \psi_0 | \hat{V} | \psi_0 \rangle \]
Correlation energy in DFT

\[ E_C[n] = \langle \psi_{gs} | \hat{T} + \hat{U} | \psi_{gs} \rangle - \langle \psi_0 | \hat{T} + \hat{U} | \psi_0 \rangle \]

\[ T_C[n] = \langle \psi_{gs} | \hat{T} | \psi_{gs} \rangle - \langle \psi_0 | \hat{T} | \psi_0 \rangle \]

\[ E_C[n] < 0 \quad T_C[n] > 0 \]

- Theorem: A physical quantity cannot have self-repulsion
- Corollary: Expectation values of physical operators are self-repulsion free
- Corollary: \(E_C\) and \(T_C\) are self repulsion-free
Hartree and Exchange energy

\[ \langle \psi_0 | \hat{U} | \psi_0 \rangle = E_H[n] + E_X[n] \]

(Self-repulsion free)

\[ E_H[n] = \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' \]

(Has self-repulsion)

\[ E_X[n] = -\frac{1}{2} \int \int \frac{\rho(r,r')^2}{|r-r'|} d^3r d^3r' \]

(Has self-attraction)
Local approximation to $E_c$

$$E_C[n] = \langle \psi_{gs} | \hat{T} + \hat{U} | \psi_{gs} \rangle - \langle \psi_0 | \hat{T} + \hat{U} | \psi_0 \rangle$$

(self repulsion-free)

$$E^{SL}_C[n] = \int f_{XC} \left( n(r), |\nabla n(r)| \right) d^3r - E_X$$

(Long range self repulsion)
New approach to hybrid functional theory

\[ E_C [n] = \langle \psi_{gs} | \hat{Y} \gamma \psi_{gs} \rangle - \langle \psi_0 | \hat{Y} \gamma | \psi_0 \rangle \]

\[ E_C [n] = \langle \psi_{gs} | \hat{Y}_\gamma \psi_{gs} \rangle - \langle \psi_0 | \hat{Y}_\gamma | \psi_0 \rangle \quad \hat{Y} = \frac{1}{2} \sum_{j \neq j'} y_{\gamma} (|r_j - r_{j'}|) \]

\[ y_{\gamma} = \frac{1 + \gamma r}{1 + \gamma r} \quad y_{\gamma} = \frac{e^{-\gamma r}}{r} \quad y_{\gamma} = \frac{\text{erfc}(\gamma r)}{r} \]

\[ y_0 (r) = \frac{1}{r} \quad y_\infty (r) = 0 \]

\[ \gamma = 0 : \langle \psi_{gs} | \hat{Y}_\gamma \psi_{gs} \rangle - \langle \psi_0 | \hat{Y}_\gamma | \psi_0 \rangle = E_C - T_C < E_C \]

\[ \gamma = \infty : \langle \psi_{gs} | \hat{Y}_\gamma \psi_{gs} \rangle - \langle \psi_0 | \hat{Y}_\gamma | \psi_0 \rangle = 0 > E_C \]

Conclusion: There exists a \( \gamma \) for which there is equality
Approximate hybrid $E_c$ functional

$$E_C[n] = \langle \psi_{gs} | \hat{Y}_\gamma | \psi_{gs} \rangle - \langle \psi_0 | \hat{Y}_\gamma | \psi_0 \rangle = \left[ \langle \psi_{gs} | \hat{Y}_\gamma | \psi_{gs} \rangle - E_H^y \right] - E_X^y$$

$$E_C^{Hyb} = \int f_{XC}^\gamma \left( n(r), \nabla n(r) \right) d^3r - E_X^y$$

$$E_X^y = -\frac{1}{2} \iiint \rho(r,r') y_\gamma \left( ||r-r'|| \right) d^3r d^3r'$$

$$y_\gamma = \frac{1}{1 + \gamma \frac{r}{r}} \frac{\text{erfc}(\gamma r)}{r} e^{-\gamma r}$$

Fix $\gamma$ and find Good approx for $f(n,dn)$:
- Becke (B3LYP)
- Savin
- Hirao
- Handy
- Baer+Neuhauser
- Yang
- Tozer
- Truhlar
- Head-Gordon
- Gerber-Angyan
- Perdew-Scuseria
- ...

“B3LYP” type
Long-range self-repulsion

“RSH” type
No long-range self-repulsion
B3LYP type in electron gas

\[
\frac{1}{1 + \gamma} = \frac{\varepsilon_c}{\varepsilon_c - t_c}
\]

\[r_s \propto \frac{1}{n^{1/3}}\]
RSH type in electron gas

Pair correlation function taken from:

E. Livshits and R. Baer, PCCP 9, 2932 (2007)
Argue against the universal $\gamma$

- In B3LYP – OK
- In RSH – NOT OK
- Must be: $\gamma$ system dependent
The IP theorem

Theorem:
The ionization potential of the system is exactly equal to the HOMO energy.

