On the decay rate of real space delocalization measures

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Outline

Introduction

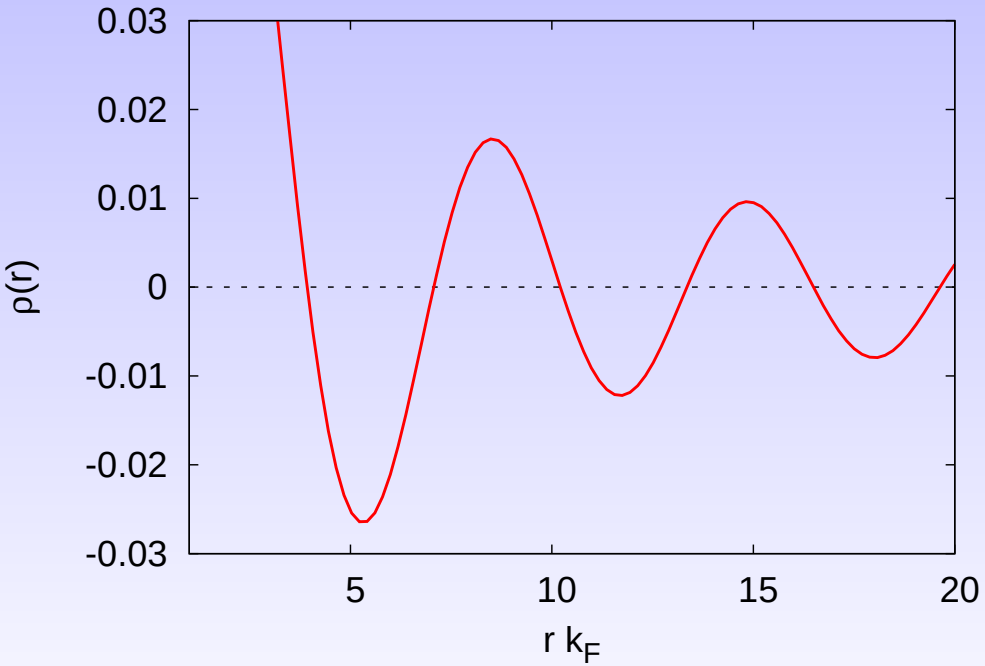
- May real space descriptors of metallic or insulating-like character be found in extended as well as molecular systems?
  - Partitioning of space provided by QTAIM
- Some initial QTAIM proposals unfruitful:
  - Non-nuclear attractors found in Li molecular clusters.
  - Present in bcc-Li, ... but not in Cu, Al.
- A seminal paper by Kohn establishes a deep link between localization and insulating character.
  - Tempting to examine real space delocalization measures.
- In solids, a lot of theoretical work has been done.
  - ... Berry phases, modern theory of polarization.
  - Link between the decay rate of $\rho(\boldsymbol{r};\boldsymbol{r}')$ with insulating nature

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
  $\rho(r) = 2(2\pi)^{-3}\int_{\boldsymbol{k}<\boldsymbol{k}_F} d\boldsymbol{k} e^{-i\boldsymbol{k}\boldsymbol{r}} = \frac{-k_F}{\pi^2 r^2}(\cos(rk_F) - \sin(rk_F)/(rk_F))$



Similar to Friedel oscillations

First zeros at $rk_F = 4.49, 7.73, 10.90$

If $k_F \approx \pi/a$ close to lattice positions

Decay as $r^{-(d+1)/2}$ in d-dimensions

Known results in extended systems

Insulators

e.g. PRL 88, 196405 (2002)

- Exponential decay for $\rho(|\boldsymbol{r}-\boldsymbol{r}'|) \approx e^{-\lambda|\boldsymbol{r}-\boldsymbol{r}'|}$
- For 2 bands tight binding (TB) models exist for a 1D chain, 2D square, 3D simple cubic lattice.
  - A prefactor $r^{d/2}$ appears.
  - ρ is anisotropic. Slowest decay along diagonals.
    - $(1,1)$ or $(1,1,1)$ directions in 2D, 3D.
  - Decay length λ depends on the gap Δ.
  - As $\Delta \to 0$, λ scales linearly with Δ.
  - Effective λ values between $\approx 1-5$.

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. $\delta \approx e^{-\lambda r}$
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Aims

- Examine Hückel finite + TB extended models in 1D, 2D, 3D.
- Compute actual DI's for H and LiH realizations of the models.
- Examine the role of electron correlation.
- Link results with chemistry.

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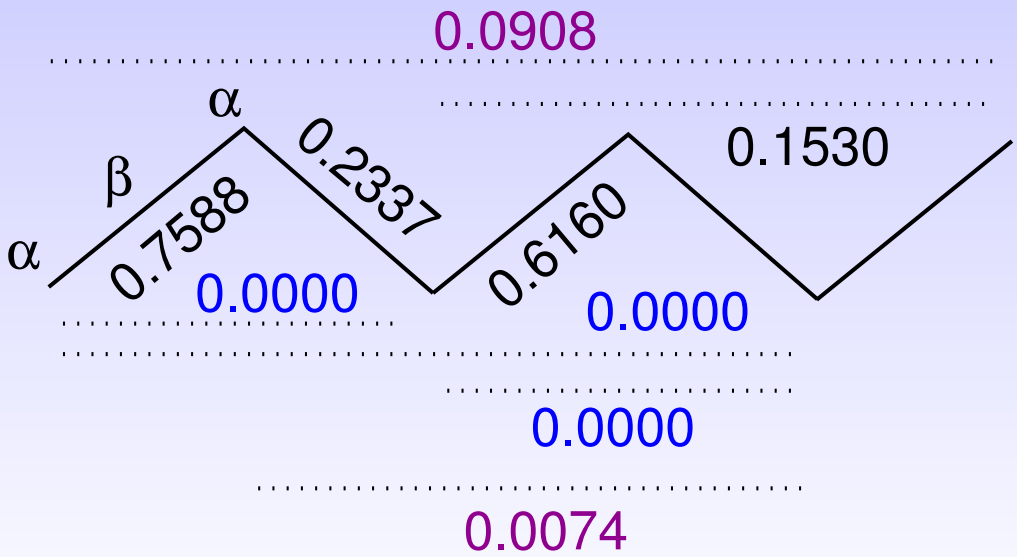
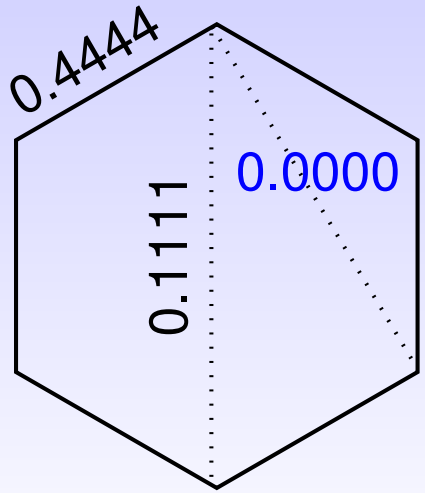
Finite analytical model systems

Hückel homoatomic systems

- $H = \alpha I + \beta T$, where $T_{ij} = \delta_{|i-j|=1}$ is Toeplitz tridiagonal if linear.
- Eigensystem $\lambda_\mu = \alpha + 2\beta \cos \frac{\mu\pi}{n+1}, \mu = 1, n$ (n even). $x^i_\mu = \sqrt{\frac{2}{n+1}} \sin \frac{\mu i \pi}{n+1}$.
- $\delta^{ij} = 2(\sum_\mu x^i_\mu x^j_\mu)^2$
- DI's predict Peierls-like distortions in linear chains.
- The p-DI in cyclic related to aromaticity.





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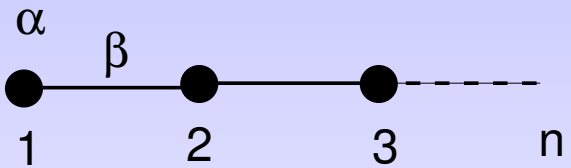
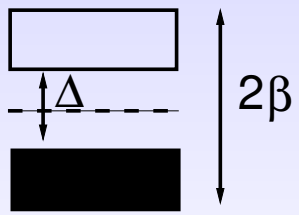
- $\delta^{ij} = 2(\sum_\mu x^i_\mu x^j_\mu)^2, \qquad \lim_{n\to\infty} \delta^{ij} = (16/\pi^2) j^2/(i^2 - j^2)^2$ ($j + i$ odd).
- Gap $\Delta(\gamma) = 2\pi(\gamma - \gamma^2) + \mathcal{O}(\gamma^3)$. (Expansion with respect to $\gamma = 1/n$)
- $\delta^{i,i+2n} = 0$, $\delta^{n/2,n/2+r} \to 4/(r^2\pi^2)$ (r odd)





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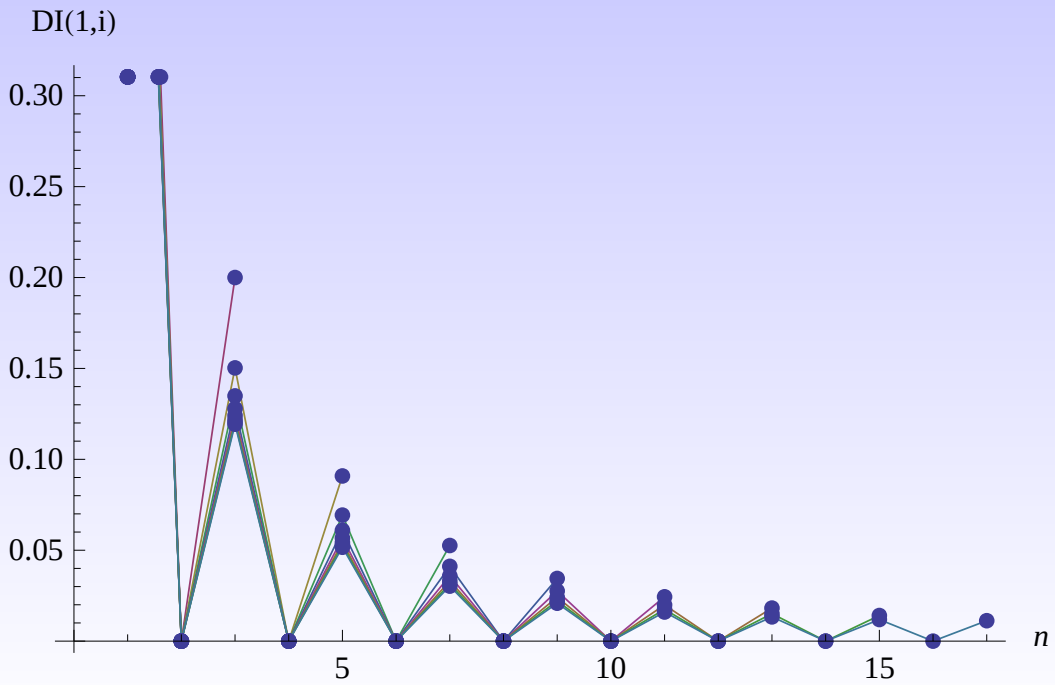

