Towards real space indicators of the metallic state: Partitioning the localization (or position spread) tensor

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Outline

Introduction

About electrical conductivity

Kohn PR 133 A171 (1964); Resta PRL 80, 1800 (1998)

- What does it characterize a metal/insulator?
  - At the mean-field level: One electron band gap (HOMO-LUMO)
  - In general: Excitation spectrum
- Is it possible to determine this character from the ground state?
  - A seminal paper by Kohn (1964) establishes this link.
  - The theory of the insulating state: Insulators display ground states with disconnected regions in the Hilbert space.
- Forgotten for long time until revisited & generalized by Resta (1998-)
  - It is the organization of electrons that renders a system conducting or insulating.
  - Broadly speaking: delocalized vs. localized.
  - A quantitative measure is provided by the localization tensor.

Introduction

Conductivity indicators in real space

- May real space descriptors of metallic or insulating-like character be found in extended as well as molecular systems?
  - Partitioning of space provided by the QTAIM
- Long-standing question without only recent clear answers.
- Some initial QTAIM proposals unfruitful:
  - Non-nuclear attractors found in Li molecular clusters.
  - Present in bcc-Li, ... but not in Cu, Al.
- From Kohn-Resta, ... it is not in the density.
- Tempting to examine real space delocalization measures.

Known results in extended systems

Metals

e.g. Goedecker, PRB 58, 3501, (1998)

- $\rho(\boldsymbol{r};\boldsymbol{r}') \equiv \rho(|\boldsymbol{r}-\boldsymbol{r}'|) \equiv \rho(\boldsymbol{r})$ decays like a power law at $T=0$.
- For free electron bands
  $\rho(r) = 2(2\pi)^{-3}\int_{\boldsymbol{k}<\boldsymbol{k}_F} d\boldsymbol{k} e^{-i\boldsymbol{k}\boldsymbol{r}} = \frac{-k_F}{\pi^2 r^2}(\cos(rk_F) - \sin(rk_F)/(rk_F))$

Insulators

e.g. PRL 88, 196405 (2002)

- Exponential decay for $\rho(|\boldsymbol{r}-\boldsymbol{r}'|) \approx e^{-\lambda|\boldsymbol{r}-\boldsymbol{r}'|}$
- Decay length λ proportional to the gap Δ.

Real space delocalization measures

- Well known in real space theories of the chemical bond.
  - Becke's & Edgecombe ELF (local, drawback).
  - QTAIM's delocalization indices δ^{AB}, extension of Wiberg-Mayer bond order.
  - etc.

Delocalization index

Bader & Stephens 1974

- $\mathrm{DI}(A,B) = \delta^{AB} = 2\int_{\Omega_A} d\boldsymbol{r}_1 \int_{\Omega_B} d\boldsymbol{r}_2 \rho_2^{xc}. \qquad \rho_2^{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \rho_1(\boldsymbol{r}_1)\rho_1(\boldsymbol{r}_2) - \rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2)$
- Scalar parameter between each pair of atoms: $1/2\sum_{A,B}\delta^{AB} = N$.
- Condenses two-center electron population fluctuations.
  - $\delta^{AB} = -2\mathrm{cov}(n_A,n_B) = -2\left[\langle n_A n_B\rangle - \langle n_A\rangle\langle n_B\rangle\right]$
  - $\langle n_A n_B\rangle = \sum_{n_A,n_B} n_A n_B p(n_A,n_B), \qquad \langle n_A\rangle = \sum_{n_A} n_A p(n_A)$
- At the single-determinant level (non-interacting effective electrons) $\rho_2^{xc} = \rho(\boldsymbol{r}_1;\boldsymbol{r}_2)\rho(\boldsymbol{r}_2;\boldsymbol{r}_1) \equiv |\rho(\boldsymbol{r}_1;\boldsymbol{r}_2)|^2$
- For interacting systems (correlated level) still dominated by Fock-Dirac.

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Real space delocalization measures

Expectations for extended systems

- DI's should fall as power-law for metals: $\delta \approx r^{-f}$
  - f depends on dimension.
  - DI's might show Friedel-like oscillations.
- DI's should fall exponentially for insulators. $\delta \approx e^{-\lambda r}$
  - λ depends on Δ.

Results

- DIs behave as predicted in models (Hückel, TB, Hubbard).
- Actual computations in real systems support results in models.

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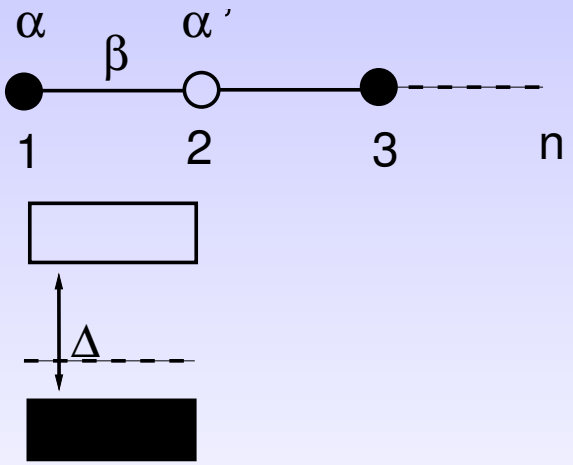
Finite analytical model systems

Hückel heteroatomic AB chain

- $H = \mathrm{diag}(\alpha_i) + \beta T$, $T = \delta_{|i-j|=1}$ is tridiagonal
- Two α and α' values ($\alpha' = 0$).
- $\lambda_k = \left(\alpha \pm \sqrt{\alpha^2 + 16\cos^2(k\pi/(n+1))}\right)/2, k = 1, n/2$
- Gap $\Delta(\gamma) = \alpha + 2\pi^2\gamma^2/\alpha + \mathcal{O}(\gamma^3)$