Basis: cc-pVTZ

Setting $\gamma$: ab initio method

\[
\varepsilon_{HOMO}^N(N;\gamma) = E(N;\gamma) - E(N - 1;\gamma)
\]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\gamma$ (a₀⁻¹)</th>
<th>IP exp</th>
<th>IP w=0</th>
<th>IP w=0.1</th>
<th>IP B3LYP</th>
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<td>-0.5</td>
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<td>RMS</td>
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</table>

E. Livshits and R. Baer, PCCP 9, 2932 (2007)
The symmetric radical cation $R_2^+$

![Graph showing E(E_h) vs. H-H distance (A) for different methods: HF, B3LYP, BLYP.](image)

**$H_2^+$**  
**QCHEM 3.1**  
**cc-pVTZ**

Same problems appear in:  
**He$_2^+$, Ne$_2^+$**  
/etc

---

Root cause: SIEs

\[ |GS\rangle = \frac{1}{\sqrt{2}} (|L\rangle \pm |R\rangle) \]

\[ E_{\text{correct}}(r) \rightarrow E(R) + E(R^+) \rightarrow + \frac{\alpha}{2r^4} + \ldots \]

Density Picture:
\[ n = \frac{1}{2} (n_L + n_R) \]
\[ E(r) = 2E(R^{0.5}) + \frac{1}{4r} \]
Usual RSH - not good enough

- By using RSH we get rid of repulsion
- But this is not enough
- There is also large error at $r = r_0$
- Wrong asymptotic curve ($\neq -\alpha/2r^4$)

Tuning $\gamma$ to obtain degeneracy

$$\Delta E(\gamma) = E_{\gamma}^{0-1} - E_{\gamma}^{0.5-0.5}$$

---

Optimized choice of $\gamma$ is blessed

- Have $\gamma$ so: localized-delocalized degenerate
- Energies in kcal/mole

<table>
<thead>
<tr>
<th>Property</th>
<th>R</th>
<th>BLYP</th>
<th>B3LYP</th>
<th>HF</th>
<th>LC BNL</th>
<th>LC* BNL*</th>
<th>Exp.</th>
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<td>H</td>
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<td>65</td>
<td>60.9</td>
<td>60.9</td>
<td>60.9</td>
<td>61</td>
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<tr>
<td>He</td>
<td>82</td>
<td>75</td>
<td>43</td>
<td>74</td>
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<tr>
<td>Ne</td>
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<td>59</td>
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<td>32</td>
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<tr>
<td>Enthalpy by asymptote</td>
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<td></td>
<td></td>
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<tr>
<td>H</td>
<td>NA</td>
<td>NA</td>
<td>60.9</td>
<td>50</td>
<td>60.9</td>
<td>61</td>
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<tr>
<td>He</td>
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<td>NA</td>
<td>43</td>
<td>42</td>
<td>59</td>
<td>55</td>
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<tr>
<td>Ne</td>
<td>NA</td>
<td>NA</td>
<td>2</td>
<td>27</td>
<td>34</td>
<td>32</td>
<td></td>
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<tr>
<td>$r_{eq}$ ($\text{A}$)</td>
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<td></td>
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<td>NA</td>
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<td>1</td>
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<td>$a_{R_{\text{aug}}} / (\alpha_0^3)$</td>
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<td>3.2</td>
<td>2.70</td>
<td>2.66</td>
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</tr>
</tbody>
</table>

$\alpha_{eff} = \frac{1}{2} E'(r) r^5$
"7 for the price of 1"

By using $\gamma^*$ several problems are solved

- Repulsion instead of attraction
- No degeneracy breaking
- Proper well depth at $r=r_0$
- Fine bond lengths
- "Good vibrations"
- Leading term in asymptotic form of potential - correct
- Excellent atomic polarizability

Applications for water dimer cation

Energies (kcal/mol) of \((\text{H}_2\text{O})_2^+\) relative to the proton-transferred geometry

<table>
<thead>
<tr>
<th>Method</th>
<th>Vertical neutral</th>
<th>Hemi-bonded</th>
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<tbody>
<tr>
<td>BLYP</td>
<td>6.7</td>
<td>-8.3</td>
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<tr>
<td>B3LYP</td>
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<td>-1.6</td>
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<tr>
<td>BNL*(0.56)</td>
<td>23.3</td>
<td>8.2</td>
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<tr>
<td>EOM-IP-CCSD</td>
<td>20.0</td>
<td>5.3</td>
</tr>
<tr>
<td>EOM-IP-CC(2.3)</td>
<td>21.8</td>
<td>7.4</td>
</tr>
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</table>

We looked into the Anthracene-TCNE charge transfer complex in solution (CH$_2$Cl$_2$).

\[
h\nu_{CT} = IP_{ArH} - EA_A - \frac{1}{\varepsilon R}
\]

