Characterization of Difficult Systems by LRC-TD-DFT

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Theory Section
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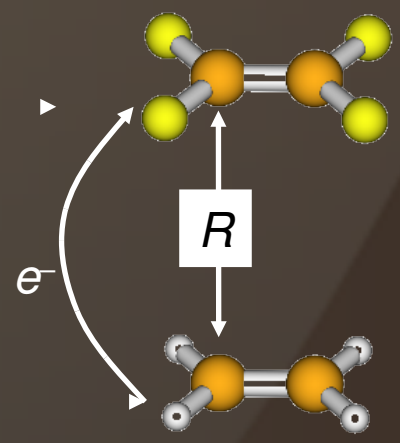
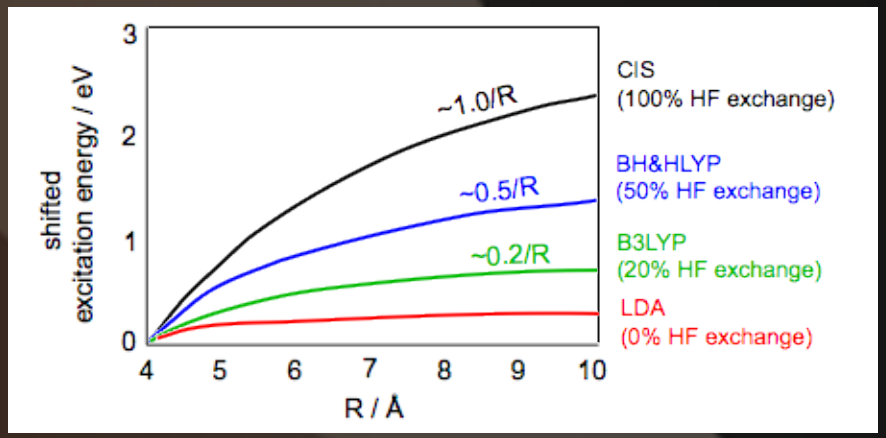
Outline

- Background: Long Range Corrected Time Dependent Density Functional Theory (LRC-TD-DFT)
- Exciton Length in DNA
- Characterization of L_a and L_b states of polycyclic aromatic hydrocarbons (PAHs)
- Conclusions

Background

- Certain traditional TD-DFT methods have incorrect asymptotic distance dependence of XC potential
  - Generalized gradient approximation
  - Do not incorporate full HF exchange
  - Leads to problems in calculations of:
    - CT states
    - Polarizabilities

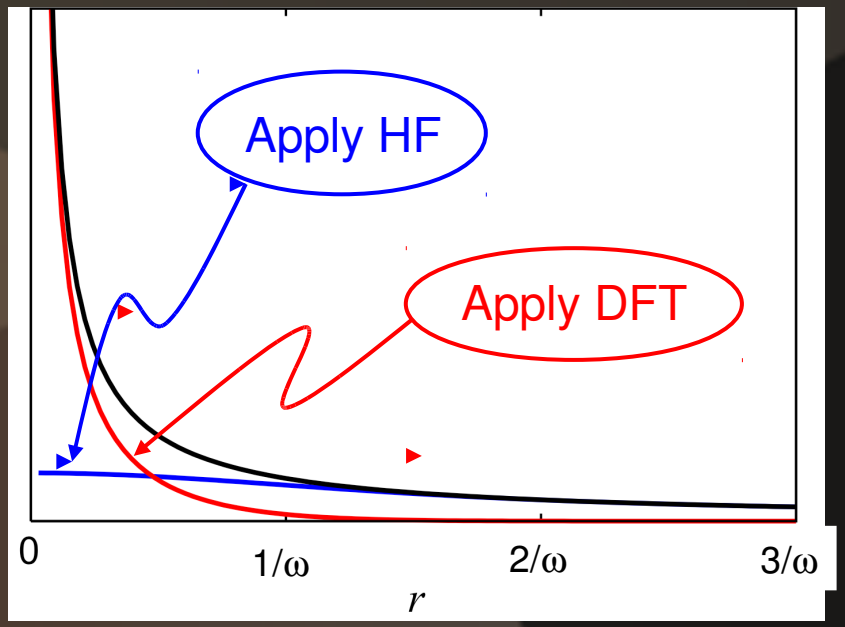




M. Head-Gordon and co-workers, *J. Chem. Phys.* **119**, 2943 (2003)

Background

$$\frac{1}{r} = \frac{\mathrm{erf}(\omega r)}{r} + \frac{1 - \mathrm{erf}(\omega r)}{r}$$



