The Self Interaction Correction revisited

- Explicit dynamics of clusters and molecules under irradiation
- Spectroscopic accuracy at low energy

**SIC problem**: one electron interacts with its own mean-field!

- Density Functional Theory (DFT) for electrons, classical ions
- From Local Density Approximation (LDA) to SIC and beyond

Toulouse-Erlangen collaboration (P. G. Reinhard)
Electronic systems

DFT and Local Density Approximation (LDA)

From Density Functional Theory (DFT) to LDA

LDA

Self Interaction problem

Ionization potential problem

Self Interaction Correction (SIC)

Optimized Effective Potential (OEP)

Simple approximations, Slater, ADSIC

Examples of application

Defects of simple approximations

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General SIC formulation

Double set formulation and Generalized Slater

Time Dependent SIC
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About electronic systems

- (Quantum) electrons and (classical) ions in molecules
  - « Who » follows « whom »
    Ex: Born Oppenheimer surface
  - Large « phase » space for deformations
    Ex: degeneracy lifting
  - Well defined center of mass

- Key role of electron exchange (and correlation)
  - Neutral systems
  - Most binding comes from exchange and correlation
    Ex: infinite jellium metal
    Ex: also in finite systems
Some observables

- **Intrinsic single particle properties**
  - Density of states (DOS), Band Gap, Ionization Potential (IP)
  - Ex: solids (DOS, gap), molecules, chemistry (IP)

- **Global structure properties**
  - Bond length, Dissociation energy, Potential barriers ...
  - Ex: potential energy surfaces in chemistry

- **Response to electromagnetic fields**
  - Static and dynamical responses
  - Polarizability, Magnetic moment, Optical response...
  - Ex: physics and chemistry of irradiation

Typical ingredients for irradiation dynamics
Electronic systems

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From DFT to LDA

- **(Time Dependent) Density Functional Theory (TD) DFT**

  Ensemble of (orthonormal) orbitals (1 electron) \( \{ \psi_{\alpha}(r), \alpha = 1, \ldots \} \)

  One body density
  \[
  \rho = \sum_{\alpha} |\psi_{\alpha}(r)|^2 = \sum_{\alpha} \rho_{\alpha}
  \]

  Effective mean field theory
  \[
  h[\rho] \psi_{\alpha} = \ldots \quad h[\rho] = -\frac{\hbar^2}{2m} \Delta + U_{H} + U_{xc}[\rho]
  \]

- **Local Density Approximation**

  LDA and TDLDA ➔ Exchange-correlation function of density \( \rho \)
Local Density Approximation (LDA)

- Local exchange-correlation term:
  \[ U_{xc} \] assumed to be a function of [\( \rho(r) \)].

- Ex: pure exchange:
  \[ \rho^{1/3} \]
  A priori not valid for rapidly varying \( \rho(r) \) ...

- In general correct for global energies
- Ex: IP from \( E(N+1) - E(N) \), dissociation energies within 10-20%.
- Exhibits good formal features.
- Many successful applications (solid state, molecules, clusters).

LDA tends to delocalize wavefunctions:

- Ex: metals (simple ones !!)

\[ U_{xc} \text{ assumed to be a function of } \rho(r) \]

Table 8.2 LSD Spectroscopic Constants for Diatomic Molecules

<table>
<thead>
<tr>
<th>( r_e ) (boh)</th>
<th>LSD</th>
<th>Expt.</th>
<th>LSD</th>
<th>Expt.</th>
<th>LSD</th>
<th>Expt.</th>
<th>LSD</th>
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<td>( r_e ) (boh)</td>
<td>Exp</td>
<td>Exp</td>
<td>Exp</td>
<td>Exp</td>
<td>Exp</td>
<td>Exp</td>
<td></td>
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<tr>
<td>H_2</td>
<td>1.40</td>
<td>1.43</td>
<td>4.8</td>
<td>4.9</td>
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<tr>
<td>Li_2</td>
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<td>3.03</td>
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<tr>
<td>B_2</td>
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<td>2.07</td>
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<td>5.3</td>
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<tr>
<td>C_2</td>
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<td>2.27</td>
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<td>5.1</td>
<td></td>
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<tr>
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<tr>
<td>Ne</td>
<td>4.24</td>
<td>4.29</td>
<td>5.1</td>
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<tr>
<td>Na_2</td>
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</tr>
<tr>
<td>S_2</td>
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<td>3.76</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
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<td></td>
</tr>
<tr>
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<td>3.76</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

Ex: \( \omega_e \) and \( D_e \) for various molecules.

