

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

Summary

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)

Problem

Optimized Effective Potential (OEP)

Simple approximations, Slater, ADSIC

Solution

Examples of application

Defects of simple approximations

Problem

SIC revisited

General SIC formulation

Solution

Double set formulation and Generalized Slater

Time Dependent SIC

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About electronic systems

➤ (Quantum) electrons and (classical) ions in molecules

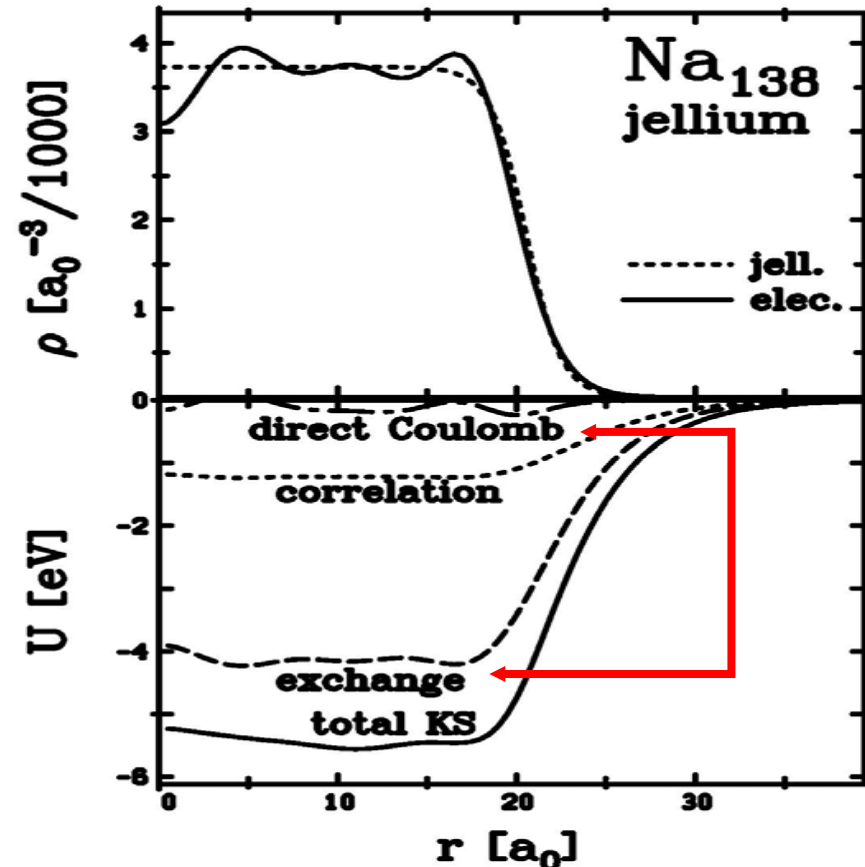
- « Who » follows « whom »
 - Ex: Born Oppenheimer surface
- Large « phase » space for d
 - Ex: degeneracy lifting
- Well defined center of mass