- Our group has developed two so called LRC-TD-DFT functionals:
  - LRC-ωPBE and LRC-ωPBEh
    - M.A. Rohrdanz, K.M. Martins, J.M. Herbert. *J. Chem. Phys.* 130 (**2009**) 054112.
    - T.M.Henderson, B. G. Janesko, G.E. Scuseria. J. Chem. Phys. 128 (2008) 194105.

Exciton Length in DNA

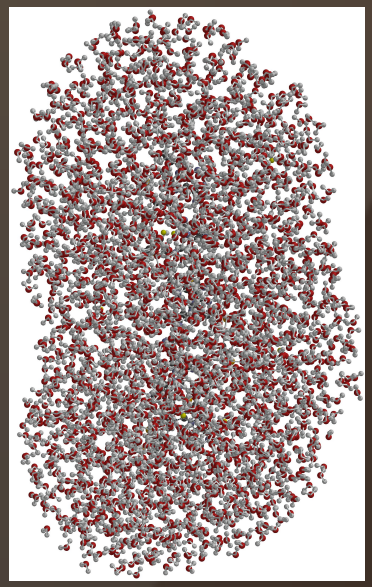
- Early reports of the spectra of DNA claim it was the sum of the bases' spectra
- Modern advances in spectroscopy have shown that the spectra are actually more complicated
- Now realize that π systems are a linear combination of coulomb coupled monomers (Exciton)

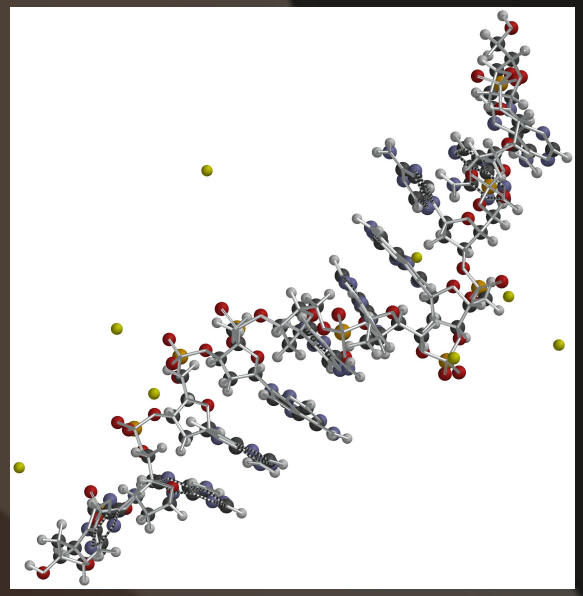
Exciton Length in DNA

- Why do we care?
  - UV excitation of DNA can lead to mutations
  - Understand the photo stabilization of DNA
    - Flourescence quantum yield of (10^{-4})
  - DNA is a unique and challenging system that incorporates: CT, excitonic states, and $\pi\pi^*$