Plasmon response

- \( E \) vs. \( \omega \)
- \( r_e \) vs. \( D_e \)
- \( \omega_e \), 24% deviation
- \( D_e \), 3% deviation
- \( \text{LSD SOV} \) vs. frequency [eV]
Electronic systems
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- **(Time Dependent) Density Functional Theory (TD) DFT**

  Ensemble of (orthonormal) orbitals (1 electron) \( \{\psi_\alpha(r), \alpha = 1, \ldots\} \)

  One body density

  Effective mean field theory

  \[ h[\rho] \psi_\alpha = \ldots \]

  \[ h[\rho] = -\frac{\hbar^2}{2m} \Delta + U_H + U_{xc}[\rho] \]

  Hartree \quad Exch. + Corr.

- **Local Density Approximation**

  LDA and TDLDA \( \Rightarrow \) Exchange-correlation function of density \( \rho \)

  Energy \( E_{\text{LDA}}[\rho] \) \( \Rightarrow \) Potential

  \[ \hat{h}_{\text{LDA}} = -\frac{\hbar^2}{2m} + U_{\text{LDA}}[\rho] \]

  \[ U_{\text{LDA}}[\rho] = \frac{\delta E_{\text{LDA}}}{\delta \rho} \bigg|_{\rho=q} \]

  Self Interaction

  Ionization Potential Problem...
The Ionization Potential Problem

- Potential and level scheme

Example of anion clusters: $K_7^-$ (8 electrons)

Exp:
Little bound system
Ionization Potential about 1 eV

$U_{KS}$ [eV]

$1p$

$1s$

$\Delta E$

$K_7^-$

soft jellium

$1p$

$\Delta E$

LDA

$\text{Adsic}$

Exp: Almost no binding
Totally wrong IP (reasonable $\Delta E$) $\rightarrow$ dynamics?
The Ionization Potential Problem (2)

Example of organic molecules:

Benzene-like cyclic structures:
\[ H \rightarrow N, O, S \]

Neutral species
Covalent bond

50% error on IP!

LDA: Totally wrong IP
Self Interaction Correction (SIC)

- **SIC energy functional**
  \[ E_{\text{SIC}} = E_{\text{LDA}}[\rho] - \sum_{\beta=1}^{N} E_{\text{LDA}}[\rho\beta] \]

- Subtract explicitly self interaction

- **One-body equations**
  \[ \hat{h}_{\text{SIC}} = \hat{h}_{\text{LDA}} - U_{\text{LDA}}[|\psi_\alpha|^2] = h_{\text{SIC}, \alpha} \]

- Orbital dependent field
- Loss of orthonormality ...
- Time dependent formulation ?

- Approximation by One potential: Optimized Effective Potential

**NB:** No SIC problem in HF due to exact cancellation by exchange
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Optimized Effective Potential (OEP)

- SIC and beyond

Try to restore a common 1-body potential by "optimal" choice of a unique common $V_0$:

$$V_S = \sum_i \frac{\left| \tilde{\varphi}_i \right|^2}{\rho} v_i ,$$

$$V_K = \sum_i \frac{\left| \tilde{\varphi}_i \right|^2}{\rho} (\tilde{\varphi}_i|V_0 - v_i|\tilde{\varphi}_i) ,$$

$$V_C = \frac{1}{2} \sum \nabla (\rho \nabla) .$$

$\to \varphi_i^{V_0}$

Full OEP « painful »...