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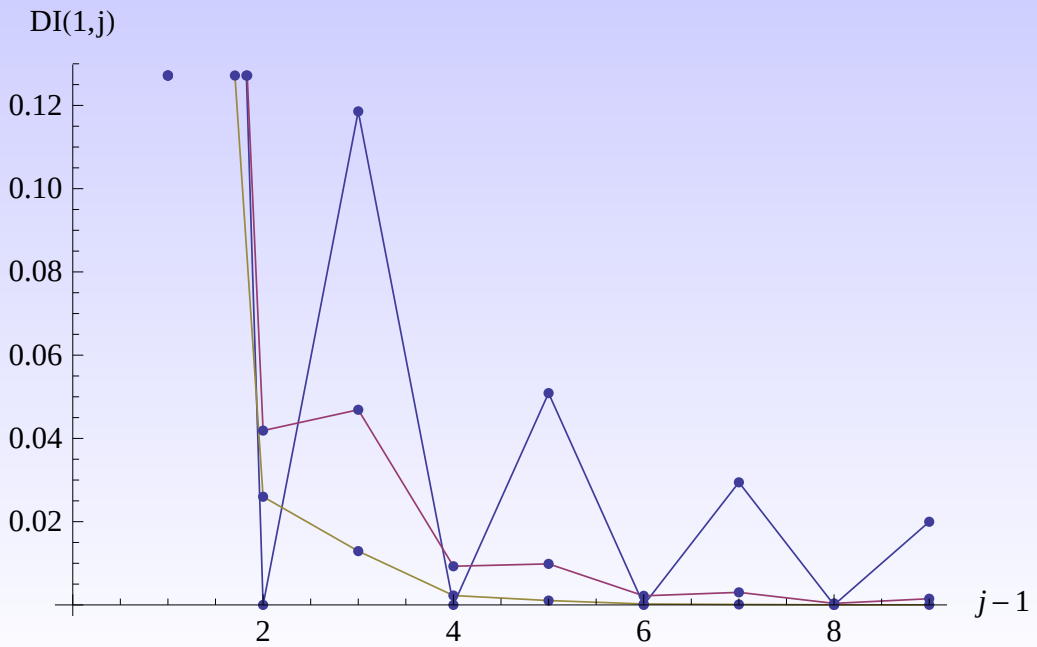
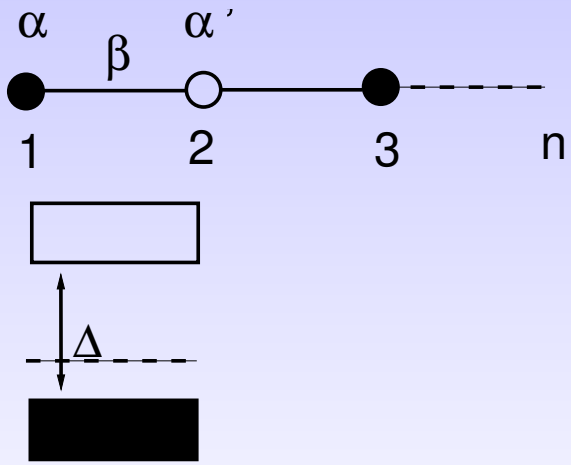
- $n = 10$ chain. $\alpha = 0, 1, 2$. From power-law to exponential





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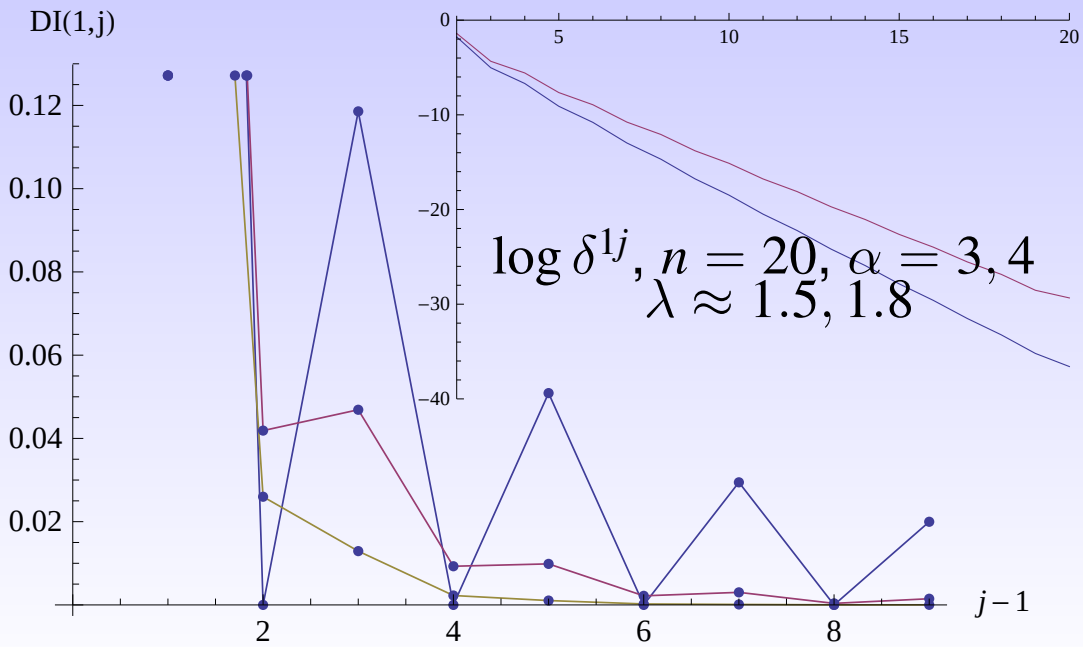
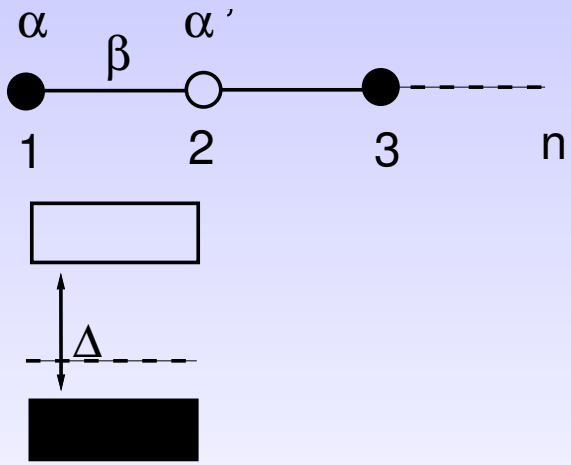
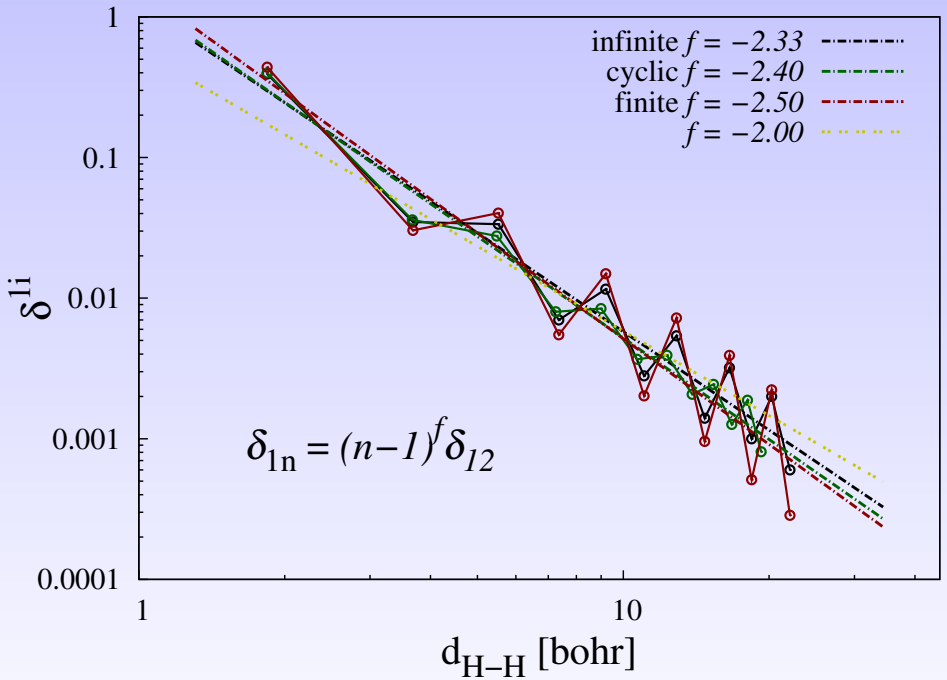