➤ Key role of electron exchange (at

- neutral systems
- most binding comes from ex and corr

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

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graph TD; A[Typical ingredients for irradiation dynamics] --> B[Ionization Potential (IP)]; A --> C[Dissociation energy]; A --> D[Static and dynamical responses];
```

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 - Ionization potential problem
 - Self Interaction Correction (SIC)
 - Optimized Effective Potential (OEP)
 - Simple approximations, Slater, ADSIC
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From DFT to LDA

➤ Electrons

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

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

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

Effective mean field theory

$$h[\rho]\psi_{\alpha} = \dots \quad h[\rho] = -\frac{\hbar^2}{2m}\Delta + \underbrace{U_{\text{H}}}_{\text{Hartree}} + \underbrace{U_{\text{xc}}[\rho]}_{\text{Exch. + Corr.}}$$

- Local Density Approximation

LDA and TDLDA \rightarrow Exchange-correlation function of density ρ

Local Density Approximation (LDA)

➤ Local exchange-correlation to

U_{xc} assumed to be a function of

Ex: pure exch

Ex:

→ In

Ex: In

→ Exhib normal features

→ Many successful applications (s)

➤ LDA tends to delocalize wavef

Table 8.2 LSD Spectroscopic Constants for Diatomic Molecules^a

	r_e (bohrs)		D_e (eV)		ω_e (cm ⁻¹)	
	Expt.	LSD	Expt.	LSD	Expt.	LSD
H ₂	1.40	1.45	4.8	4.9	4400	4190
Li ₂	5.05	5.12	1.1	1.0	350	330
B ₂	3.00	3.03	6.3	7.3	1050	1030
C ₂	2.35	2.35	9.9	9.9	1860	1880
N ₂	2.07	2.07	5.2	5.2	2360	2380
O ₂	2.28	2.27	1.7	1.6	1580	1620
F ₂	2.68	2.61	0.8	0.8	890	1060
Na ₂	5.82	5.67	1.8	1.8	160	160
Al ₂	4.66	4.64	3.1	3.1	350	350
Si ₂	4.24	4.29	5.1	5.1	490	490
P ₂	3.58	3.57	4.4	4.4	780	780
S ₂	3.57	3.57	2.5	2.5	730	720
Cl ₂	3.76	3.74			560	570

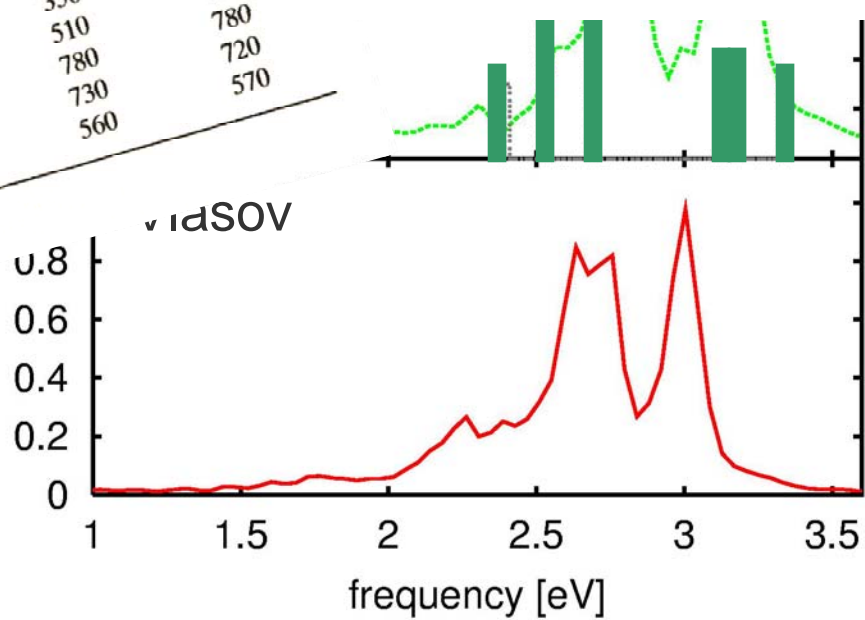
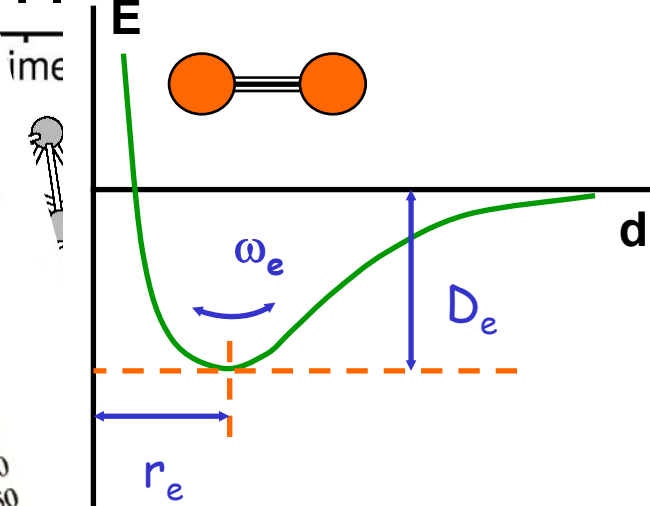
^a From Becke (1986a).

24%

3%

1%

Plasmon response



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But...

➤ Electrons

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

One body density

$$\rho = \sum_{\alpha} |\psi_{\alpha}(\mathbf{r})|^2 = \sum_{\alpha} \rho_{\alpha}$$

Effective mean field theory

$$h[\rho]\psi_{\alpha} = \dots$$

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

Hartree

Exch. + Corr.

- Local Density Approximation

LDA and TDLDA → Exchange-correlation function of density ρ

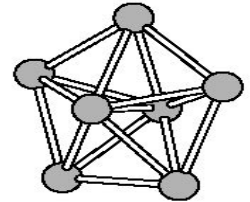