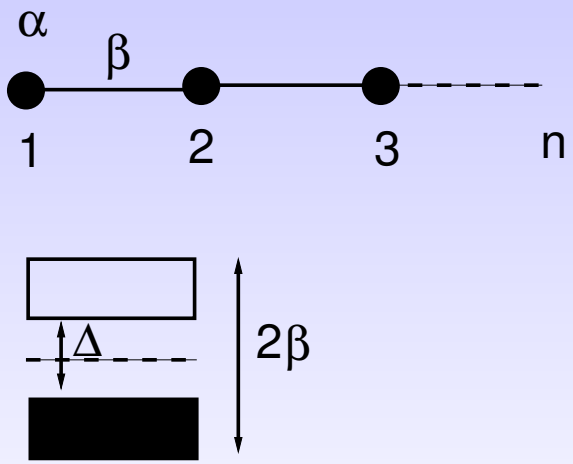

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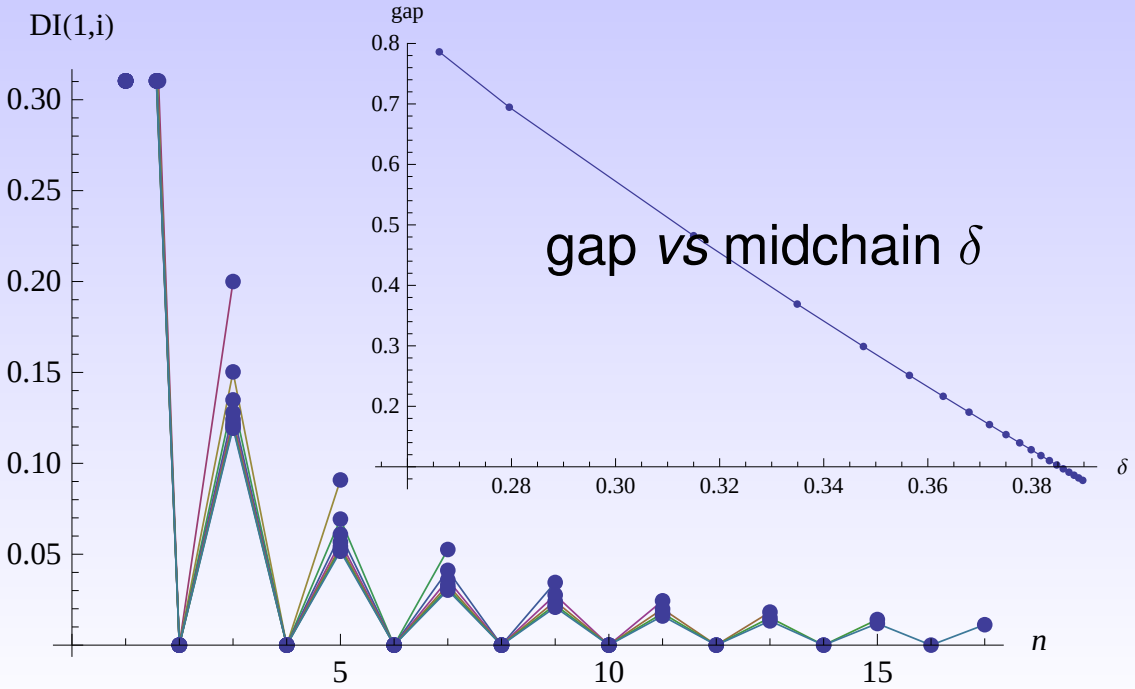

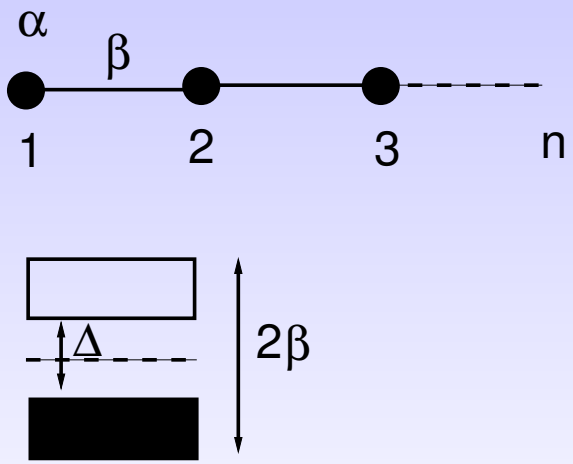

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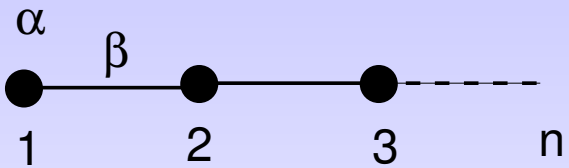
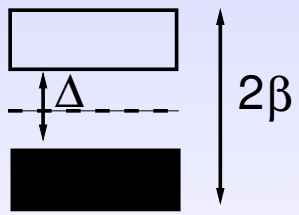
Equivalence to TB:

- 1D lattice, a
- Occ. BZ $\equiv -\pi/(2a) \le k < \pi/(2a)$
- $\phi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}} e^{i\boldsymbol{k}\boldsymbol{R}} \phi(\boldsymbol{r} - \boldsymbol{R})$
- $\delta^{0r} = 4\{\frac{a}{2\pi} \int_{-\pi/(2a)}^{-\pi/(2a)} dk\, e^{ikra}\}^2 =$
  $4\sin^2(\pi r/2)/(r^2\pi^2) =$
  $4/(r^2\pi^2), (r\,\text{odd})$





Finite analytical model systems

Hückel heteroatomic AB chain

- Two different α and α' values. ($\alpha' = 0$).
- Analytically solved through a generalization of the Coulson-Rushbrooke theorem.
- $\lambda_k = \left(\alpha \pm \sqrt{\alpha^2 + 16\cos^2(k\pi/(n+1))}\right)/2, k = 1, n/2$
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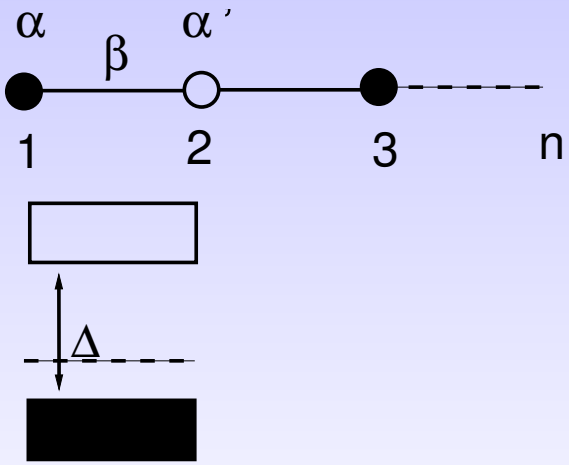

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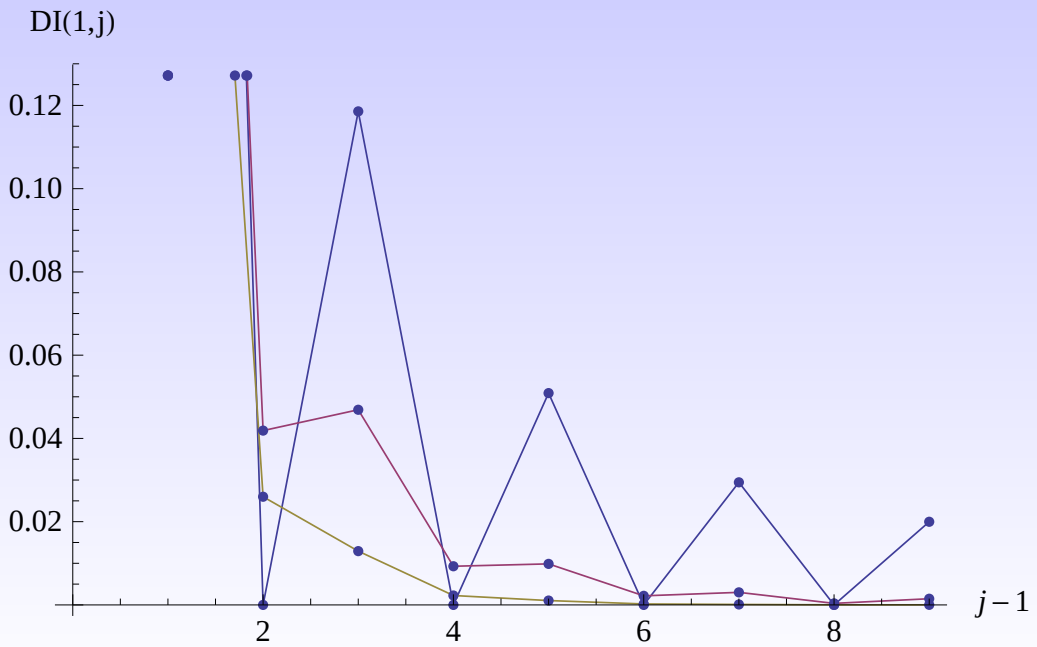

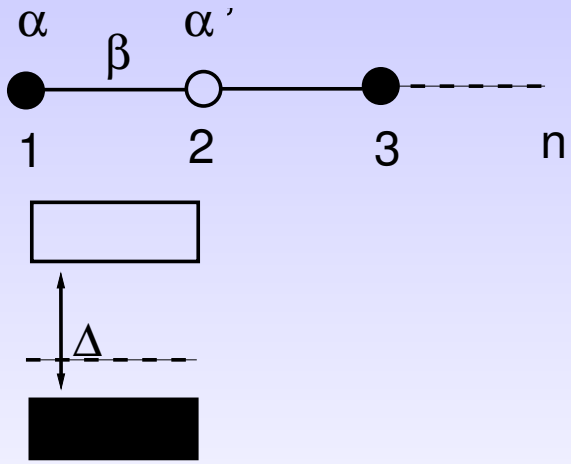

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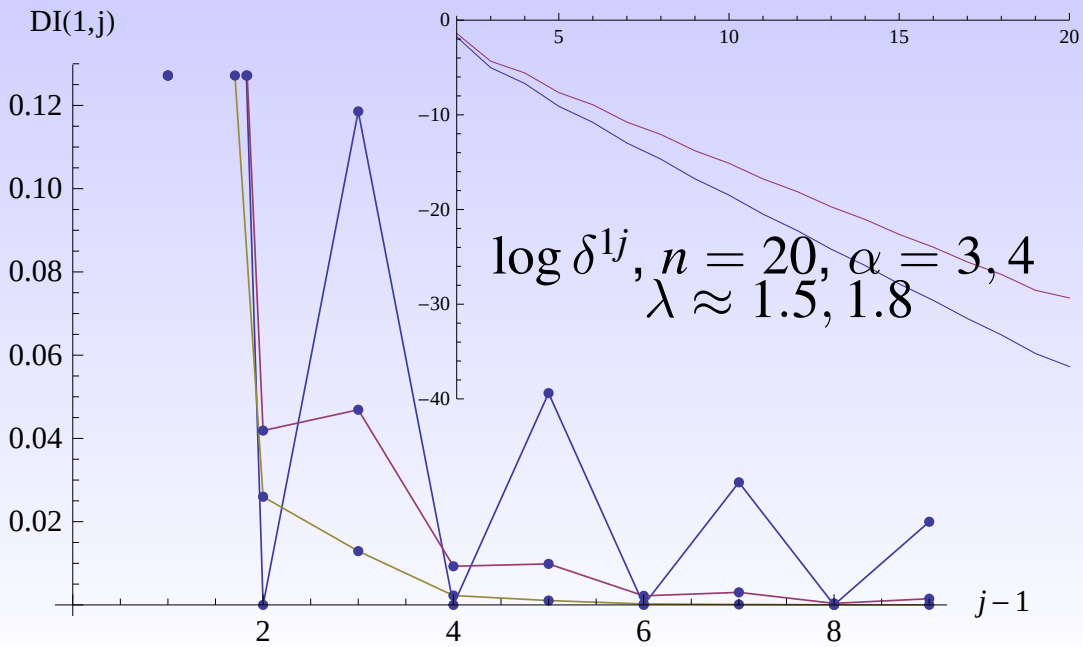
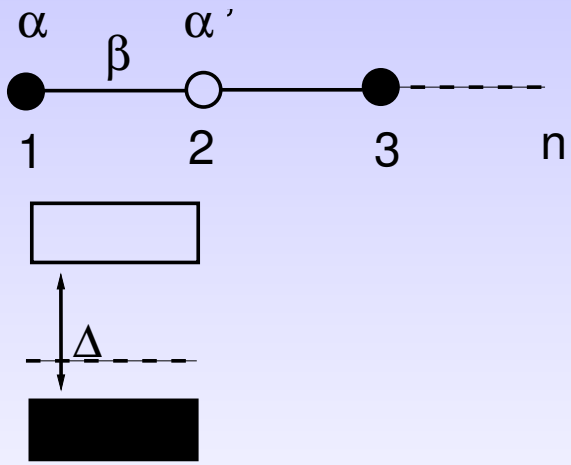
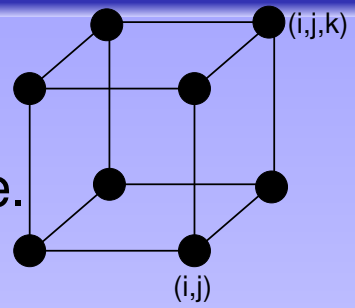