In ideal CT excitation:

Stage 1: Determine $\gamma$

- First stage is to find the appropriate $\gamma$
- This requires finding a $\gamma$ that gives proper HOMO energies for IP(ArH) and EA(TCNE)

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>IP (ANT) (eV)</th>
<th>IP (TCNE$^-$) = EA (eV)</th>
<th>$\Sigma r$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta E_{\text{SCF}}$</td>
<td>$-\varepsilon_{\text{HOMO}}$</td>
<td>$r$</td>
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<tr>
<td>0.01</td>
<td>6.09</td>
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<tr>
<td>0.02</td>
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<td>0.5</td>
<td>7.08</td>
<td>7.56</td>
<td>-0.07</td>
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</tbody>
</table>

- One obtains an optimal value of 0.3
Stage 2: check Mulliken

- Checking the Mulliken law in gas phase

\[ h\nu_{CT} = I_{ArH} - E A_A - \frac{1}{R} \]
Stage 3: do TDDFT

- We took a B3LYP optimized geometry for the complex and performed TDDFT calculation

<table>
<thead>
<tr>
<th>Ar</th>
<th>B3LYP</th>
<th>BNL γ=0.5</th>
<th>BNL γ*</th>
<th>Exp</th>
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<td>$f$</td>
<td>$γ^*$</td>
<td>$E$</td>
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<td>0.32</td>
</tr>
</tbody>
</table>

# Anthracene and substituents

<table>
<thead>
<tr>
<th>Substituent</th>
<th>PBE</th>
<th>B3-LYP</th>
<th>BNL E(γ=0.5)</th>
<th>BNL γ*</th>
<th>BNL E(γ=0.3)</th>
<th>Exp^{26}</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.9</td>
<td>1.0</td>
<td>2.3</td>
<td>0.31</td>
<td>1.82</td>
<td>1.73</td>
</tr>
<tr>
<td>9-cyano</td>
<td>Fail</td>
<td>0.5</td>
<td>2.6</td>
<td>0.30</td>
<td>2.03</td>
<td>2.01</td>
</tr>
<tr>
<td>9-chloro</td>
<td>0.9</td>
<td>1.0</td>
<td>2.3</td>
<td>0.31</td>
<td>1.82</td>
<td>1.74</td>
</tr>
<tr>
<td>9-carbomethoxy</td>
<td>0.8</td>
<td>0.9</td>
<td>2.4</td>
<td>0.30</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>9-methyl</td>
<td>1.0</td>
<td>1.1</td>
<td>2.1</td>
<td>0.30</td>
<td>1.71</td>
<td>1.55</td>
</tr>
<tr>
<td>9-nitro</td>
<td>0.6</td>
<td>0.9</td>
<td>2.8</td>
<td>0.30</td>
<td>2.12</td>
<td>2.03</td>
</tr>
<tr>
<td>9.10-dimethyl</td>
<td>1.3</td>
<td>1.4</td>
<td>2.1</td>
<td>0.30</td>
<td>1.77</td>
<td>1.44</td>
</tr>
<tr>
<td>9-formyl</td>
<td>0.8</td>
<td>1.0</td>
<td>2.5</td>
<td>0.30</td>
<td>1.95</td>
<td>1.90</td>
</tr>
<tr>
<td>9-formyl 10-chloro</td>
<td>0.8</td>
<td>0.9</td>
<td>2.5</td>
<td>0.30</td>
<td>1.96</td>
<td>1.96</td>
</tr>
</tbody>
</table>

Band gap in solids

- Kohn-Sham $\rightarrow$ bad gaps (50-70% too small)
- Because missing “derivative discontinuity”
- Hartree-Fock theory terrible: 500% too large.
Looks like NOT???

\[
\frac{E_g^\gamma - E_g^{LDA}}{E_g^{Hartree-Fock} - E_g^{LDA}}
\]
\[ \gamma^* = \frac{C}{\varepsilon_{opt} - A} \]

\begin{align*}
C &= 0.22 \\
A &= 0.8
\end{align*}

\( \gamma^* \) vs optical permittivity \( \varepsilon_{opt} \)
Low band gap materials

H. Eisenberg, R. Baer, work in progress (2008).
High band gap materials

H. Eisenberg, R. Baer, work in progress (2008).
**Spirits - summary**

**Dogmatic spirit**
- Hybrid (B3LYP/RSH) theory
- In B3LYP: \( \gamma \) insensitive to density (factor 3)
- In RSH: \( \gamma \) very sensitive (factor \(~100\))

**Pragmatic spirit**
- \( \gamma \) system dependent
- Ab initio ways to determine \( \gamma \)
- “Systems too difficult for DFT”
- Symmetric cation radicals
- Charge-transfer excitations
- Band gaps

*Note: \( \gamma \) is a parameter in DFT calculations that affects the exchange-correlation functional.*