Energy $E_{\text{LDA}}[\rho]$ → Potential $U_{\text{LDA}}[\rho] = \left. \frac{\delta E_{\text{LDA}}}{\delta \rho} \right|_{\rho=\rho}$

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

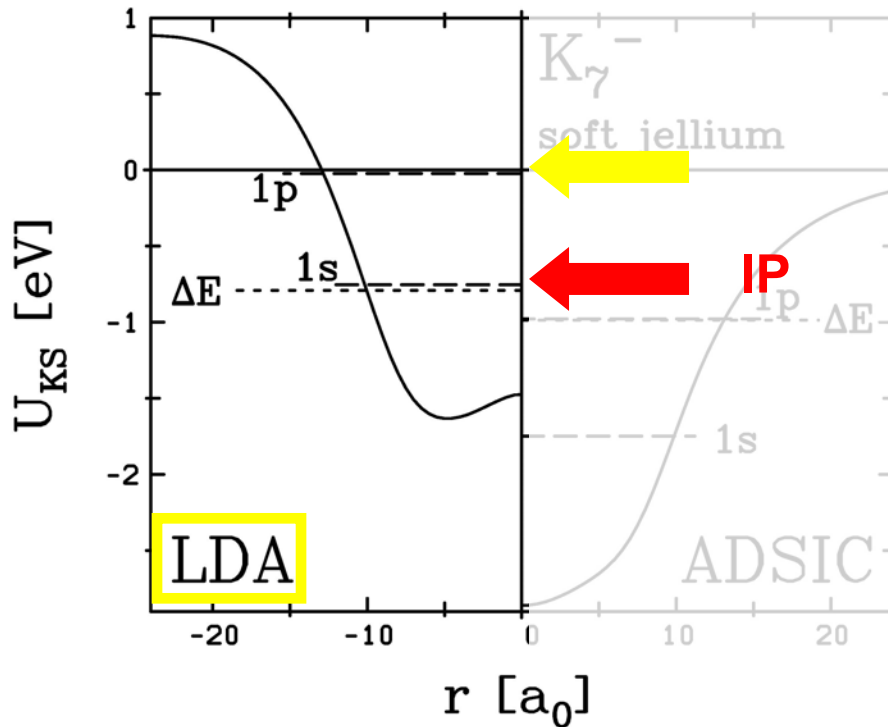
Self Interaction

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

↪ **LDA : Almost no binding**
Totally wrong IP (reasonable ΔE) → dynamics ?



The Ionization Potential Problem (2)

Example of organic molecules:

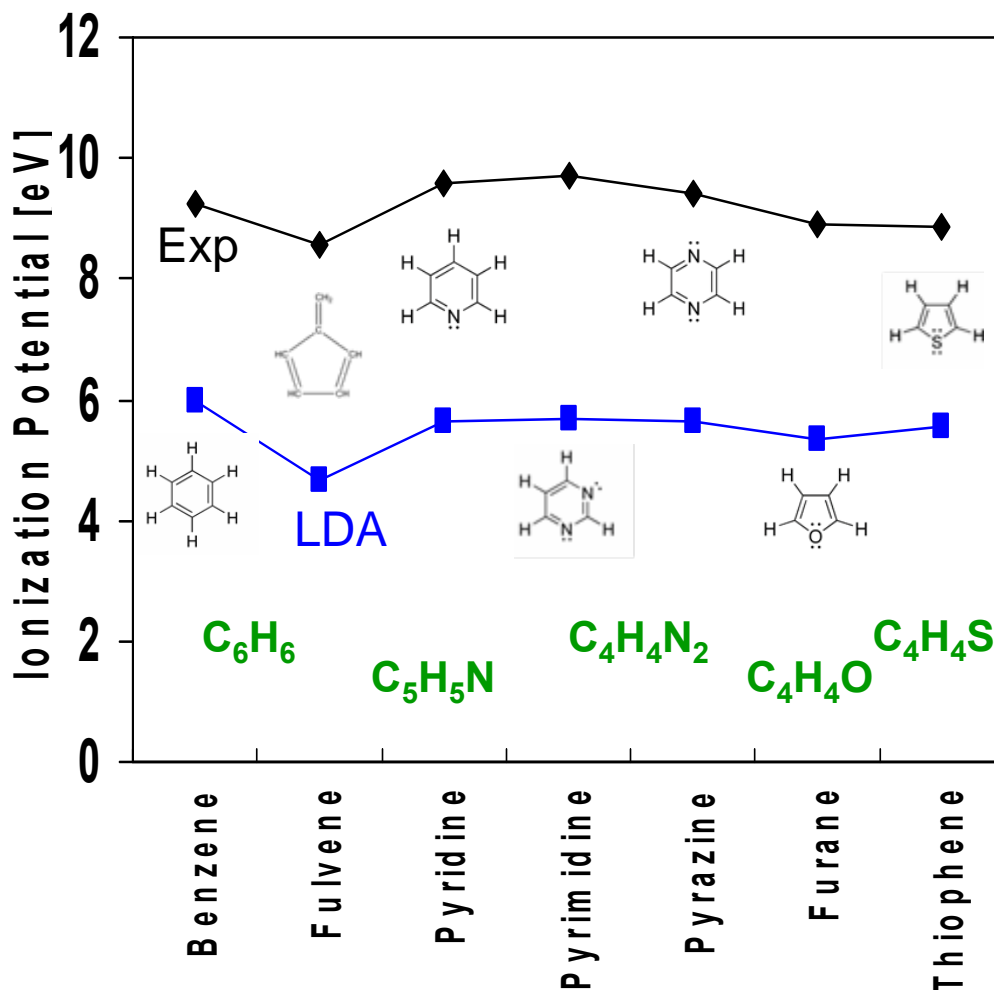
Benzene-like cyclic structures:

$H \rightarrow N, O, S$

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

$$\hat{h}_{\text{SIC}} = \hat{h}_{\text{LDA}} - U_{\text{LDA}}[|\psi_{\alpha}|^2] = \hat{h}_{\text{SIC}, \alpha}$$

Orbital dependent field

Loss of orthonormality ...

Time dependent formulation ?

Approximation by **O**ne potential: **O**ptimized **E**ffective **P**otential

NB: No **SIC** problem in **HF** due to exact cancellation by exchange

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Optimized Effective Potential (OEP)

➤ **SIC and**

Try to restore
of a **unique c**

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

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

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

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