The 2D,3D TB limit

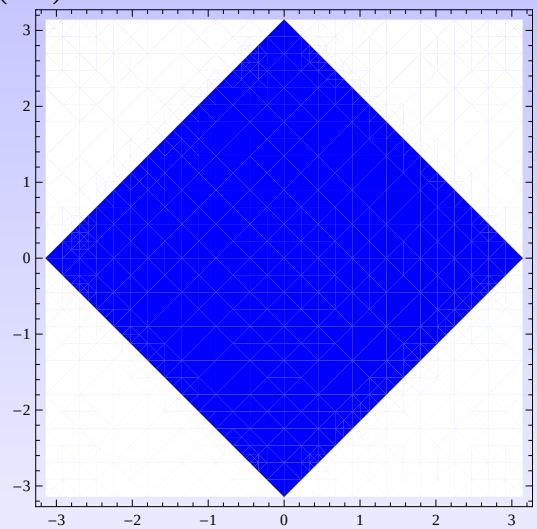
R. Ponec JCTC (2012)



- The linear 1D and square 2D lattices are analytically solvable.
- The simple cubic 3D lattice reduces to simple quadratures.

2D

$$\delta^{0,rs} = 4\{\frac{a^2}{(2\pi)^2}\int_{\in FS} dk_x dk_y\, e^{i(rak_x + sak_y)}\}^2$$



$\delta^{0,rs} = 16/(\pi^4(-r^2+s^2)^2$, $r+s$ odd.

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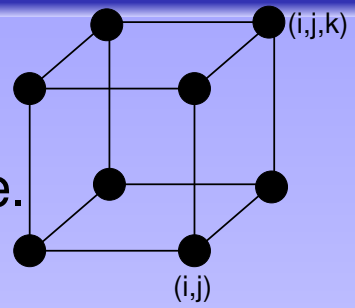

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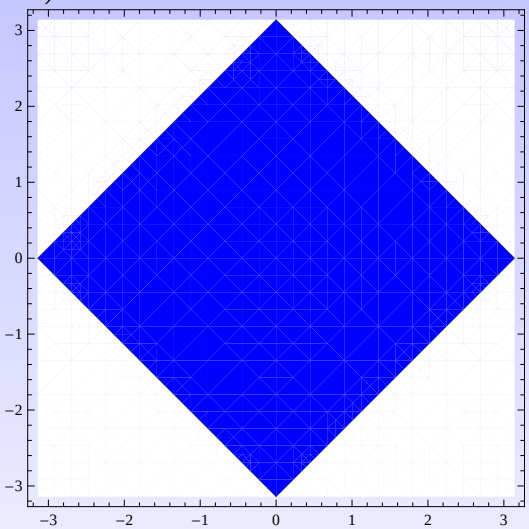	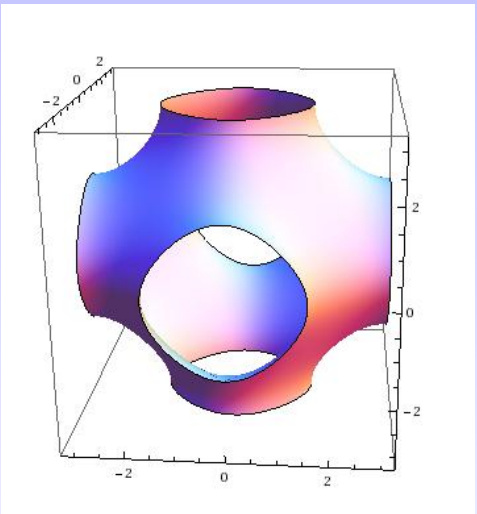
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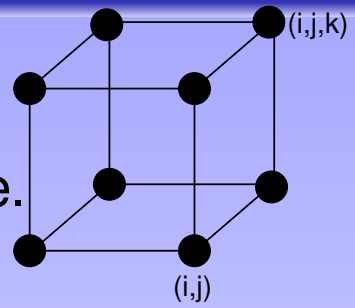

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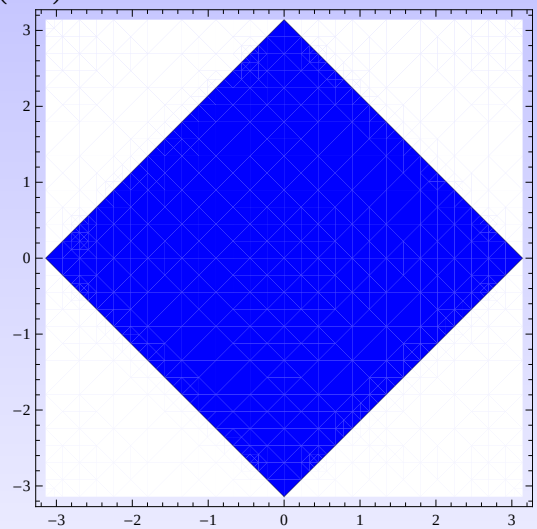	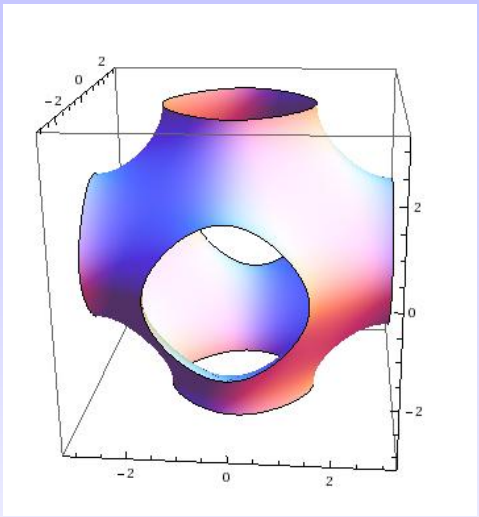
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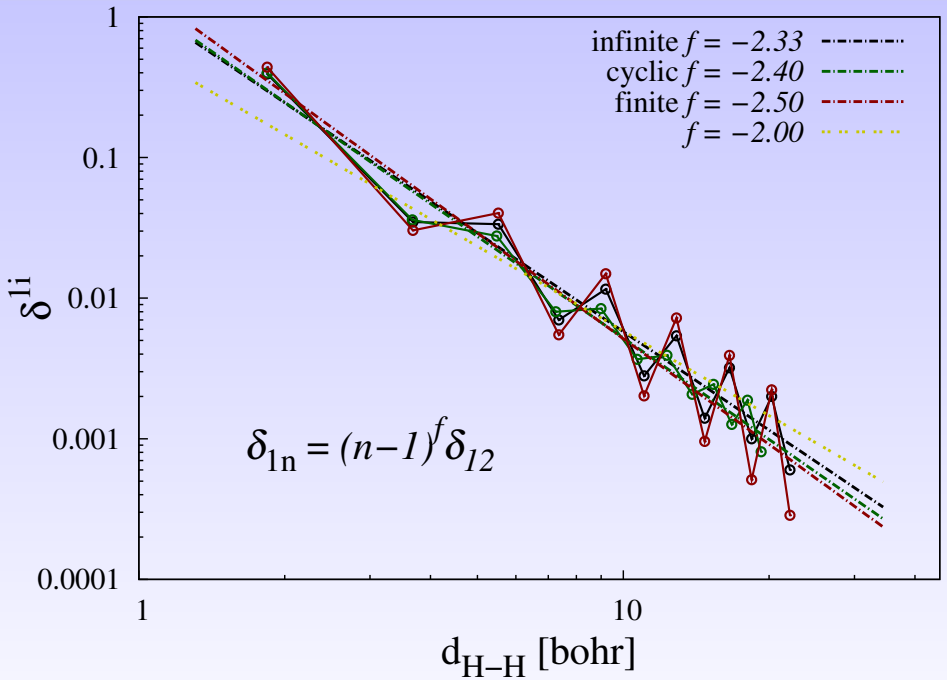
δ(1st neighbor)$= 0.405, 0.164, 0.112$ in 1D,2D,3D.

Metallic-like behavior

Hydrogen toys

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.

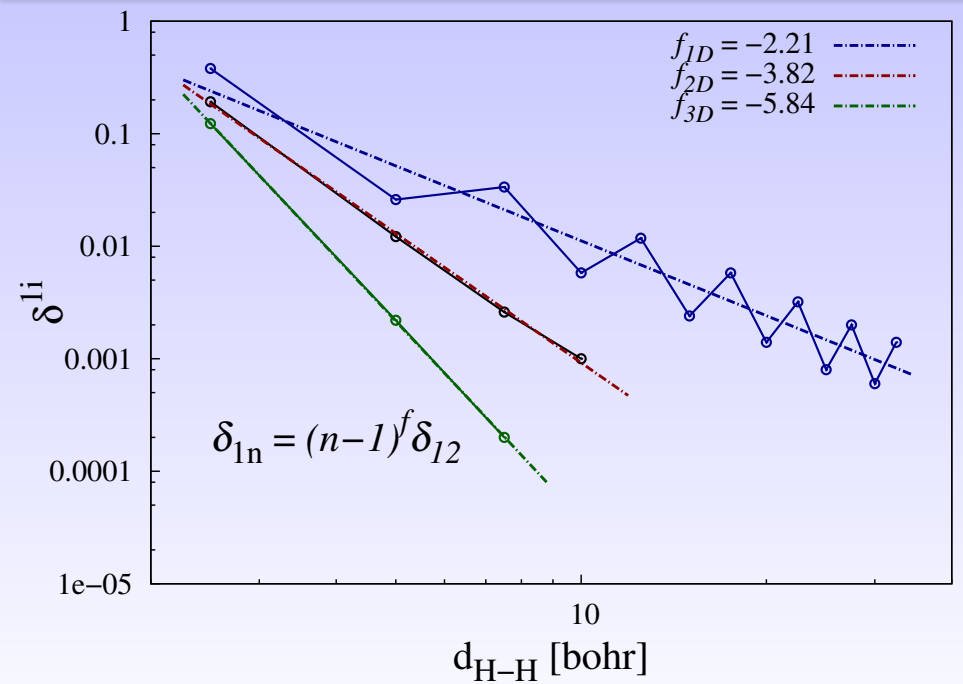
$\delta^{1,2(4)}$ close to models: $0.44(0.40), 0.04(0.04)$ for infinite chain.