Metallic-like behavior
Hydrogen chains

H chains

- Fixed nearest neighbors distance.
- 6-311G(p) Hartree-Fock finite data.
- Elk+DGRID 1D Kohn-Sham periodic calculations.



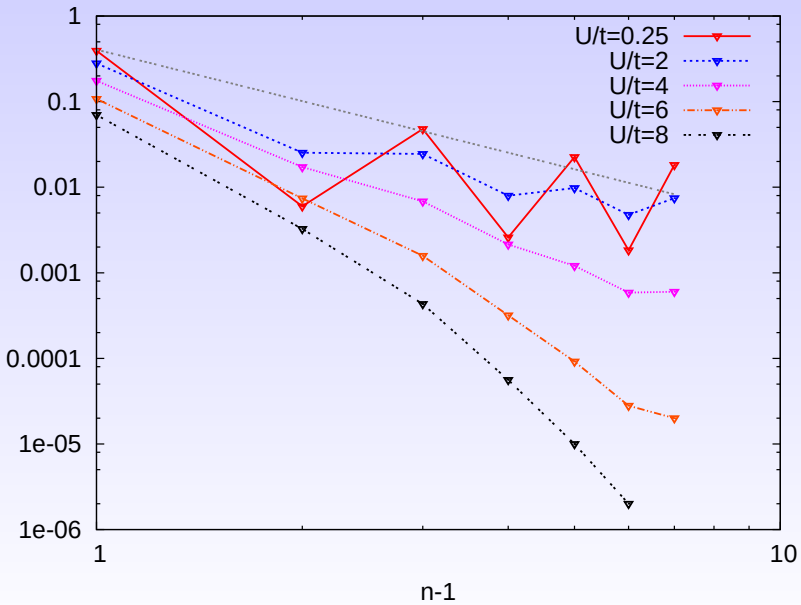
- $a = 1.84$ au.
- $\delta^{1,2i+1} \neq 0$ but small.
- Friedel-like oscillations clear even for finite chains
- f values larger than Hückel or TB, but definitely power-law scaling.

$\delta^{1,2(4)}$ close to models: $0.44(0.40), 0.04(0.04)$ for infinite chain.

Effect of correlation

Mapping to Hubbard Hamiltonian

- $H = -t\sum_{\langle i,j\rangle,\sigma}(c^{+}_{i\sigma}c_{j\sigma} + c^{+}_{j\sigma}c_{i\sigma}) + U\sum_i n_{i\uparrow}n_{i\downarrow}$
- U/t measures correlation
  - $U = 0 \equiv$ TB: independent electrons, 1SD.
  - $U/t \to \infty \equiv d \to \infty$ dissociation limit
  - $U/t \approx d$ mapping
- Lieb-Wu exact solution: No Mott transition for 1D Hubbard. AF singlet solution for any U/t



- $\delta^{1,n}$ for H_{14}
- Wild oscillations for small U/t
- Dampening on growing U/t
- Change above $U/t = 4$ to exponential

The theory of the insulating state

The localization tensor (LT)

Resta JCP 124 104104 (2006)

- $\boldsymbol{\lambda}$ is the second cumulant moment of the total position operator $\hat{\boldsymbol{R}} = \sum_i^N \hat{\boldsymbol{r}}_i$
- The $\hat{\boldsymbol{R}}$ operator is ill-defined under periodic boundary conditions $\Rightarrow$ Berry phases, nice stuff.

$$\boldsymbol{\lambda} = \frac{1}{N}\left\{\langle\Psi|\hat{\boldsymbol{R}}\otimes\hat{\boldsymbol{R}}|\Psi\rangle - \langle\Psi|\hat{\boldsymbol{R}}|\Psi\rangle\otimes\langle\Psi|\hat{\boldsymbol{R}}|\Psi\rangle\right\}$$

- Example $\lambda_{xy} = \frac{1}{N}\left\{\langle\Psi|\hat{X}\hat{Y}|\Psi\rangle - \langle\Psi|\hat{X}|\Psi\rangle\langle\Psi|\hat{Y}|\Psi\rangle\right\}$