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

$$V_C = \frac{1}{2} \sum \frac{\nabla \cdot (n \nabla \varphi_i)}{\rho_A(|\varphi_i|^2)}$$

Full OEP « painful » ...

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

$$G_i(\mathbf{r}, \mathbf{r}') = \sum_{j \neq i} \frac{\tilde{\varphi}_j^*(\mathbf{r}) \tilde{\varphi}_j(\mathbf{r}')}{\epsilon_j - \epsilon_i} .$$

al » choice
is φ_i by V_0

$$\rightarrow \varphi_i^{V_0}$$

$$V_K + V_C$$

Optimized Effective Potential (OEP)

➤ SIC and beyond

Try to restore a common potential by « optimal » choice of a **unique common V_0** : « parametrize » wavefunctions φ_i by V_0

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

➤ Practically

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

KLI, Slater, ADSIC...

From full OEP to ...

$$\rho = \sum_{\alpha} |\psi_{\alpha}(\mathbf{r})|^2 = \sum_{\alpha} \rho_{\alpha}$$

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

Krieger Li Iafrate (KLI)

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

« Local » Average (Slater)

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

« Global » Average

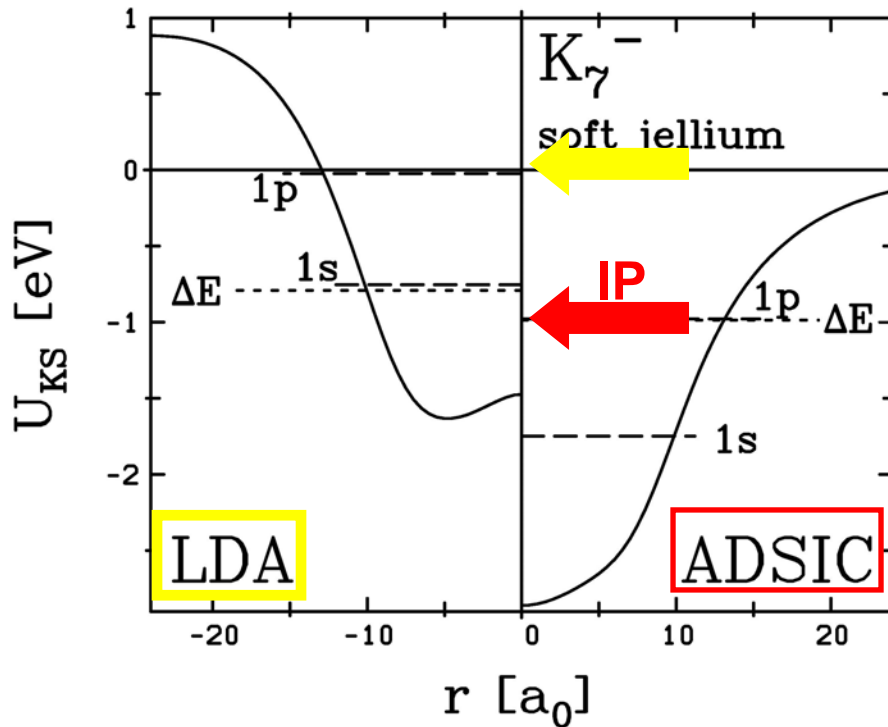
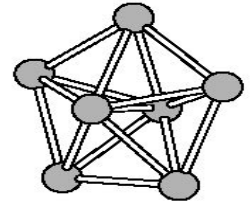
$$U^{\text{ADSIC}} = U_{\text{LDA}} - \left[U_{\text{H}} \left(\frac{\rho}{N} \right) + U_{\text{xc}} \left(\frac{\rho}{N} \right) \right]$$