Metallic-like behavior

Hydrogen toys

2D, 3D periodic H lattices

- Elk+DGRID KS periodic calculations
- $a = 2.5$ au.
- Only (1,0) or (1,0,0) directions shown



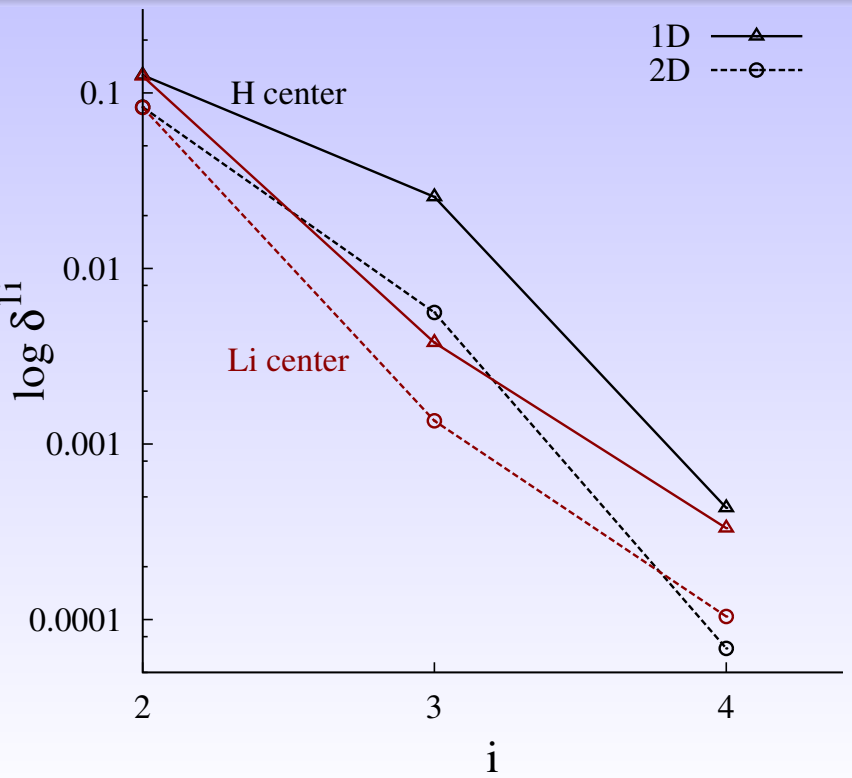
- Directional profiles.
- Clear power law for DIs.
- Tight binding (TB) oscillations damped.
- $f_{2D} \approx 3.8$, close to TB. $\delta^{12} = 0.19, 0.164$ for KS, TB.
- f_{3D} close to 6. $\delta^{12} = 0.12, 0.112$ for KS, TB.

Insulating-like behavior

LiH toys

1D, 2D models

- 6-311G(p) Hartree-Fock calculations.
- $a = 3.0$ au.
- Only (1,0) directions shown



- 9-1D, 9x9-2D
- $\delta^{HX} + \delta^{LiX}$
- δ's decrease exponentially or even faster.
- λ grows with D
- No oscillations
- Numerical precision?

Back to Chemistry. The profile of DI's

The role of correlation

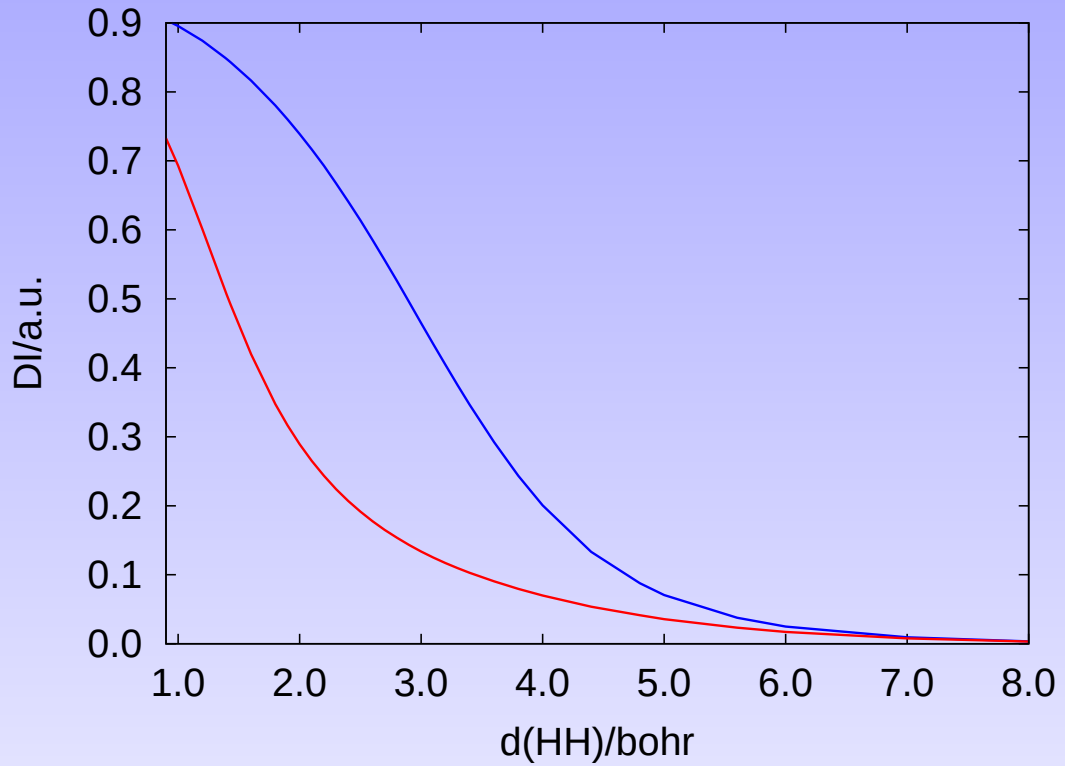
JCTC 7, 1704 (2011)

- Reliable correlated $\rho(\boldsymbol{r}, \boldsymbol{r}')$ in solids?
- DI's measure covalent bond order in molecules
  - $\delta \approx 1$ in H_2, ethane, 2 in ethylene, etc.
- Correlation effects have been investigated.
  - Homolytic dissociation $\equiv$ switch on correlation
- May we learn something from this?

- Study the profile of DI's in chemical processes
  - Bonded & non-bonded interactions.

Diatomics

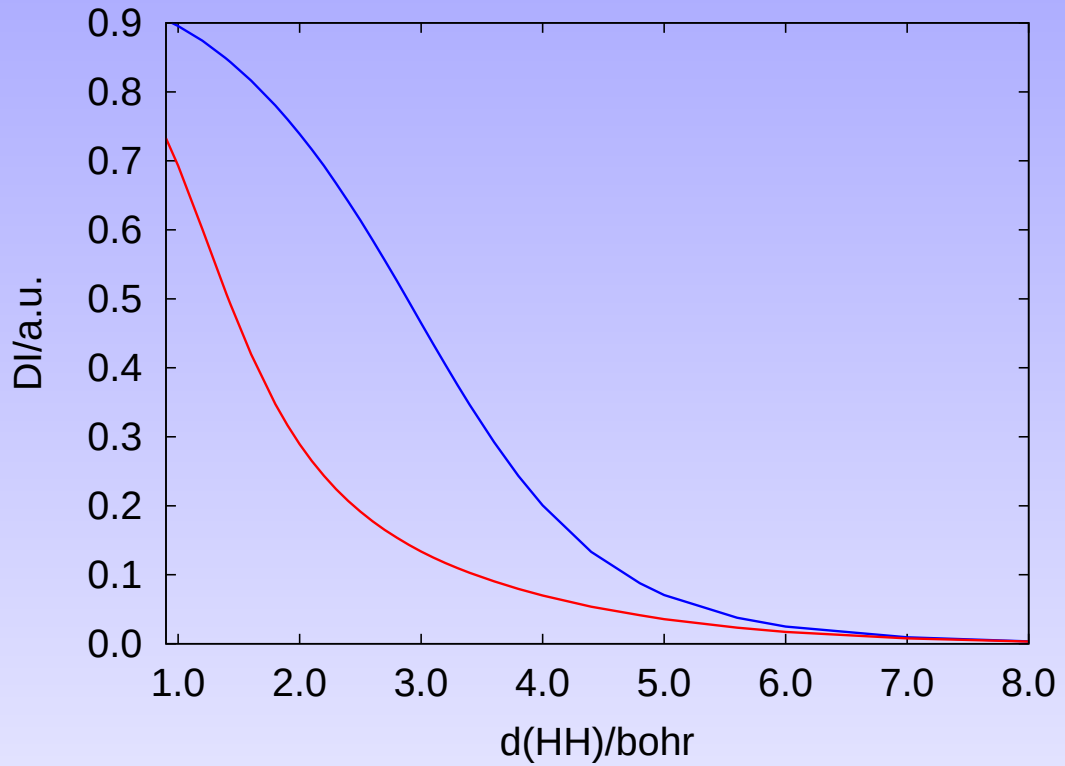
H_2



- Singlet and Triplet behave very differently.
- Singlet shows inflection point.
  - Hückel DI$= 1$
  - singlet $\rightarrow$ metallic
- Triplet decays exponentially.
  - Hückel DI$= 0$
  - triplet $\rightarrow$ insulating