Thermodynamic limit

- λ diverges for conductors
- λ converges for insulators

The theory of the insulating state

Why? Fluctuation-dissipation theorem

- if $\boldsymbol{\alpha}(\omega)$ is the polarizability tensor,
  $\boldsymbol{\lambda} = (1/N)\int_0^\infty d\omega\ \mathrm{Im}\boldsymbol{\alpha}(\omega)$
- With PBC, $\sigma(\omega)$ the conductivity,
  $(\pi e^2/\hbar)\lambda_{\beta\gamma} = \delta_{\beta\gamma}(V/N)\int_0^\infty d\omega\ \mathrm{Re}\sigma(\omega)/\omega$
- If E_g is the optical gap, $\lambda_{\alpha\alpha} \leq \hbar^2/(2m_e E_g)$

Invariant formulation

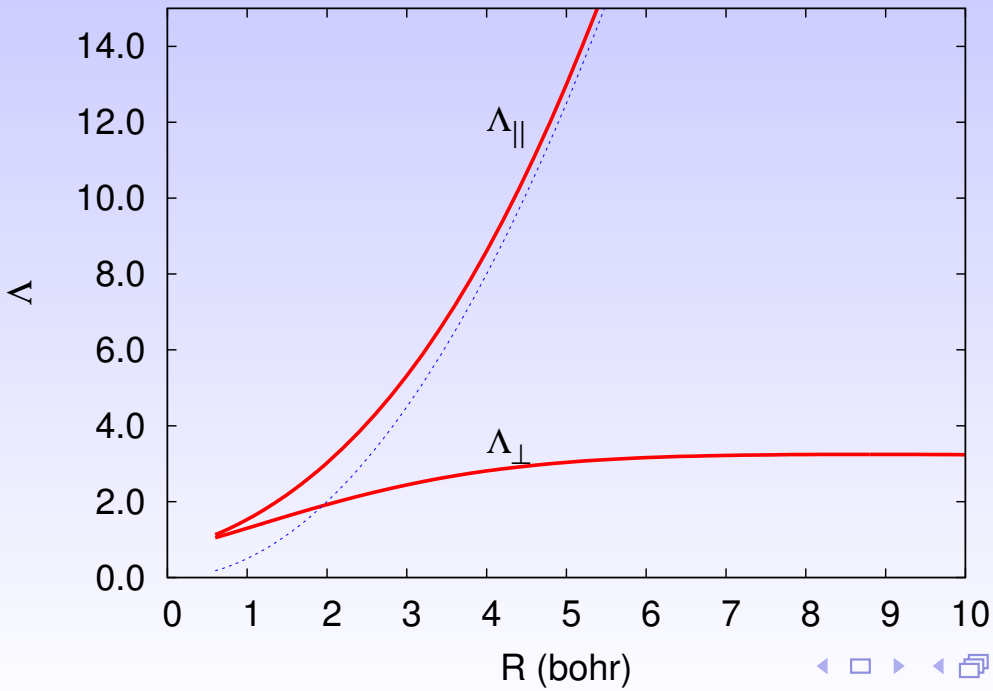
- After a little playing,
  $\lambda = \frac{1}{2N}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2\ \ (\boldsymbol{r}_{12}\otimes\boldsymbol{r}_{12})\,\rho_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2).$
- Interelectron spread...

The LT in finite systems

The total position spread tensor (PST)

Leininger JCTC 9 5286 (2013)

- Evangelisti and Leininger have proposed to used $\Lambda = N\lambda$
- The PST has been used as a chemical bonding indicator
  - It captures dissociations & other processes.
- H_2 dissociation. HF (CAS)//aug-cc-pVTZ ($\langle <^2 \rangle = 1$ for H)



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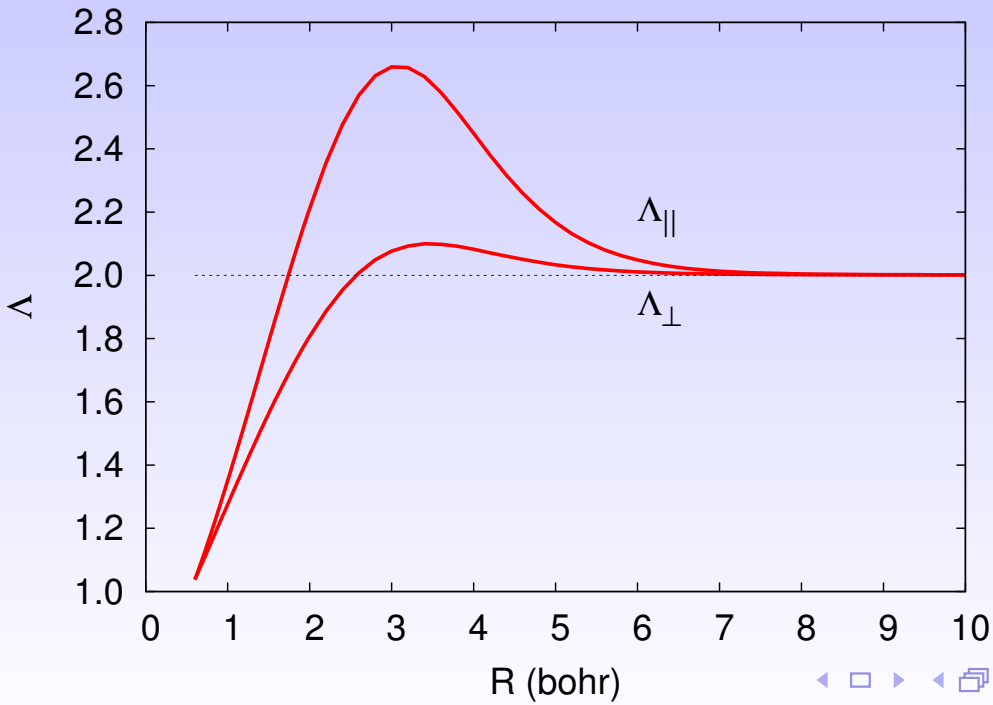
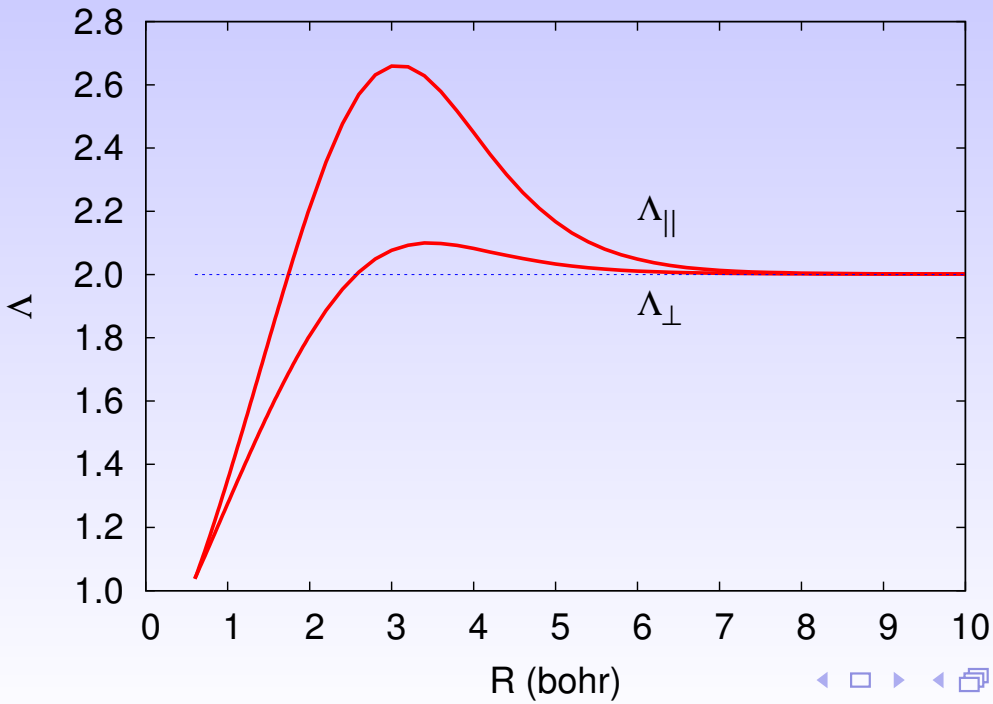