Averaged Density SIC (ADSIC)

$$\rho_{\alpha} \rightarrow \rho/N$$

Back to anion clusters

➤ Potential and level scheme



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

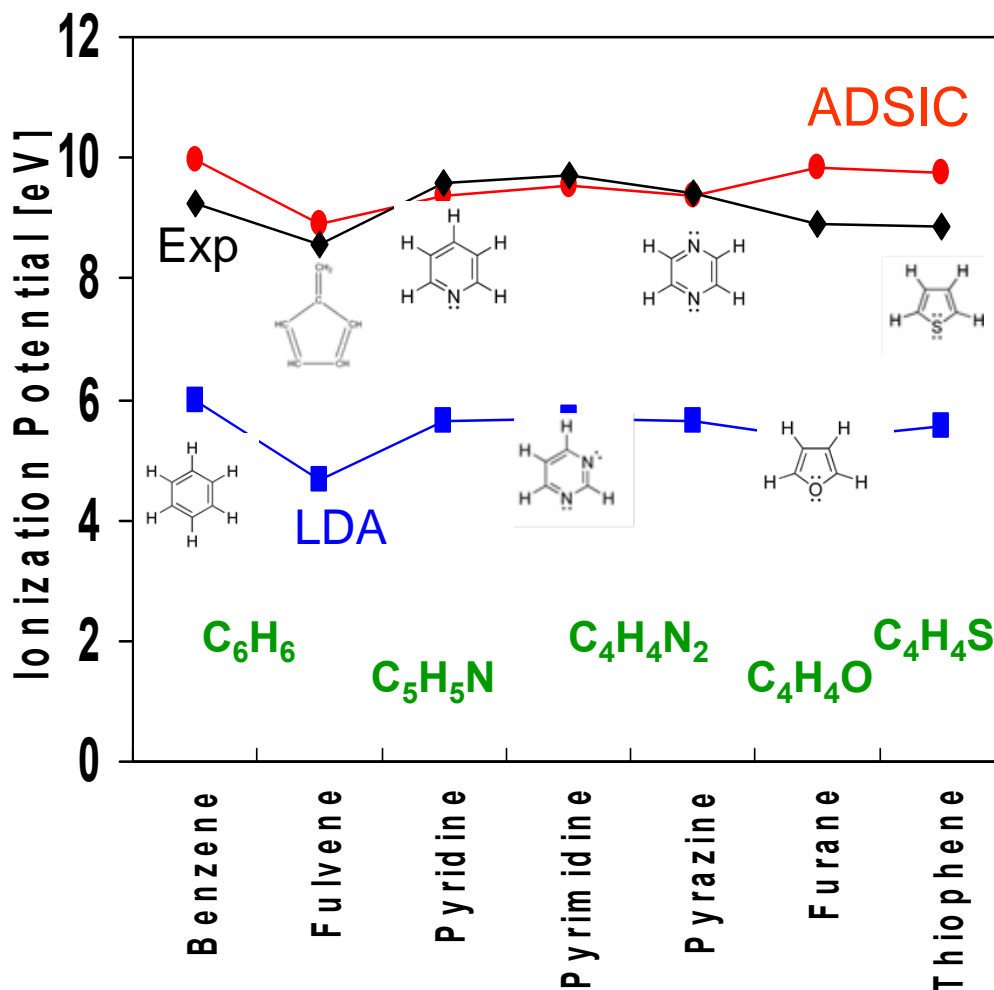
Exp:
Little bound system
Ionization Potential about 1 eV

↻ **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

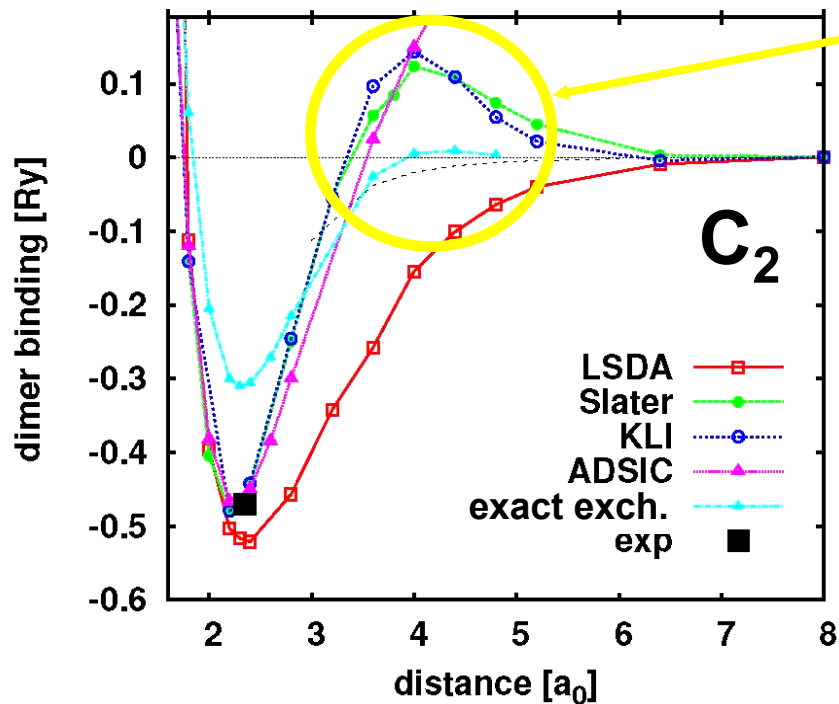


ADSIC : Correct IP

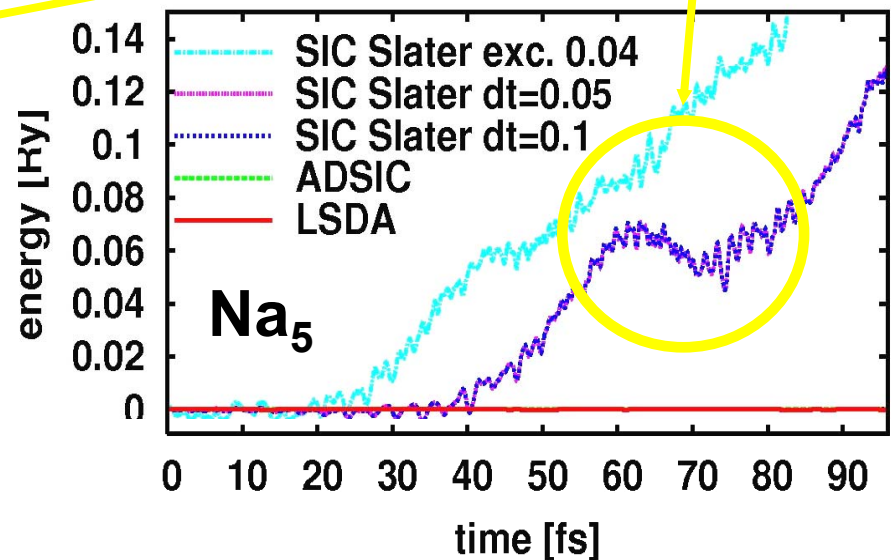
New bad surprises ...

Orthonormality violation

Potential energy surface



Time variation of localization/delocalization?



Dissociation problem
Polarizability problem

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

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➤ **New variational principle**

$$\delta_{\psi_{\alpha}^*} (E_{\text{SIC}} - \sum_{\beta, \gamma} (\psi_{\beta} | \psi_{\gamma}) \lambda_{\gamma\beta}) = 0$$

➤ **One-body equations**

$$\hat{h}_{\text{SIC}} |\psi_{\alpha}\rangle = \sum_{\beta} |\psi_{\beta}\rangle \lambda_{\beta\alpha}$$

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

(Key) Symmetry condition

Orthonormality

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

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

➤ **Double set of wavefunctions**