Exciton Length in DNA

- B-DNA: $(dA)_{10}$
  - Molecular dynamics simulation
  - QM/MM on snapshots





Exciton Length in DNA

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} = w\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix}$$

$$D^{e}_{ab} = \sum_{i} (x+y)_{ia}(x+y)_{ib}$$

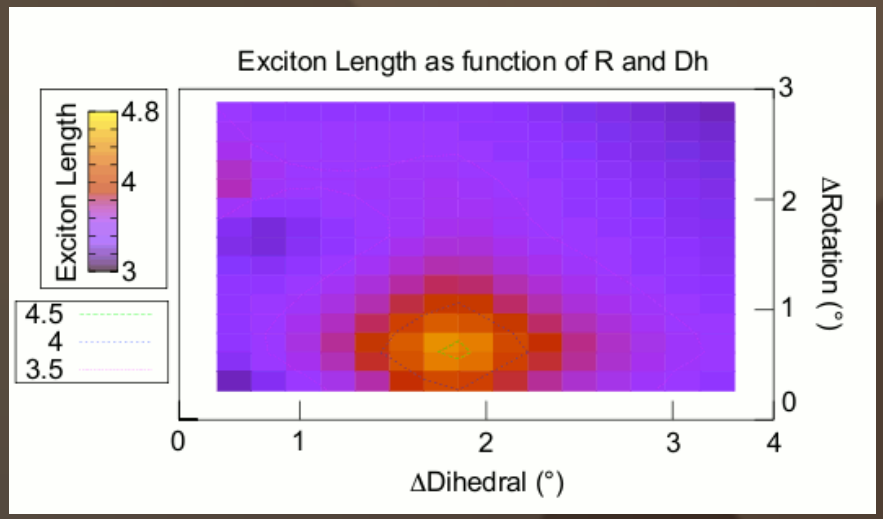
$$D^{H}_{ij} = \sum_{a} (x+y)_{ia}(x+y)_{ja}$$

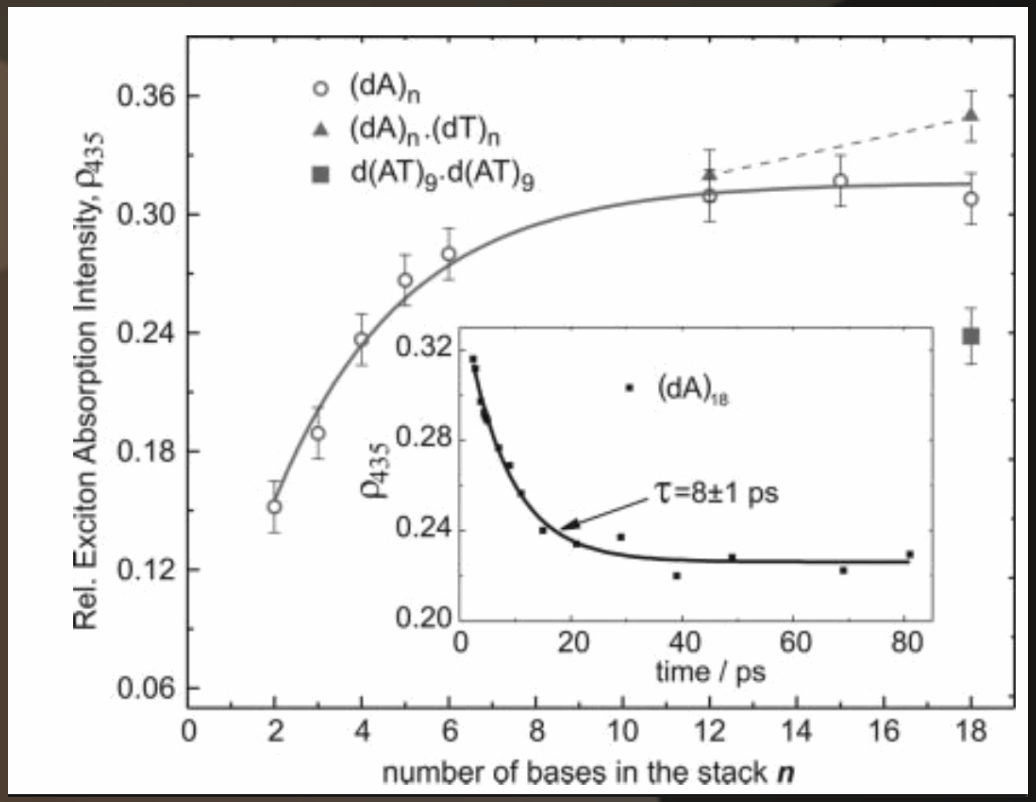
- Can do population analysis on states in the AO basis
- Summation over AOs on a base gives the amount of e^- or H^+ on that base