The LT in finite systems

The total position spread tensor (PST)

Leininger JCTC 9 5286 (2013)

- Why does it diverge in the HF approx.?
- How to get insights in polyatomics?
  - All processes appear at the same time
- Can we partition Λ and learn?



Partitioning Λ in real space

Recall that $\Lambda = \frac{1}{2}\int_A d\boldsymbol{r}_1 \int_A d\boldsymbol{r}_2\ (\boldsymbol{r}_{12} \otimes \boldsymbol{r}_{12})$

Real space partition, $R^3 = \bigcup A$

$$\begin{aligned}
\Lambda &= \sum_{A \geq B} \Lambda^{AB}, \\
\Lambda^{AA} &= \frac{1}{2}\int_A d\boldsymbol{r}_1 \int_A d\boldsymbol{r}_2\ (\boldsymbol{r}_{12} \otimes \boldsymbol{r}_{12})\rho_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2), \\
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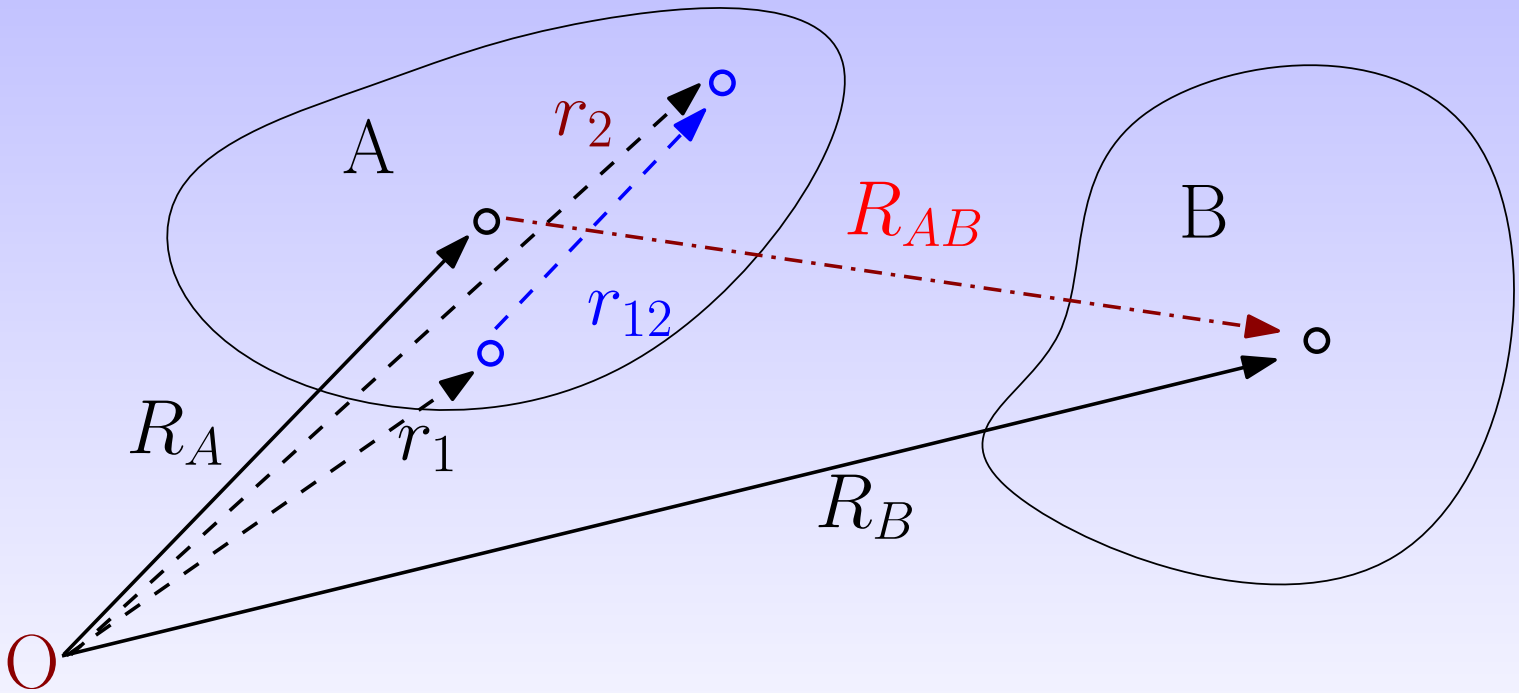
\end{aligned}$$