Diatomics

H_2



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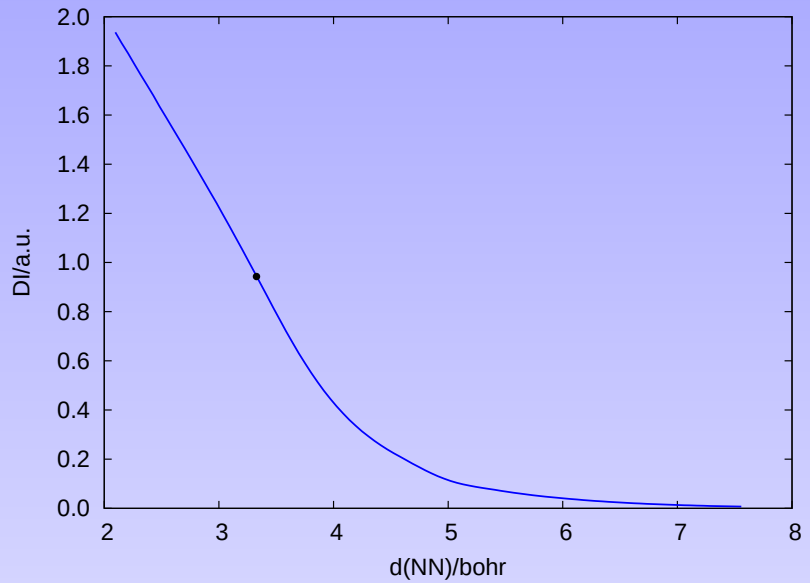
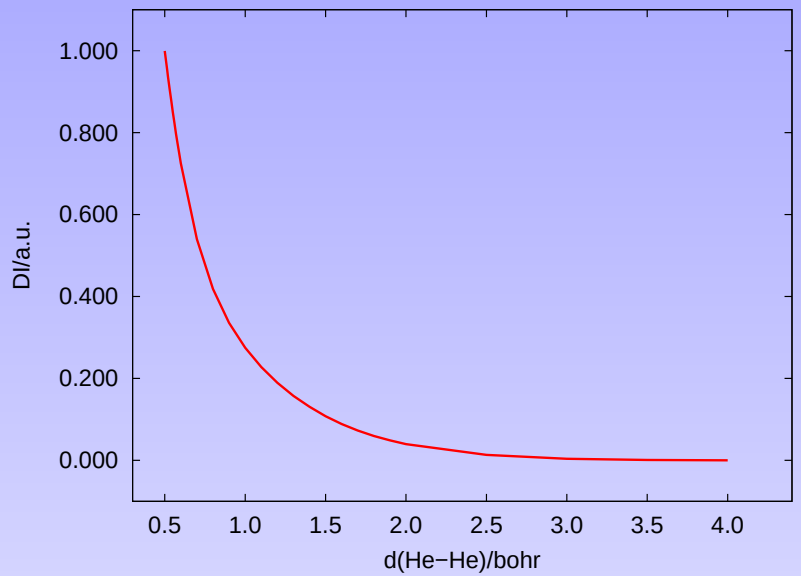
- Singlet shows inflection point.
  - Hückel DI$= 1$
  - singlet $\rightarrow$ metallic
- Triplet decays exponentially.
  - Hückel DI$= 0$
  - triplet $\rightarrow$ insulating

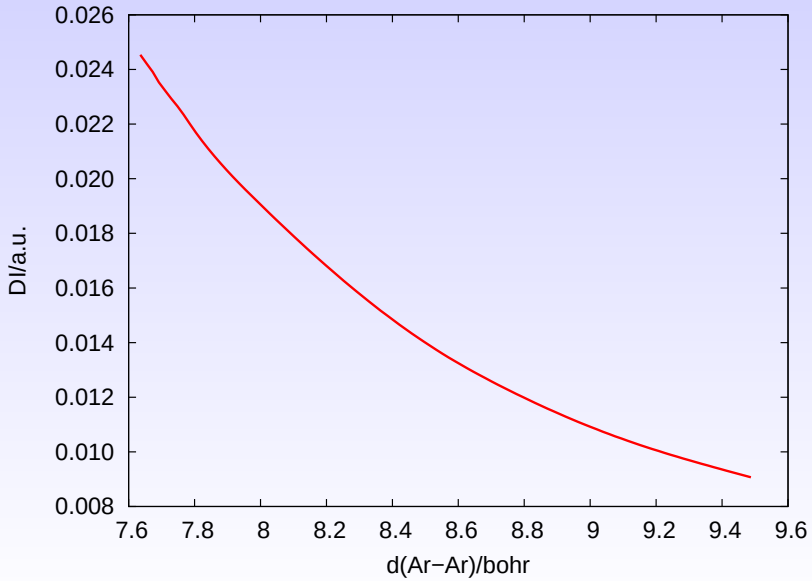
- DI=$2(1 - p(1,1)) = 4p(2,0) \equiv$ Probability of *hopping*.
- Inflection at $\approx 2.90 \pm 0.1$ a.u.
- DI $\approx 0.5 \pm 0.1$

Diatomics

Bonded *vs.* non-bonded Interactions

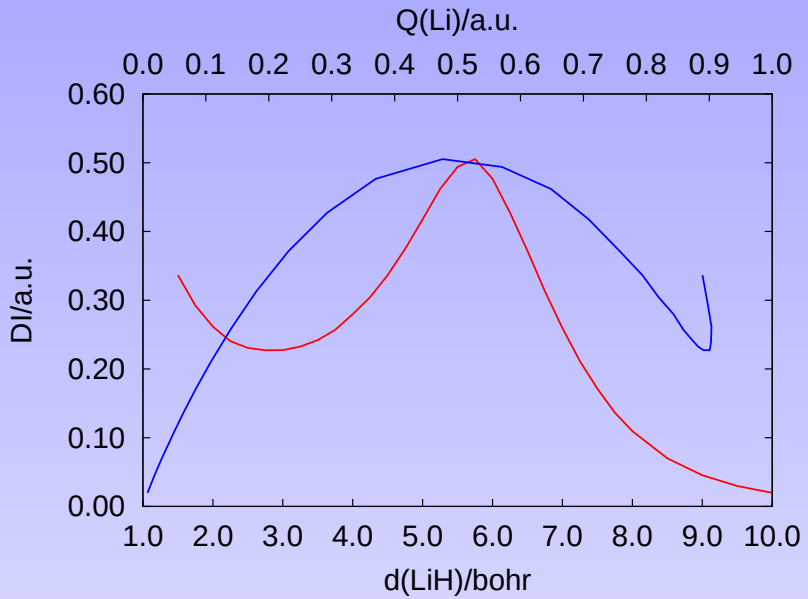


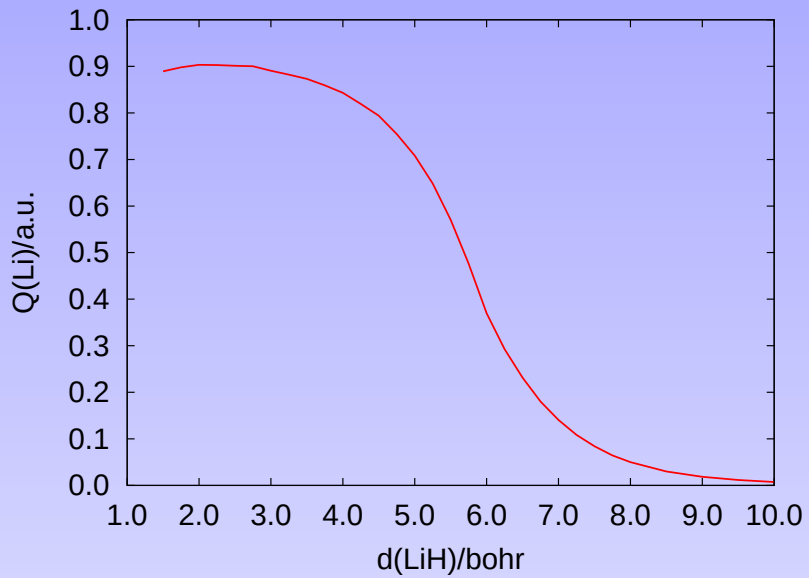




- CAS[10,8] for N_2: IP at 3.3 ± 0.1 bohr
- DI $\approx 0.9 \pm 0.1$
- IP at about half eq. value
- CISD He_2 and Ar_2.

Diatomics
Effect of charge transfer



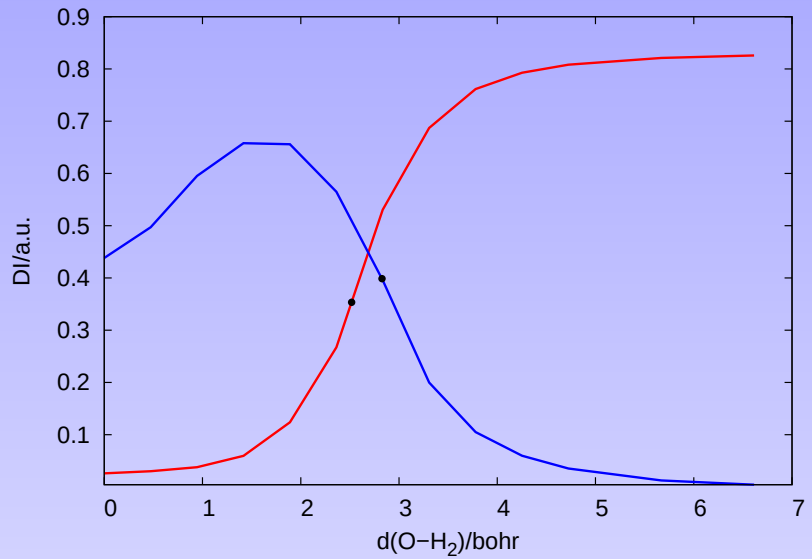


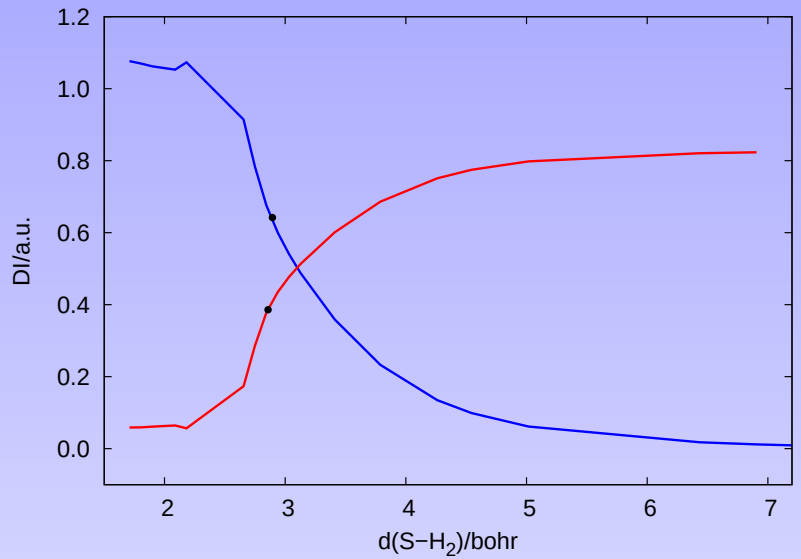
- $r \approx 5.5$ bohr $\equiv$ avoided crossing
- $Q(\mathrm{Li}) = p(2,2) = t$
- CT coordinate t models the process.
  - $\mathrm{DI} = 2t(1-t)$
  - $\mathrm{DI}(t = 1/2) = 1/2$

- H_2 Hopping $t \equiv p(2,0)$
- LiH Hopping $t \equiv p(2,2)$
- Sigmoidal $Q \equiv t$ *vs.* Distance

Other dissociations

X(^{1}D)+H_2 $\rightleftharpoons$ H_2X, C_{2v} δ^{HH} **in red.**





- In H_2O:
  - Covalent one-parameter dissociation of H-H
  - covalent formation + CT for O-H (peak DI>0.5)
  - Successfully modeled by 2 parameters.
- Similar in H_2S:
  - Larger covalency.
  - CT maximum barely visible.