Exciton Length DNA

- Impose a threshold to get exciton length
  - 10% of particle or hole on base
- Effect of base stacking on length
  - Define two parameters:
    - Rotation angle
    - Dihedral angle
  - Calculate the absolute value of the difference of these values from the mode of the simulation

Exciton Length in DNA



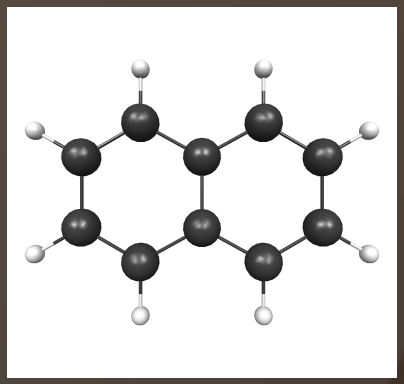


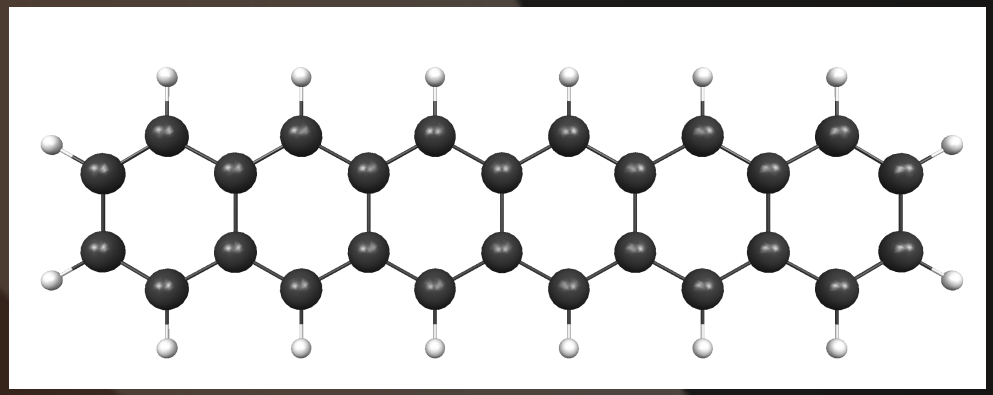
- Buchvarov et al. Measured a length of 3.3 bases +/- 0.5 bases
- Tonzani and Schatz computed a value of 3.3 bases

- Buchvarov, I.; Wang, Q.; Raytchev, M.; Trifonov, A.; Fiebig, T. *PNAS* (**2007**) 104 4794.
- Tonzani, S.; Schatz, G. C. *J. Am. Chem. Soc.* (**2008**) 130, 7607.

L_a and L_b States of PAHs

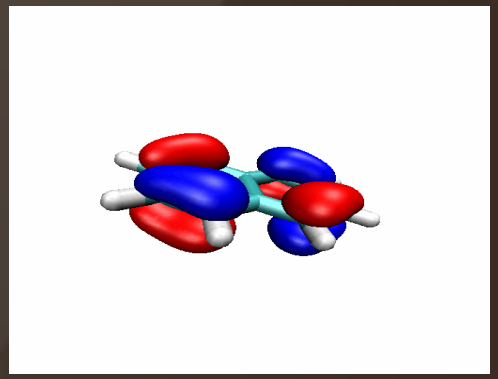
- Interested in replicating the experimental excitation energies of the linear condensed acene (LCA) series
- Look at n=2 through n=6