Partitioning Λ in real space

Convergence/Divergence

- Λ^{AA} is bounded
- Λ^{AB} behaves as $\sim (\boldsymbol{R}_{AB} \otimes \boldsymbol{R}_{AB})\delta^{AB}/2$ at large R_{AB}



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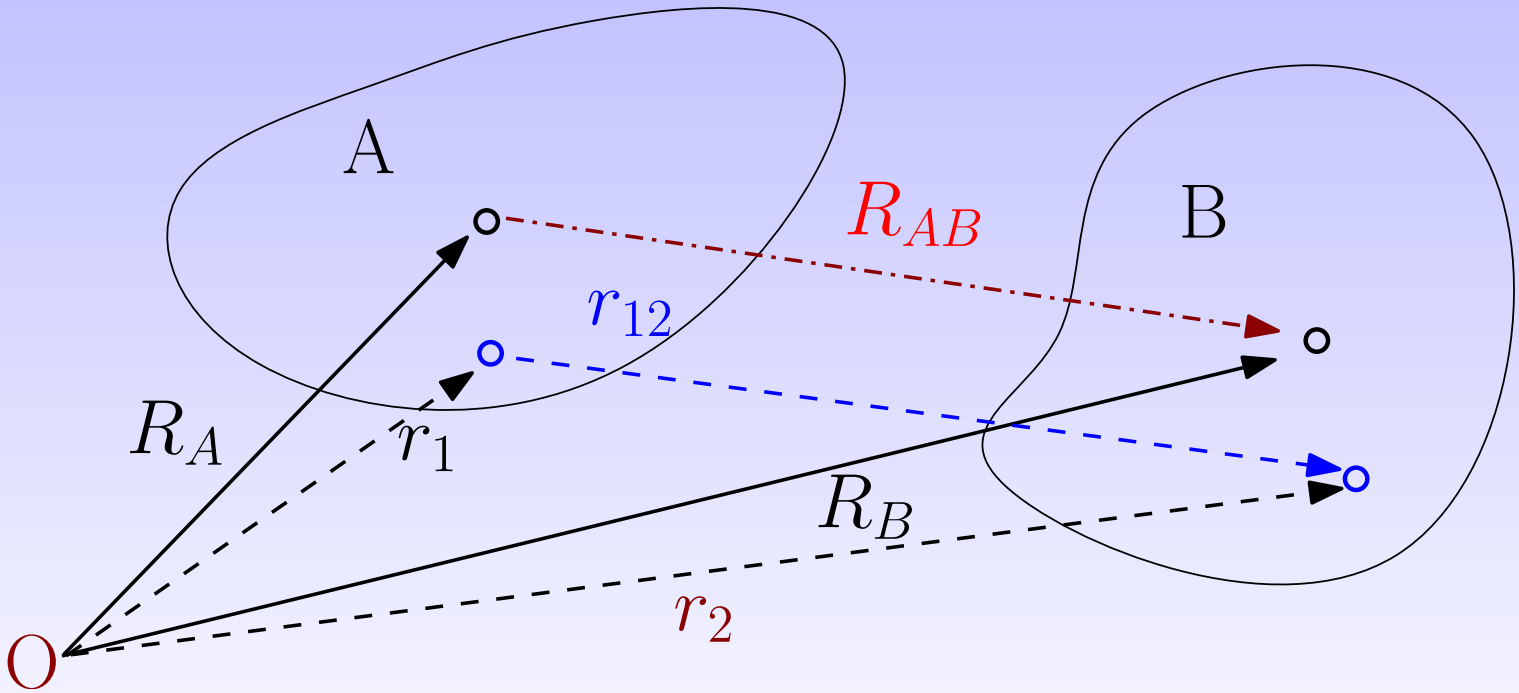
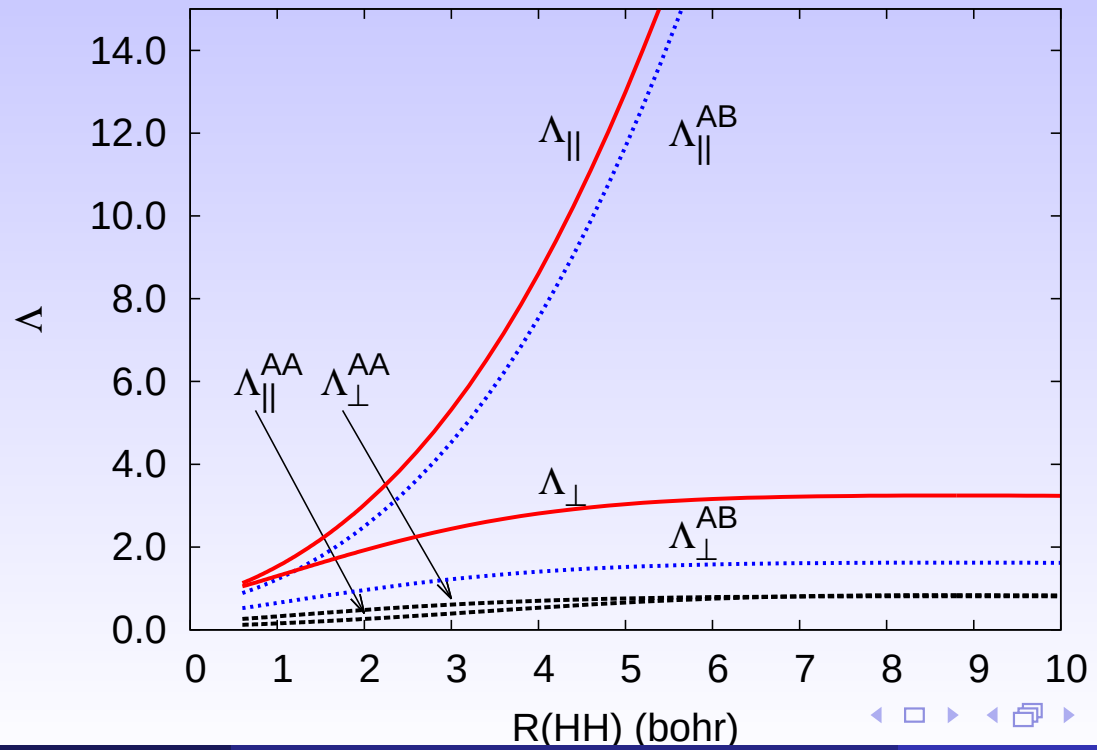