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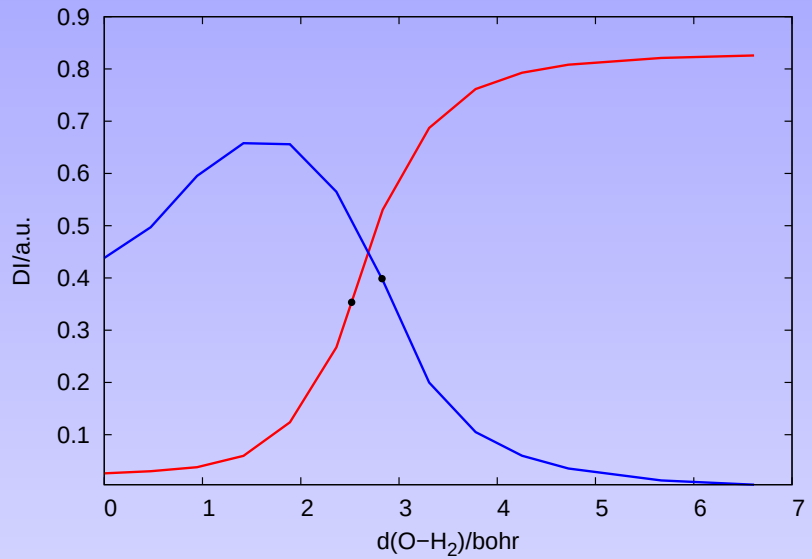

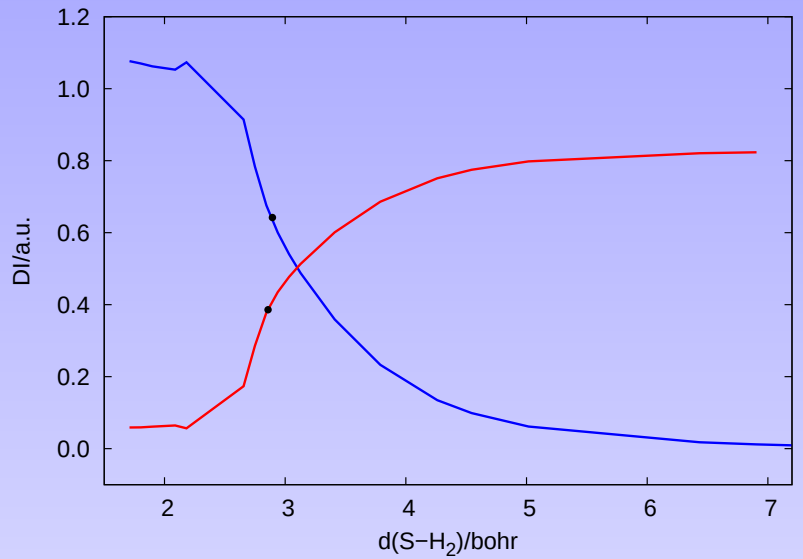

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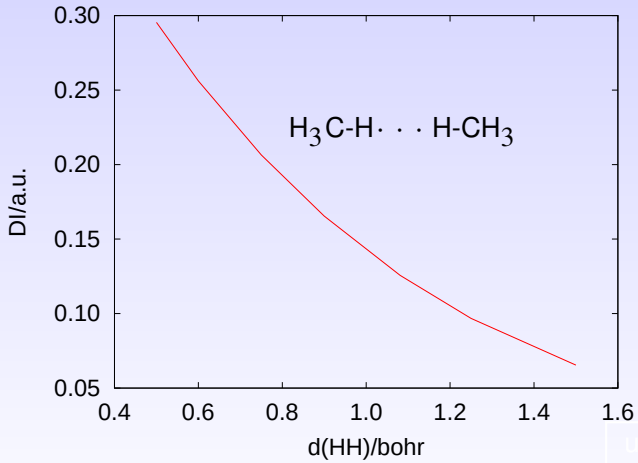
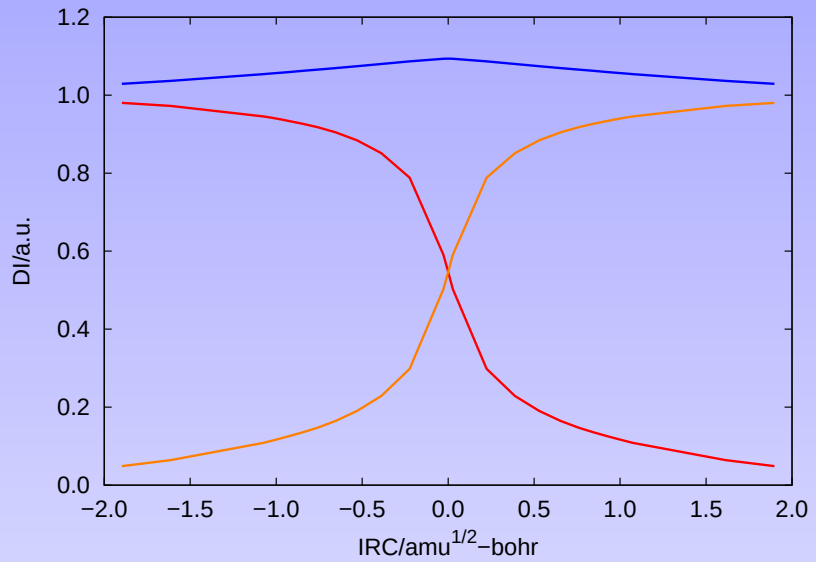
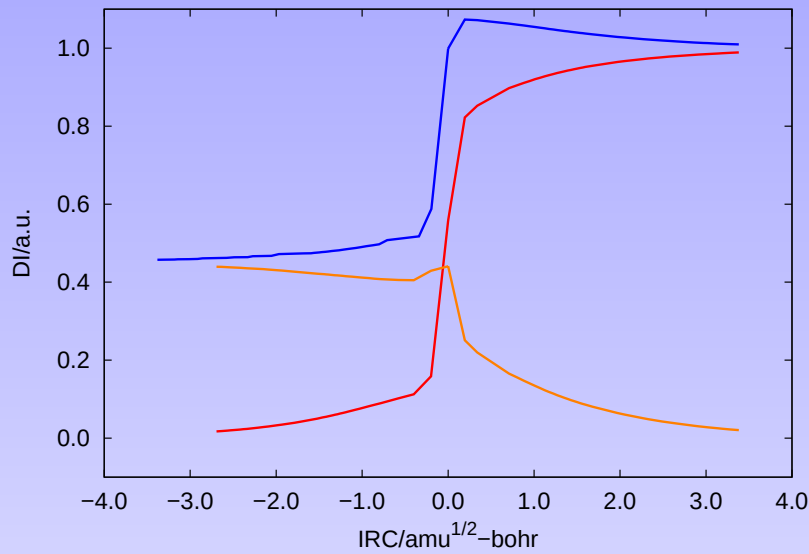


Atomic & Bond Exchanges

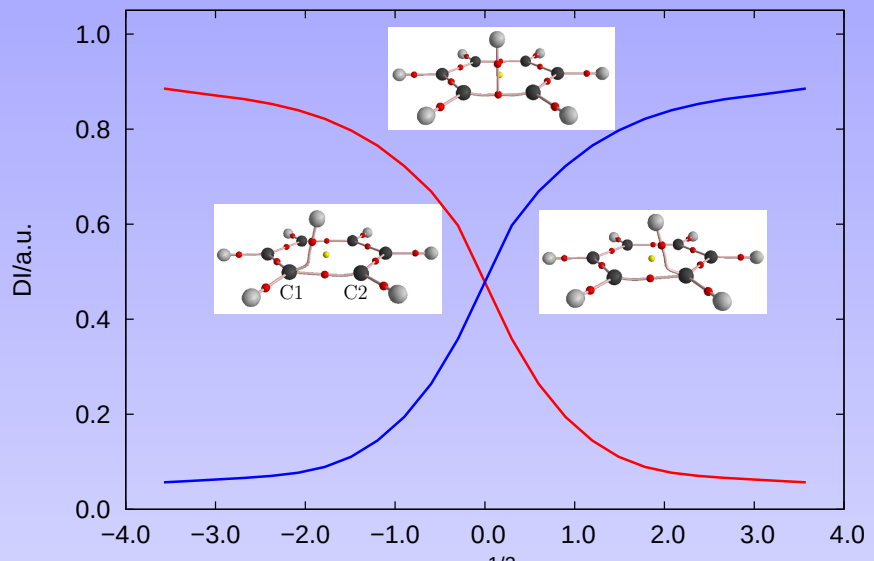
H+H-H⇌H-H+H **H+H-F⇌H-H+F**

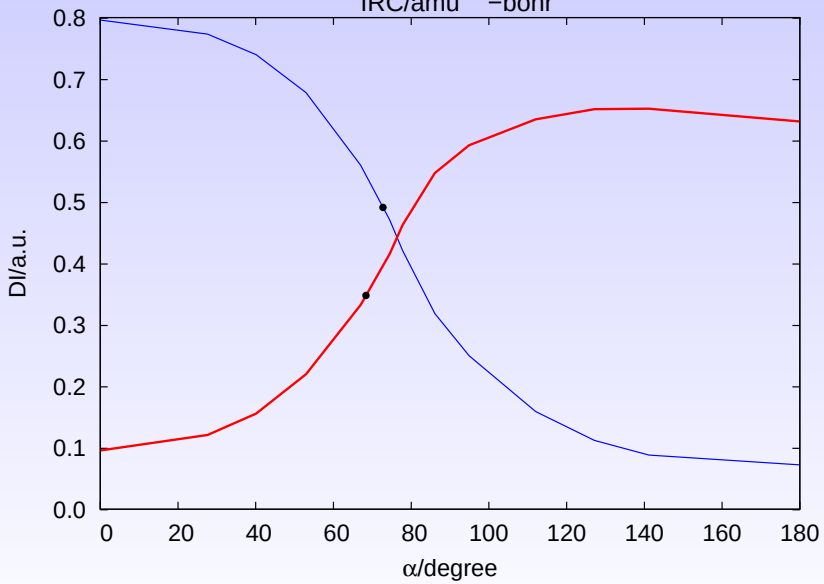


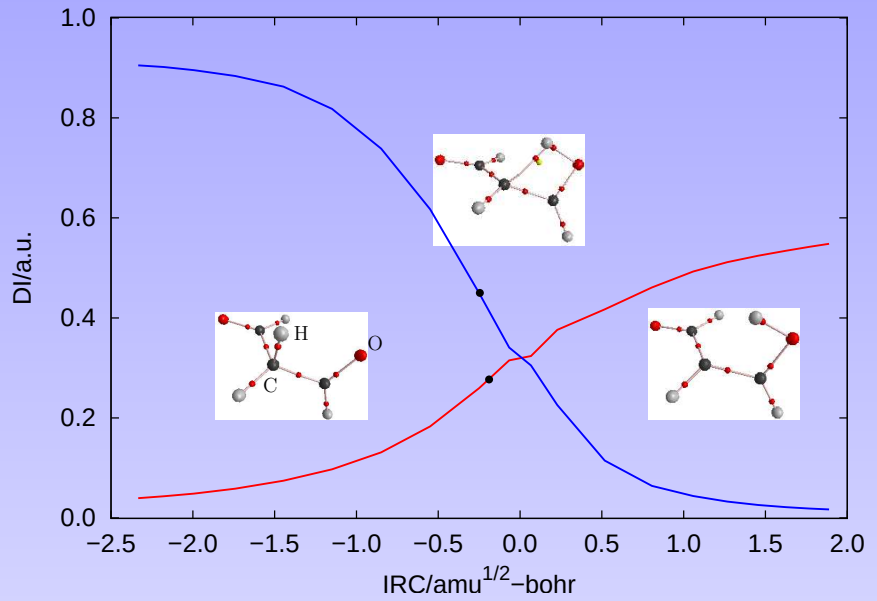


- Chemistry easy to decode.
- $\sum_i \mathrm{DI}_i$ valuable $\equiv$ free valence.
- The jump in $\sum$ DI for H+H-F related to charge transfer.
  - If washed out $\Rightarrow$ similar to H+H-H
  - For HF, $Q(\mathrm{F}) = -0.74$. At peak, $Q(\mathrm{F}) = -0.13$,