- Idea: Exploit a left over degree of freedom : unitary transform

- Localized vs physical wavefunctions

Symmetrizing vs diagonalizing wavefunctions

- Several new possibilities

Application to OEP → Generalized Slater becomes accurate

Time dependent calculations in full SIC possible

OEP with double set: Generalized Slater

« Natural » Slater approximation on
« localized » wavefunctions ψ_α
Generalized Slater (GSlat)

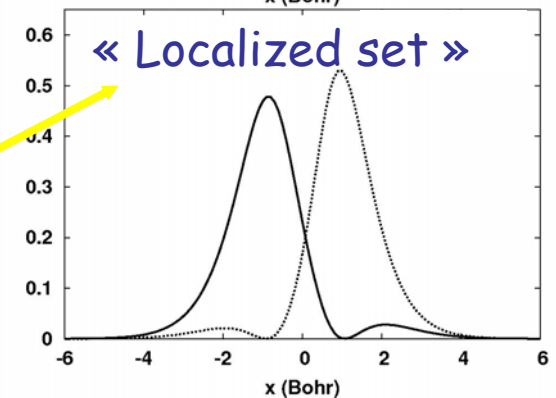
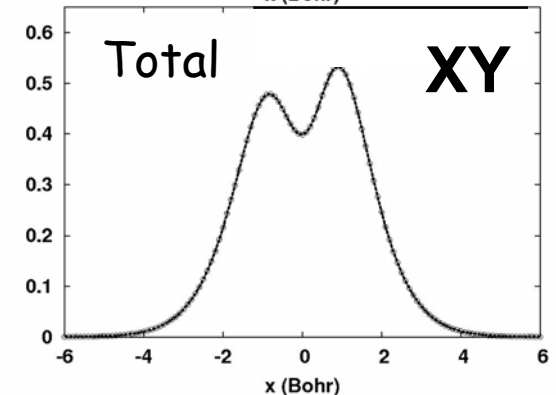
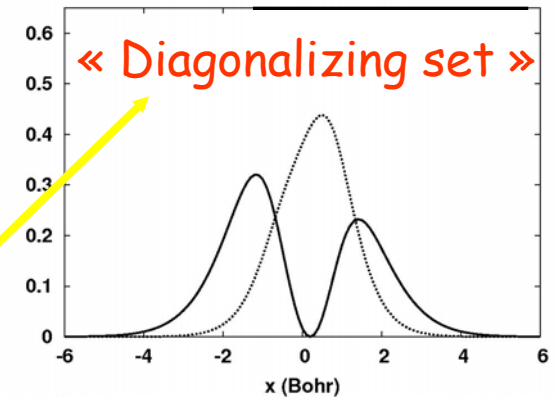
$$\varepsilon_i \tilde{\varphi}_i(\mathbf{r}) = \left[\hat{h}^{(\text{LDA})}(\mathbf{r}) - V_0(\mathbf{r}) \right] \tilde{\varphi}_i(\mathbf{r})$$

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

$$0 = (\tilde{\psi}_{\beta} | U_{\text{LDA}}[|\tilde{\psi}_{\alpha}|^2] - U_{\text{LDA}}[|\tilde{\psi}_{\beta}|^2] | \tilde{\psi}_{\alpha})$$

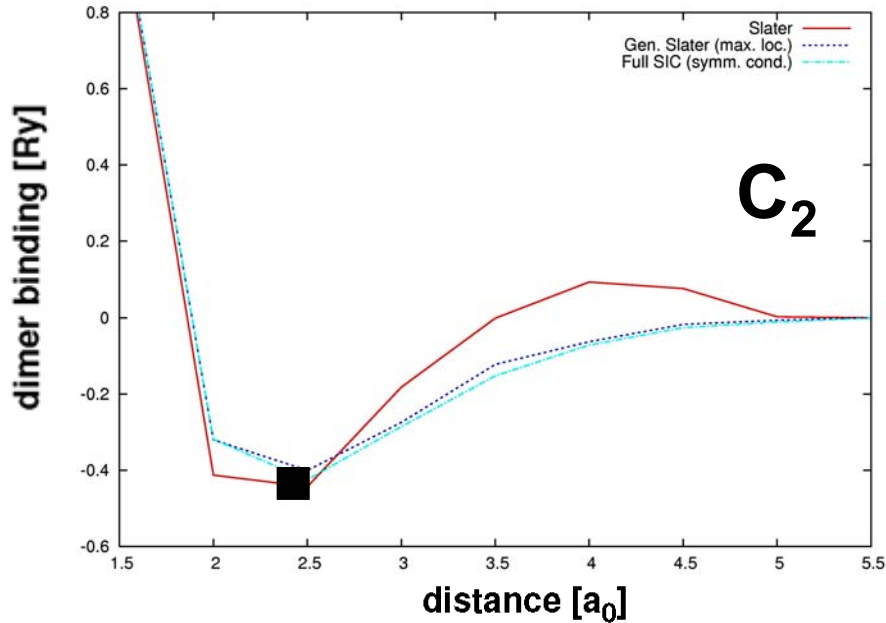
$$\tilde{\psi}_{\alpha} = \sum_i \tilde{\varphi}_i u_{i\alpha}$$

Single electron density



Generalized Slater

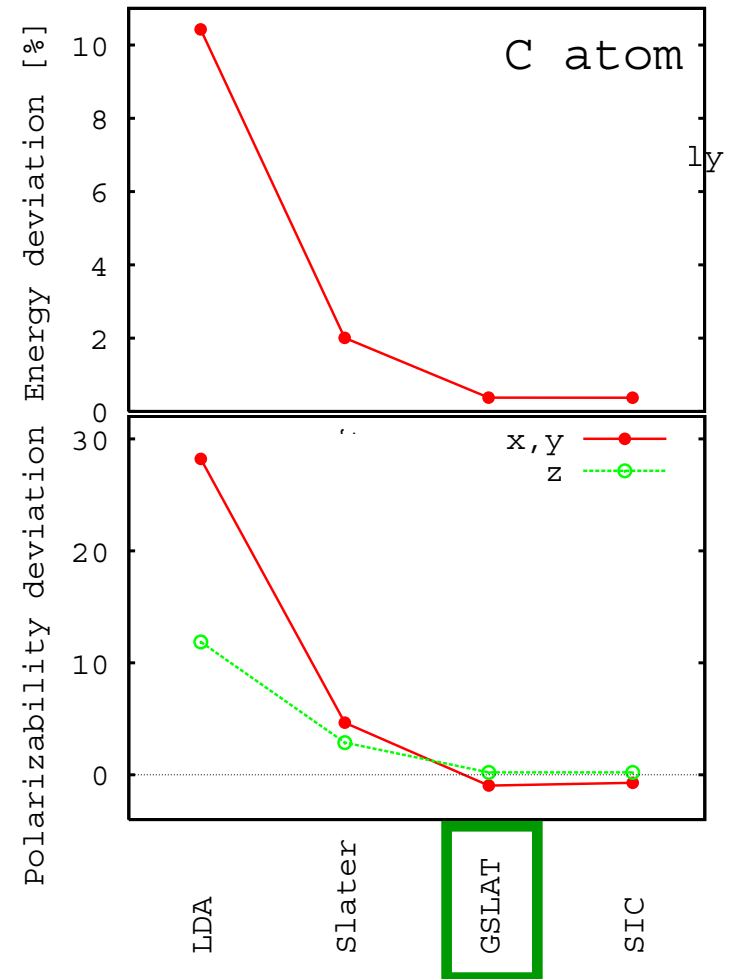
Potential energy surface



GSlater \approx full SIC \approx HF
 GSlater and SIC restore
 dissociation properties of C₂

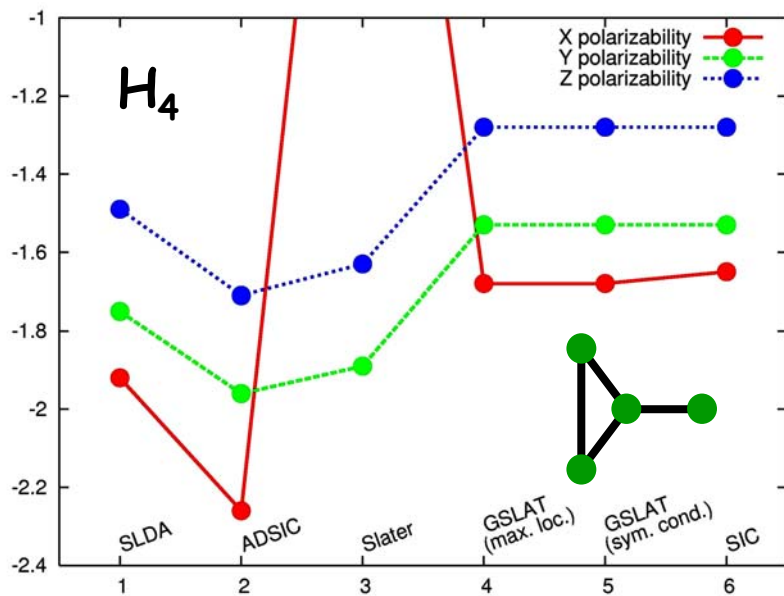
Energy and polarizability