Partitioning Λ in real space

Examples

The H_2 molecule revisited

- At the HF level, $\Lambda_{\parallel}^{AB}$ diverges as $R^2/2$, since $\delta = 1$
- At the CAS level, Λ^{AA} is finite, goes to 1. $\Lambda_{\parallel}^{AB}$ shows localization, δ decreases to 0 exponentially.



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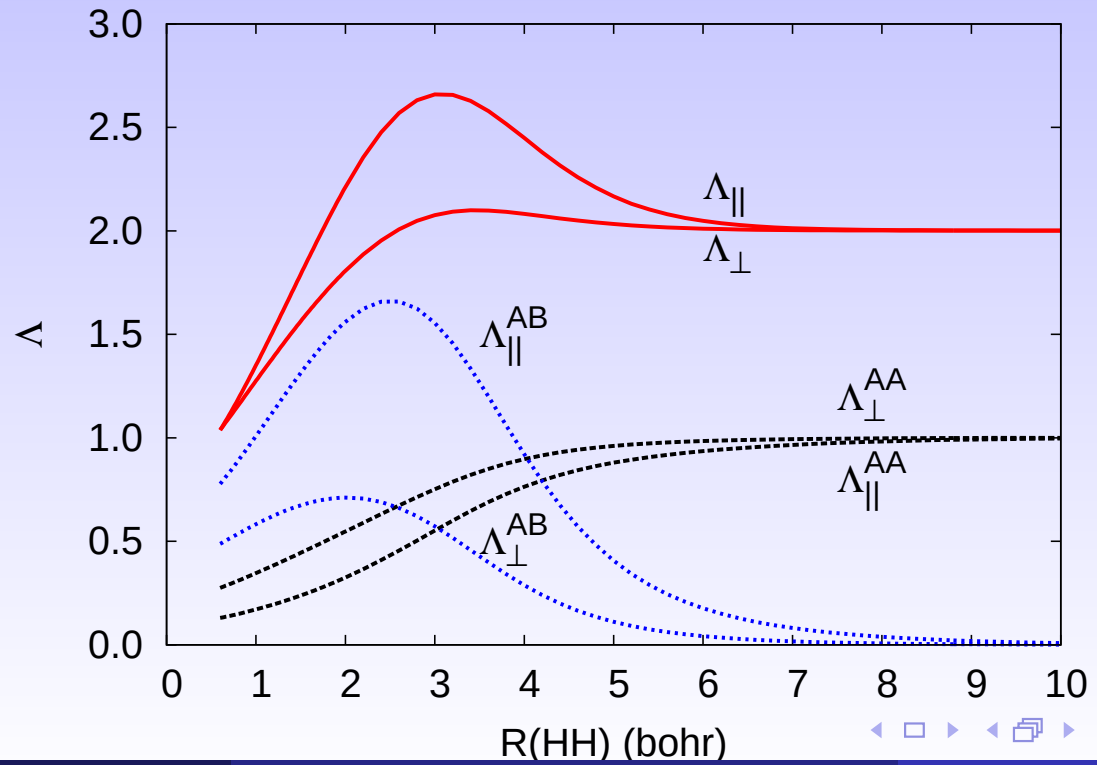
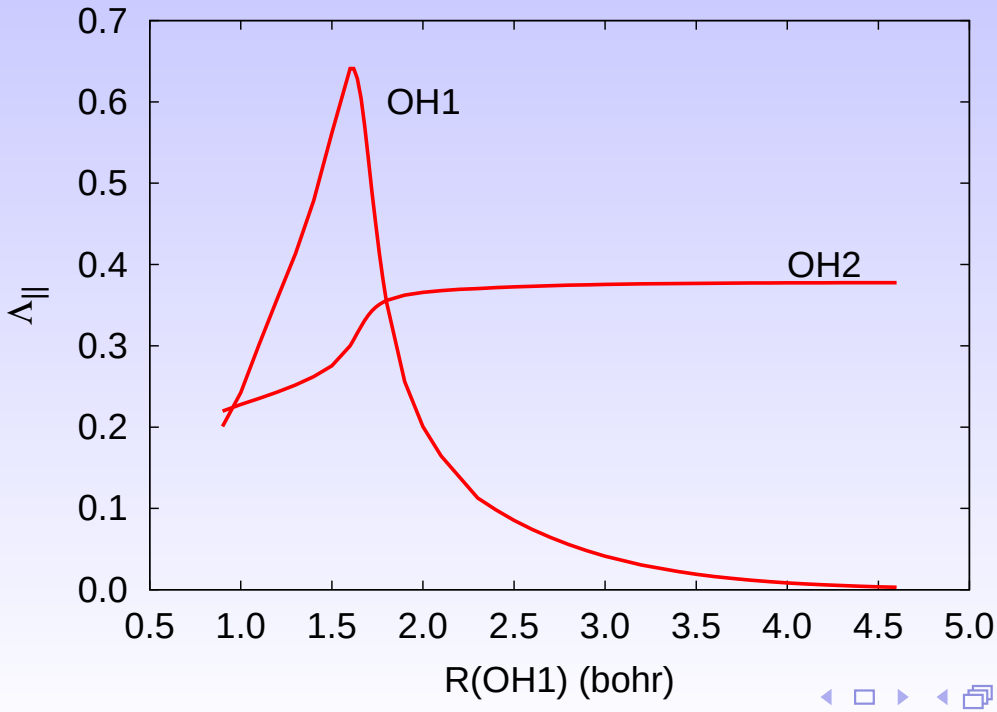


Partitioning Λ in real space

Examples

The H_2O molecule CAS[8,8]//6-311G*

- Dissociation of the OH1 bond
  - We differentiate the essential/spectator interactions.
  - The OH1 bond dissociates.
  - The OH2 bond jumps from the initial to the final bonding situation.