$$h_{\text{OEP}} =$$

$$h_{\text{OEP}} \varphi_i =$$

$$E_{\text{OEP}} =$$

$$\int dr' \{V_0(r') - v_i(r')\} \frac{\tilde{\varphi}_i(r')}{\tilde{\varphi}_i(r)} G_i(r, r')$$

$$G_i(r, r') = \sum_{j \neq i} \frac{\tilde{\varphi}_j^\ast(r)\tilde{\varphi}_j(r')}{\varepsilon_j - \varepsilon_i} .$$
Optimized Effective Potential (OEP)

- **SIC and beyond**

Try to restore a common potential by «optimal» choice of a unique common $V_0$: «parametrize» wavefunctions $\varphi_i$ by $V_0$

\[
\begin{align*}
  h_{\text{OEP}} &= -\frac{\hbar^2 \Delta}{2m} + V_0 \\
  h_{\text{OEP}} \varphi_i &= \varepsilon_i \varphi_i = \varepsilon_i \varphi_i^{V_0} \\
  E_{\text{OEP}} &= E_{\text{SIC}}[\{\varphi_i^{V_0}\}] \\
  \frac{\delta E_{\text{OEP}}}{\delta V_0} &= 0 \rightarrow V_0 \rightarrow \varphi_i^{V_0} \\
  V_0 &= V_S + V_K + V_C
\end{align*}
\]

- **Practically**

Almost only approximate versions of OEP are numerically tractable...

KLI, Slater, ADSIC...
From full OEP to ...

$$
U^{\text{SIC}}_\alpha = U_{\text{LDA}} - [U_H(\rho_\alpha) + U_{\text{xc}}(\rho_\alpha)]
$$

Krieger Li Iafrate (KLI)

$$
U^{\text{KLI}} = \sum_{\beta} \frac{\rho_\beta}{\rho} \left\{ U_{\text{LDA}} - \int d^3 r' \rho_\beta [U^{\text{KLI}}(r') - U_{\text{LDA}}(r')] \right\}
$$

« Local » Average (Slater)

$$
U^{\text{Slater}}(r) = \sum_{\beta} \frac{\rho_\beta(r)}{\rho(r)} U^{\text{SIC}}_\beta(r)
$$

« Global » Average

$$
U^{\text{ADSIC}} = U_{\text{LDA}} - \left[ U_H\left(\frac{\rho}{N}\right) + U_{\text{xc}}\left(\frac{\rho}{N}\right) \right]
$$

Averaged Density SIC (ADSIC)

$$
\rho = \sum_\alpha |\psi_\alpha(r)|^2 = \sum_\alpha \rho_\alpha
$$
Back to anion clusters

- Potential and level scheme

Example of anion clusters: $K_7^-$ (8 electrons)

Exp:
Little bound system
Ionization Potential about 1 eV

Correct IP, restoration Koopmann's theorem
Access to 1-photon processes (anions)
Back to carbon cycles

Case of Organic molecules
Good reproduction of IP with ADSIC

ADSIC : Correct IP
New bad surprises ...

Dissociation problem
Polarizability problem

Orthonormality violation

Violation of
Energy conservation...
Momentum conservation...

Potential energy surface

C₂

Na₅
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**SIC revisited**

- **New variational principle**
  
  $\delta \psi_*^\dagger(E_{\text{SIC}} - \sum_{\beta, \gamma} (\psi_\beta | \psi_\gamma) \lambda_{\gamma \beta}) = 0$

- **One-body equations**
  
  $\hat{h}_{\text{SIC}} |\psi_\alpha\rangle = \sum |\psi_\beta\rangle \lambda_{\beta \alpha}$

  $U_\alpha = \hat{U}_{\text{LDA}}[|\psi_\alpha|^2]$

  $\hat{h}_{\text{SIC}} = \hat{h}_{\text{LDA}} - \sum_{\alpha} U_\alpha |\psi_\alpha\rangle (\psi_\alpha |$

- **Double set of wavefunctions**

  - Idea: Exploit a leftover degree of freedom: unitary transform
  - Localized vs physical wavefunctions
  - Symmetrizing vs diagonalizing wavefunctions
  - Several new possibilities

  Application to OEP $\rightarrow$ **Generalized Slater** becomes accurate

  Time dependent calculations in full **SIC** possible
OEP with double set: Generalized Slater