 of Carbon atom

Exchange only calculation
 Hartree-Fock exact « 0% »



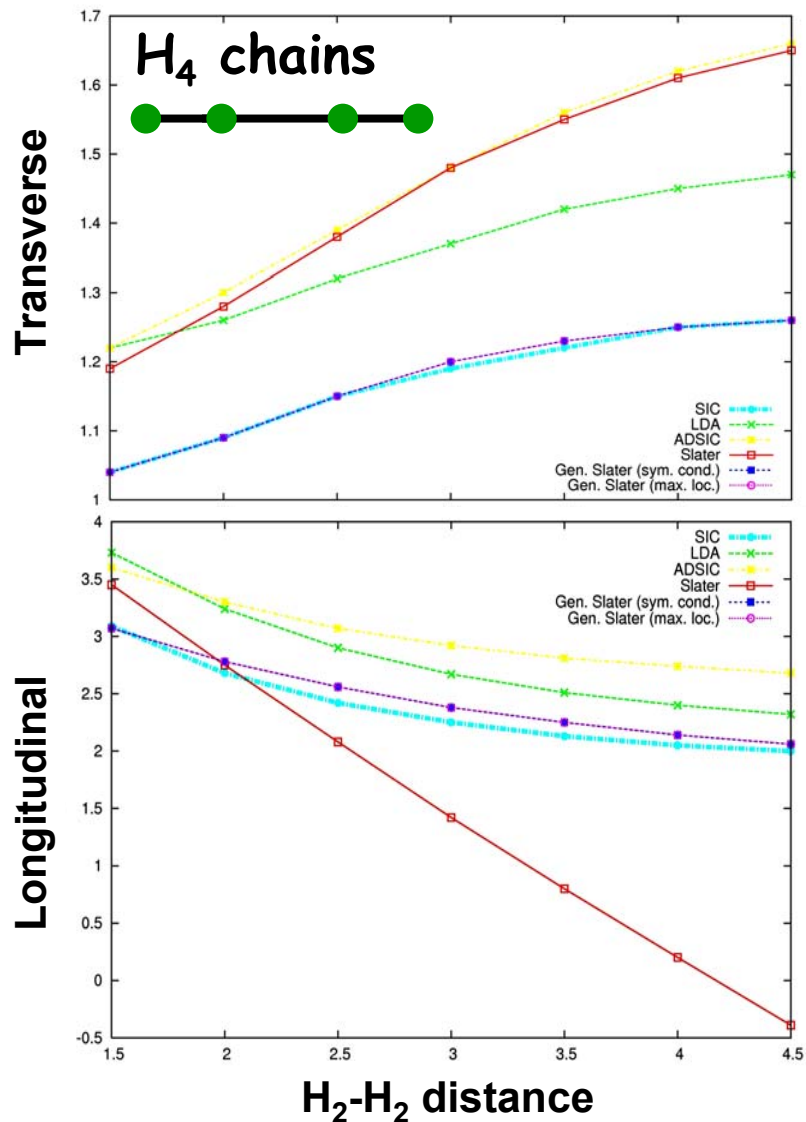
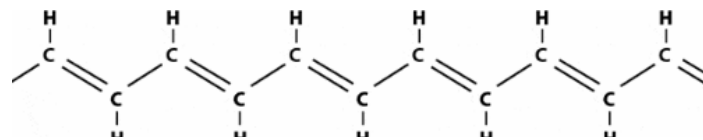
Application to Polarizabilities

Standard **DFT** test case
Hydrogen chains



GSlater \approx full SIC

Polyacetylene



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Time Dependent SIC

Time Dependent SIC (TDSIC)

➤ Variational principle

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

Orthonormality

➤ TDSIC equation

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

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

← Symmetry condition

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

← Propagation, puzzle

TDSIC made practical

➤ Propagation scheme

Choice : $(\hat{h}_{\text{SIC}} - i\hbar\partial_t) |\varphi_i\rangle = 0$

$$|\varphi_i(t)\rangle = \exp\left\{-\frac{i}{\hbar} \int_{t_0}^t dt' \hat{h}_{\text{SIC}}(t')\right\} |\varphi_i(t_0)\rangle$$

$$v_{i\beta}(t) : 0 = (\psi_\beta | U_\beta [|\psi_\beta|^2] - U_\alpha [|\psi_\alpha|^2] | \psi_\alpha)$$

➤ An example from molecular physics

Simple 1D dimer

$$w_{ij} = \frac{e^2}{\sqrt{(x_i - x_j)^2 + a_{ij}^2}}$$

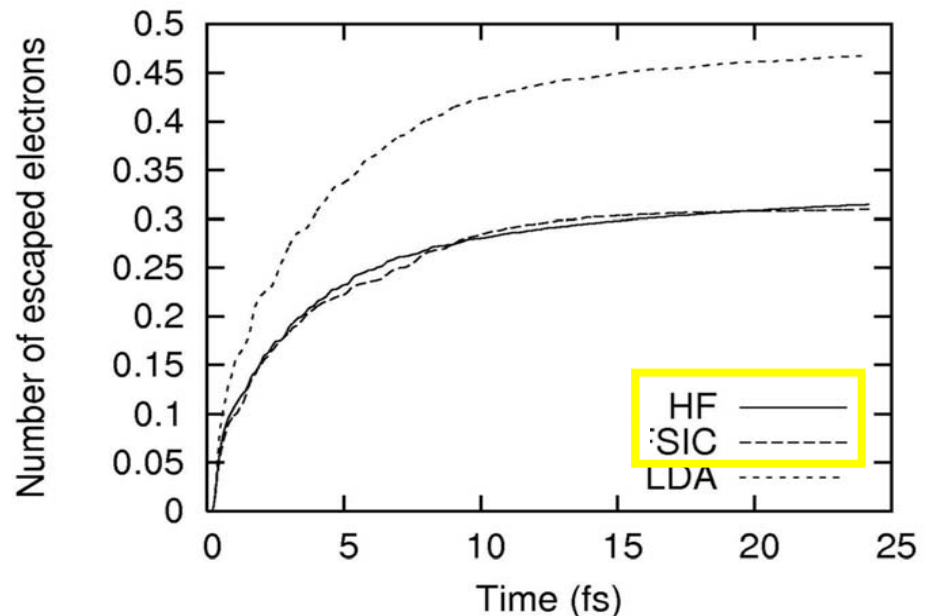
Benchmark SIC calculation

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