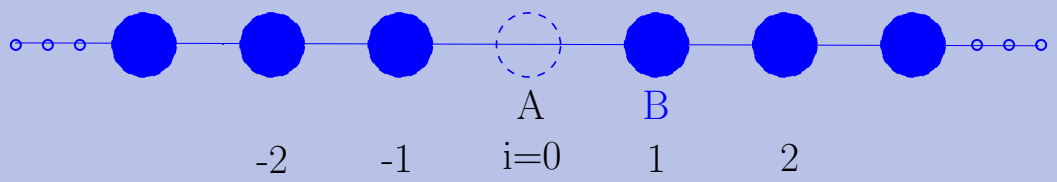
Partitioning Λ in real space

Convergence/Divergence

The thermodynamic limit of $\lambda = \Lambda/N$

- $\Lambda = \sum_A \Lambda^A$ with $\Lambda^A = \Lambda^{AA} + \frac{1}{2}\sum_{B\neq A} \Lambda^{AB}$
- If $\langle \Lambda^A \rangle$ is the atomic average of Λ^A and κ the average number of electrons per atom, $\boldsymbol{\lambda = \langle \Lambda^A \rangle / \kappa}$.
- The divergence is that of $\langle \Lambda^A \rangle$
  - Some (or all) of Λ^A must diverge.
  - Some (or all) of $\sum_{B\neq A} \Lambda^{AB}$ must diverge.

1D $\Lambda^{AB} \sim (R_{AB} \otimes R_{AB})\delta^{AB}/2$ $\Sigma_{i=-\infty}^{\infty} R_i^2 \delta(R_i)$



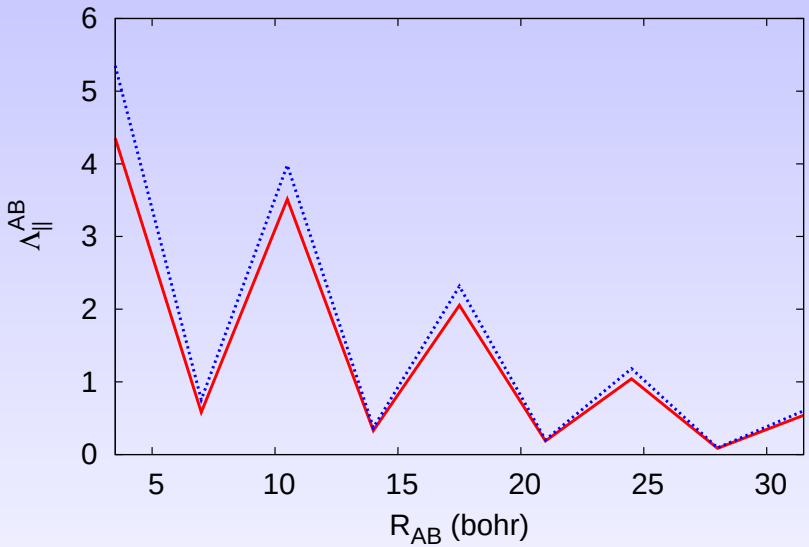
- In 1D,2D,3D λ diverges if δ decays faster than R^{-d} with $d = 2, 3, 4$.

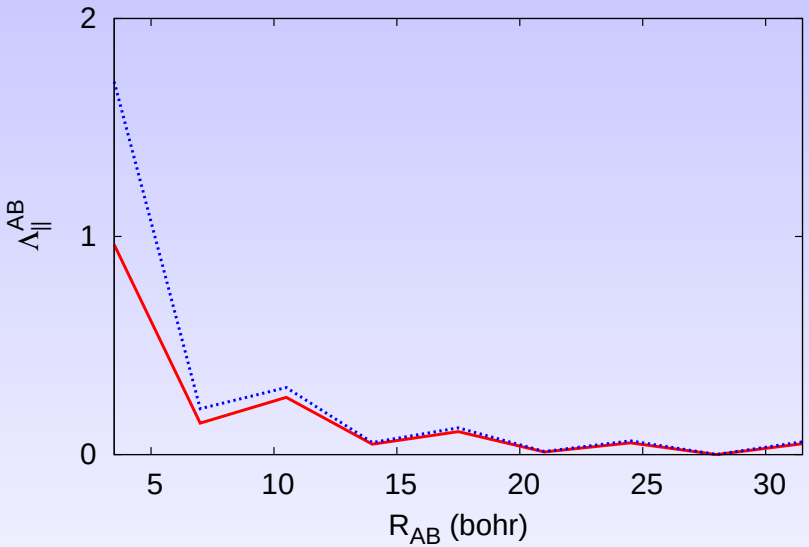
Partitioning Λ in real space

Examples II

The H_{10} linear chain. HF, CAS[10,10]//6-311G*

- $\Lambda_{||}^{AB}$ Atom on one end with all the others.
- Oscillations, R^{-d}, $d = 2.5, 4.1$ at the HF, CAS levels.
- $R_{AB}^2 \delta/2$ is the long-range limit.





Localization, as measured by δ determines conductivity

Summary, Conclusions

- As noted by Kohn (1964), insulators are characterized by exponentially separated regions in Ψ.
- Quantified (Resta) by the LT.
  - λ diverges/converges in metals/insulators.
- Previous work shows that δ decays algebraically/exponentially in metals/insulators.
- In molecules, Leininger & Evangelisti have shown that $\Lambda = N\lambda$ informs about chemical bonding.
  - Λ is global! No individual bonds, atoms, whatsoever.
  - Λ may be partitioned in real space
- The global problem in chemistry is solved.
  - It is the interatomic terms that may diverge...
    ... If our previously found conditions in δ are met.
- Chemistry of ground states and physics of conductivity intertwinned.