« Natural » Slater approximation on « localized » wavefunctions \( \psi_\alpha \)

Generalized Slater (GSlat)

\[
\varepsilon_i \tilde{\phi}_i(r) = \left[ \hat{h}^{(\text{LDA})}(r) - V_0(r) \right] \tilde{\phi}_i(r)
\]

\[
V_0 \approx \sum_\alpha \frac{|\tilde{\psi}_\alpha|^2}{\rho} U_{\text{LDA}}[|\tilde{\psi}_\alpha|^2]
\]

\[
0 = \langle \tilde{\psi}_\beta | U_{\text{LDA}}[|\tilde{\psi}_\alpha|^2] - U_{\text{LDA}}[|\tilde{\psi}_\beta|^2] | \tilde{\psi}_\alpha \rangle
\]

\[
\tilde{\psi}_\alpha = \sum_i \tilde{\phi}_i u_{i\alpha}
\]
Energy and polarizability of Carbon atom
Exchange only calculation
Hartree-Fock exact $\ll 0\%$
Application to Polarizabilities

Standard DFT test case
Hydrogen chains

\[ G\text{Slater} \approx \text{full SIC} \]
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  **SIC revisited**
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  **Problem**
  **Solution**

Time Dependent SIC
Time Dependent SIC (TDSIC)

- Variational principle

\[ 0 = \delta \int_{t_0}^{t} dt' \left( \sum_{\alpha} (\psi_{\alpha} | i \hbar \partial_t | \psi_{\alpha}) - E_{\text{SIC}} + \sum_{\beta, \gamma} (\psi_{\beta} | \psi_{\gamma}) \lambda_{\gamma\beta} \right) \]

- TDSIC equation

\[ (\hat{h}_{\text{SIC}} - i \hbar \partial_t) | \psi_{\alpha} \rangle = \sum_{\beta} | \psi_{\beta} \rangle \lambda_{\beta\alpha} \]

\[ 0 = (\psi_{\beta} | U_{\beta} - U_{\alpha} | \psi_{\alpha}) \]

\[ \lambda_{\beta\alpha} = (\psi_{\beta} | h_{\alpha} - i \hbar \partial_t | \psi_{\alpha}) \]

- Orthonormality
- Symmetry condition
- Propagation, puzzle
TDSIC made practical

- Propagation scheme
  \[
  \text{Choice:} \quad \left(\hat{h}_{\text{SIC}} - i\hbar \partial_t\right) |\varphi_i(t)\rangle = 0
  \]
  \[
  |\varphi_i(t)\rangle = \exp\left\{-\frac{i}{\hbar} \int_{t_0}^{t} dt' \hat{h}_{\text{SIC}}(t')\right\} |\varphi_i(t_0)\rangle
  \]
  \[
  v_{i\beta}(t) : \quad 0 = (\beta|U_\beta|\psi_\beta|^2 - U_\alpha|\psi_\alpha|^2|\psi_\alpha)
  \]

- An example from molecular physics
  
  Simple 1D dimer
  \[
  w_{ij} = \frac{e^2}{\sqrt{(x_i - x_j)^2 + a_{ij}^2}}
  \]
  Benchmark SIC calculation

2 sets of wavefunctions linked by a unitary transform

\[
|\varphi_i(t)\rangle = \sum_{\beta=1}^{N} |\psi_\beta(t)\rangle \; v_{i\beta}^*(t)
\]

- Propagating set $|\varphi_i(t)\rangle$
- Symetrizing set $|\psi_\beta(t)\rangle$
Some conclusions and perspectives

- From LDA to SIC and beyond
  - **SIC** schemes solve the electronic IP problem
  - Several difficulties remain: formal and numerical challenges
  - Localized vs delocalized wavefunctions
  - **GSlater** provides an appealing alternative to OEP
  - Full **TDSIC** provides the first benchmark calculation

- Applications
  - Cluster dynamics from linear to non linear domain
    - Ex: optical response, photoelectrons spectra, pump/probe dynamics ...
  - Dynamics of organic molecules
    - Ex: irradiation of biological molecules ...
Thank you for your attention