Migrations



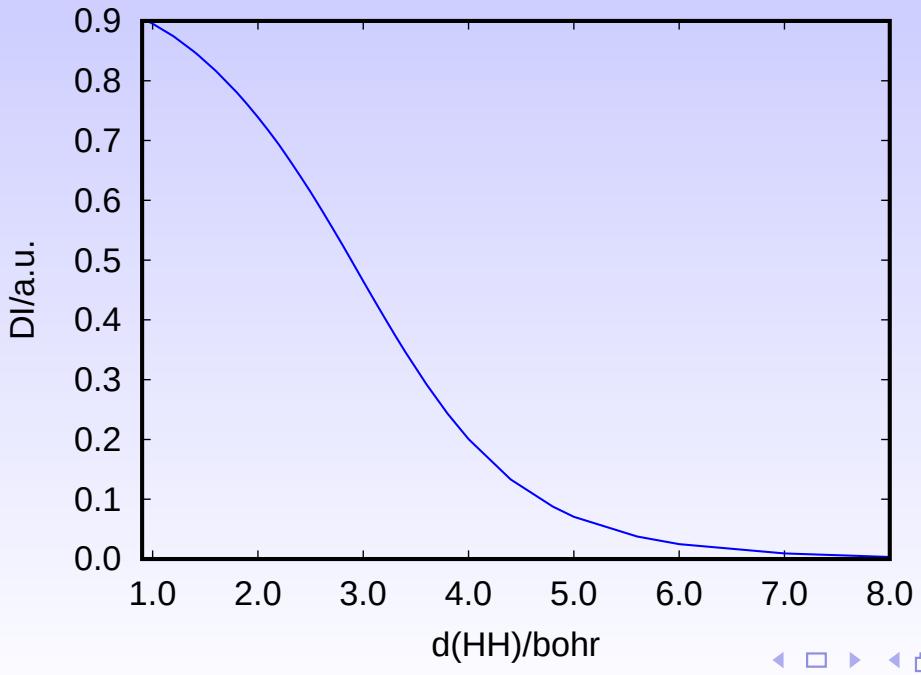




- 1,2 H migration in $C_6H_7^+$.
- keto-enol tautomerism in malonaldehyde.
- HCN isomerization.
- Even a CT step may be distinguished in HCN

Correlation: collective effects

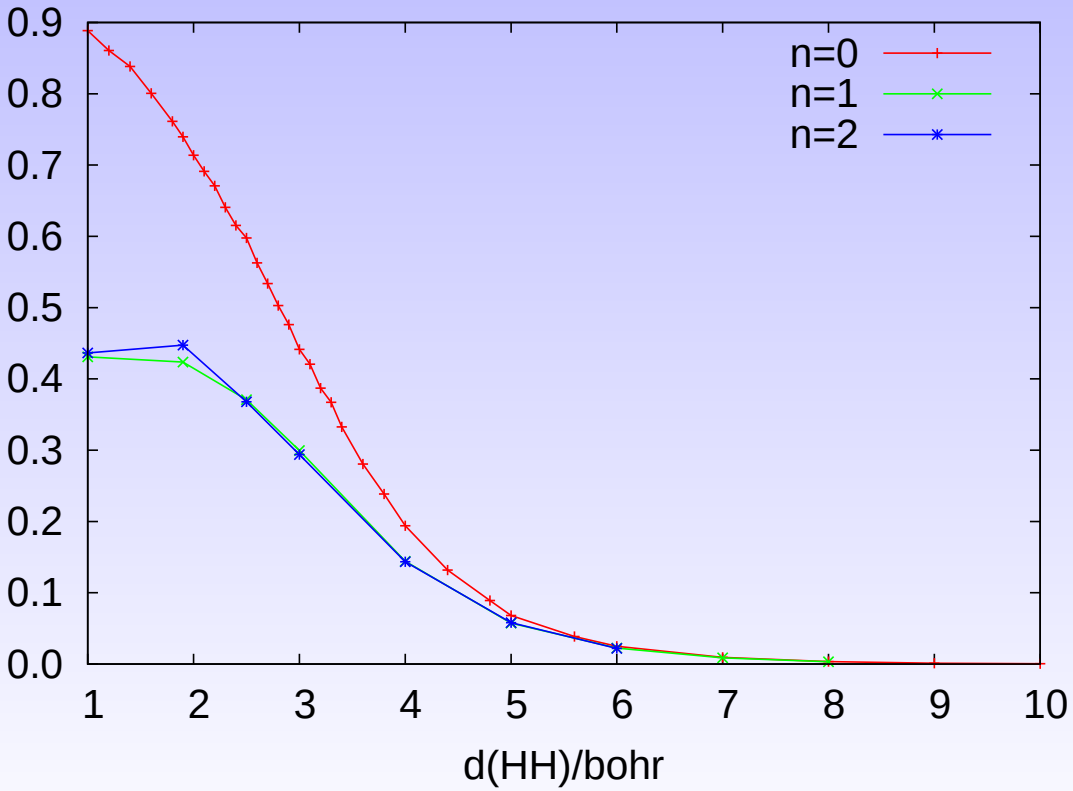
- Sigmoid $\equiv$ onset of delocalization.
- What happens as n grows?
- Baranov & Kohout have computed DI's in H chains (UKS):
  - Sharp transition form low to high DI as d(HH) decreases
  - Metal-insulator (Mott)?
  - Is the H-H DI sigmoid a precursor of the transition?



Sigmoids, Cooperativity, Phase transitions?

First attempt: Size extensive CAS

- Cyclic chains: $4n+2$ (Aromatic). $n = 0, 1, 2$ 6-311G(p)
  - Quick saturation

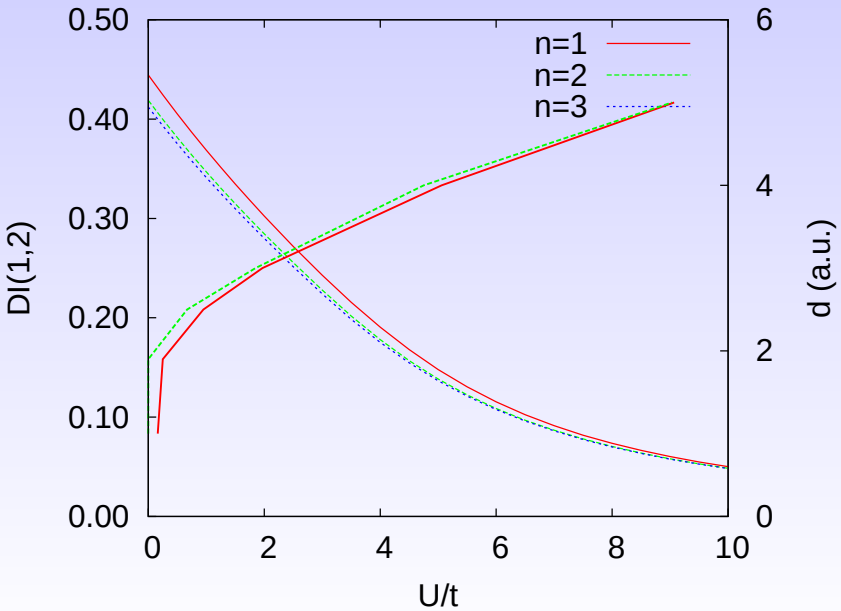


- H_2 different from real $4n+2$ cycles.
- Inflection point at $d \approx 3.6$ au quickly converged.

Sigmoids, Cooperativity, Phase transitions?

Second attempt: 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



- δ^{12} saturates quickly.
- $\lim_{n\to\infty} \delta^{12}(U=0) = 4/\pi^2 \approx 0.405$
- The U/t to d map is non-linear $\Rightarrow$ Sigmoid.
- Inflection point at about $U/t = 4$ where $\delta \approx \delta_{\text{max}}/2$

Sigmoids, Cooperativity, Phase transitions?

Second attempt: Mapping to Hubbard Hamiltonian

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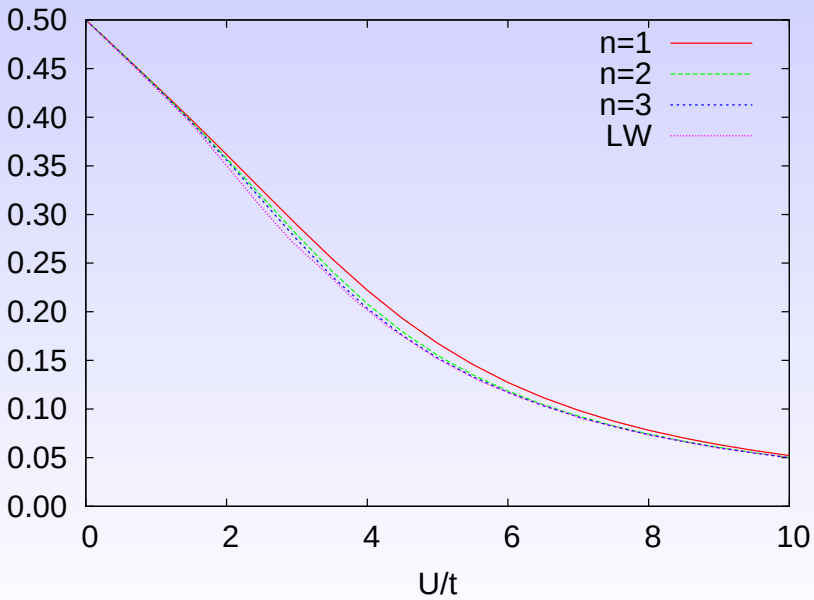

- variance=$1 - \lambda$
- Again, it quickly saturates
- Small inflection point.
- No sign of abrupt transition

Sigmoids, Cooperativity, Phase transitions?

Second attempt: Mapping to Hubbard Hamiltonian

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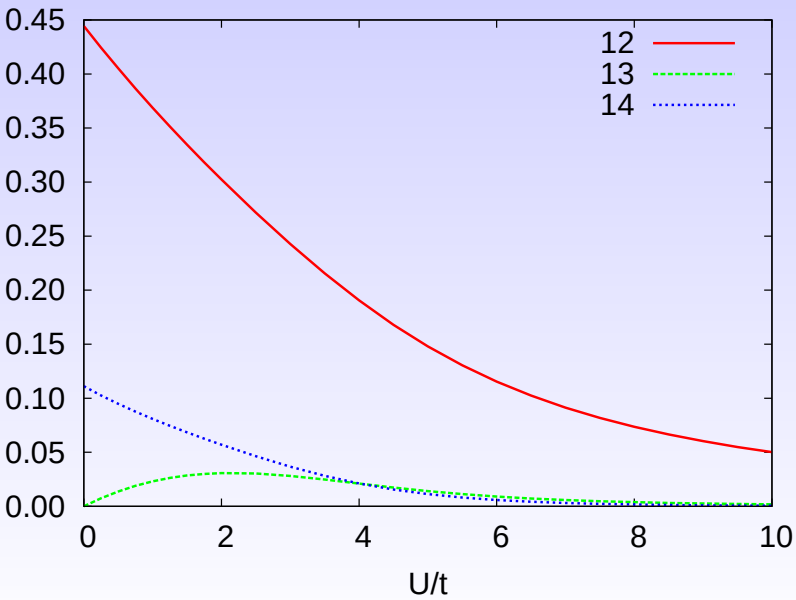

- $\delta^{1,n}$ for H_6
- Hückel ($U = 0$) $DI^{1,n}$ vanishes for odd n
- Interference effects vanish upon dissociation.
- First crossing at $U/t = 4$!

Sigmoids, Cooperativity, Phase transitions?

Second attempt: Mapping to Hubbard Hamiltonian

- $H = -t \sum_{\langle i,j \rangle, \sigma} (c^+_{i\sigma} c_{j\sigma} + c^+_{j\sigma} c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow}$
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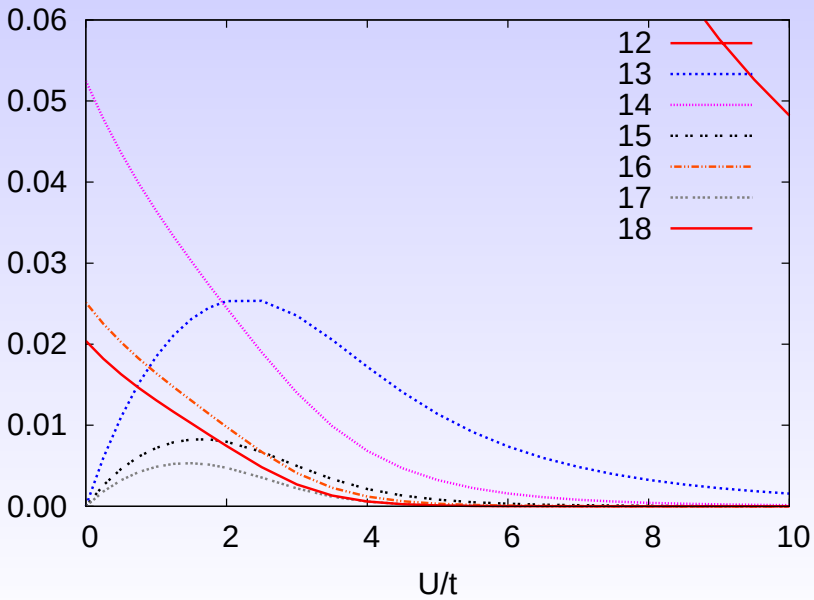

- $\delta^{1,n}$ for H_{14}
- Hückel ($U = 0$) $DI^{1,n}$ vanishes for n odd
- Hückel ($U = 0$) p-DI ($n = m/2 + 1$) $= 4/n^2$
- First crossing at $U/t = 4$!
- Interference effects vanish upon dissociation.

Sigmoids, Cooperativity, Phase transitions?

Second attempt: Mapping to Hubbard Hamiltonian

- $H = -t\sum_{\langle i,j\rangle,\sigma}(c^{+}_{i\sigma}c_{j\sigma} + c^{+}_{j\sigma}c_{i\sigma}) + U\sum_i n_{i\uparrow}n_{i\downarrow}$
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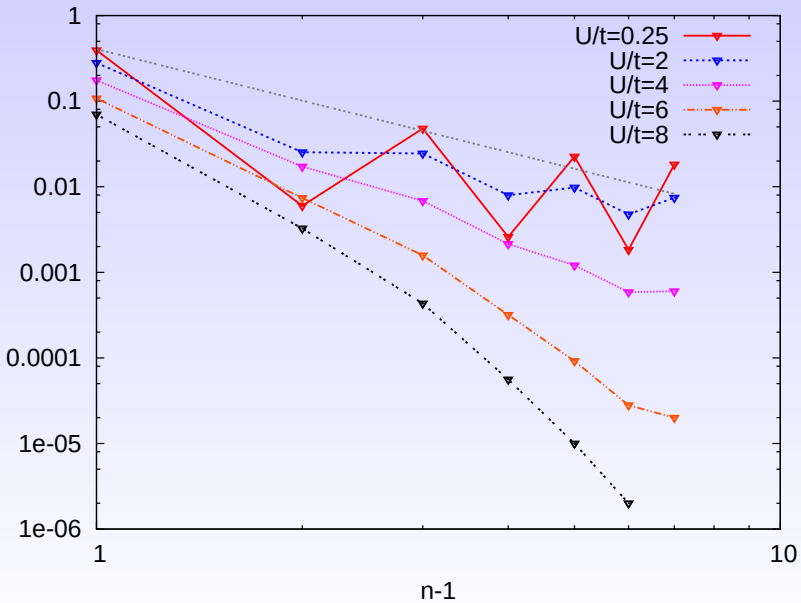
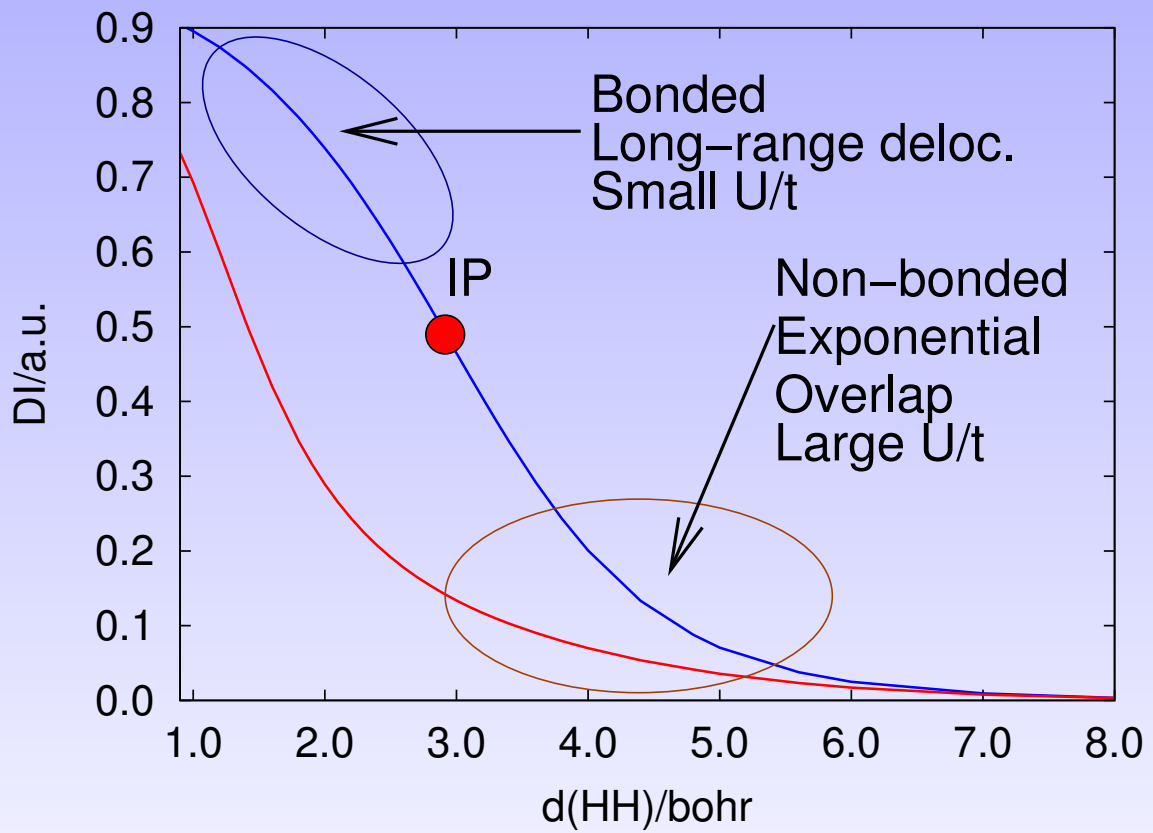


- $\delta^{1,n}$ for H_{14}
- Wild oscillations for small U/t
- Dampening on growing U/t
- Change above $U/t = 4$ to exponential

Meaning of DI profiles?

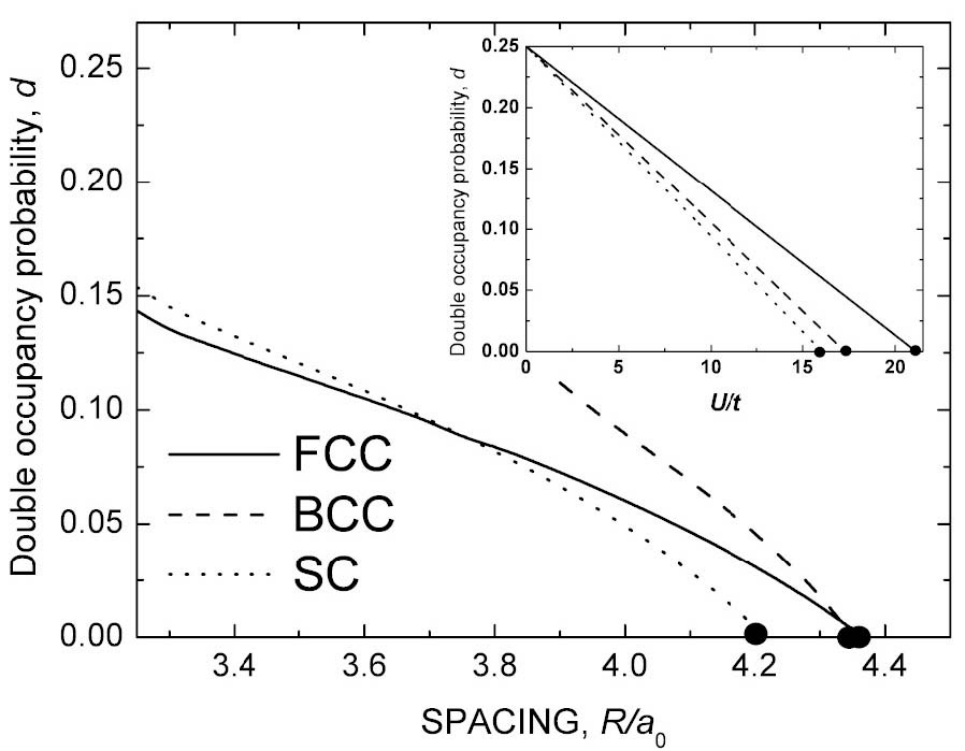
H_2



- Inflection signals the onset of QM *interference*.
  - Covalency
  - If extended, metallicity
- Featureless overlap leads to short-range delocalization
  - Non-bonded
  - Insulating
- Large U/t will kill covalency

Sigmoids, Cooperativity, Phase transitions?

Other results, Kurzyk *et. al.* Eur. Phys. J. B 66, 385 (2008)



- 3D variational Hubbard H lattices.
- All show MT.
- Almost Linear $p(2)(U/t)$
- Continuous transitions.

Summary, Conclusions

- As noted by Kohn (1963), ρ unrelated to insulating/metallic character.
- This leads to different decay rates for $\rho(\boldsymbol{r};\boldsymbol{r}')$
  - Models predict power-law in metals
  - Exponential decays in insulators
- We have shown, both analytically in simple models, and computationally that δ's behave in the same way.
- δ oscillations found in alternant hydrocarbons are analogous to Friedel oscillations in metals.
- There remains the question of numerical precision for usefulness.
- Correlation adds interesting insights
  - Profiles of DI's related to nature of interactions
  - Inflection points mark the onset of *long range* delocalization
  - Correlation suppresses fluctuations and interference.