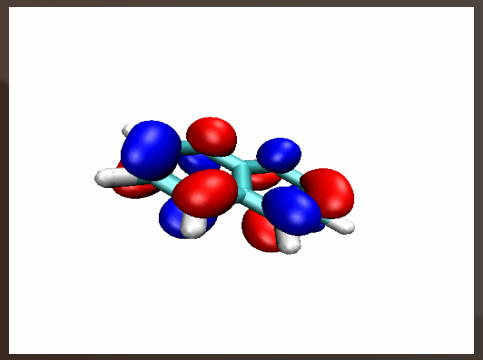




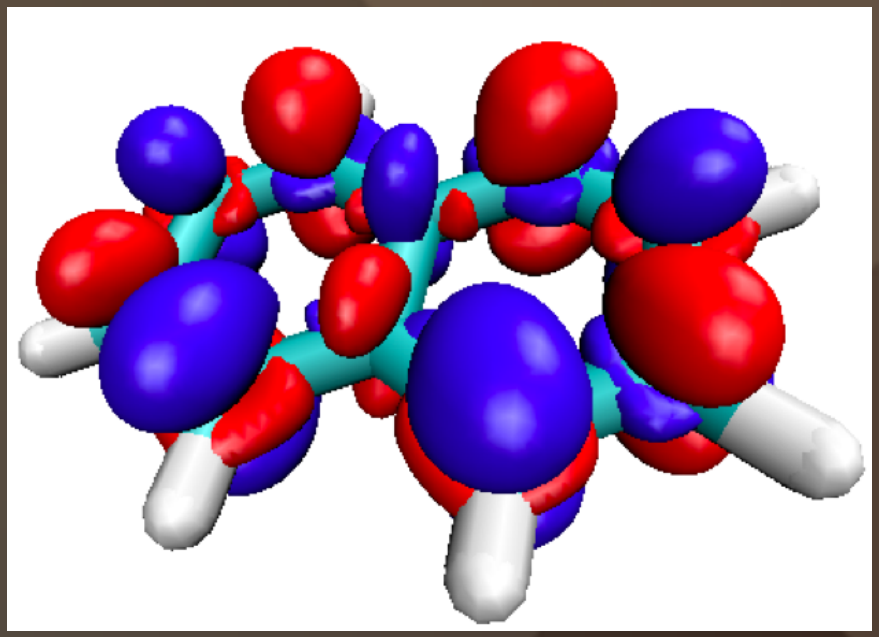
L_a and L_b States of PAHs

- Interested in the two lowest lying ππ* states
  - Termed the L_a and L_b states
- L_a is primarily the result of a HOMO to LUMO transition
- L_b is the result of either a linear combination of:
  - LUMO – 1 to HOMO and LUMO to HOMO + 1
  - LUMO – 2 to HOMO and LUMO to HOMO + 2



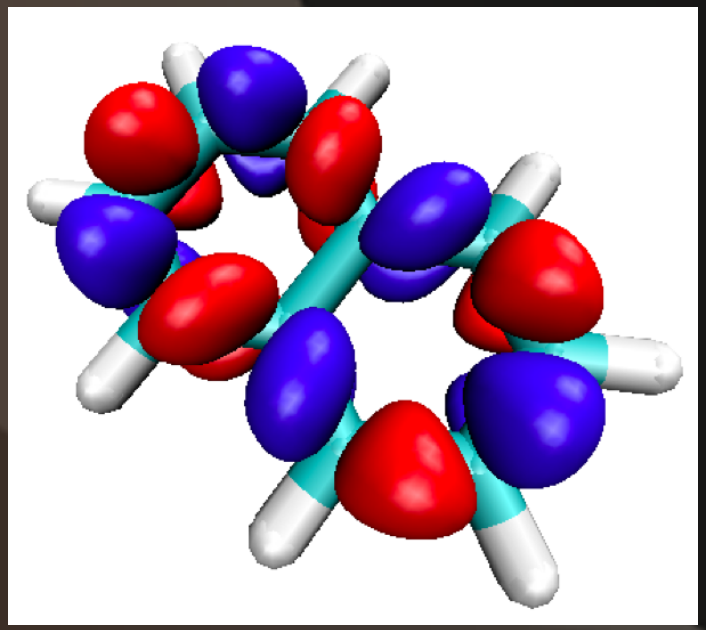


L_a and L_b States of PAHs



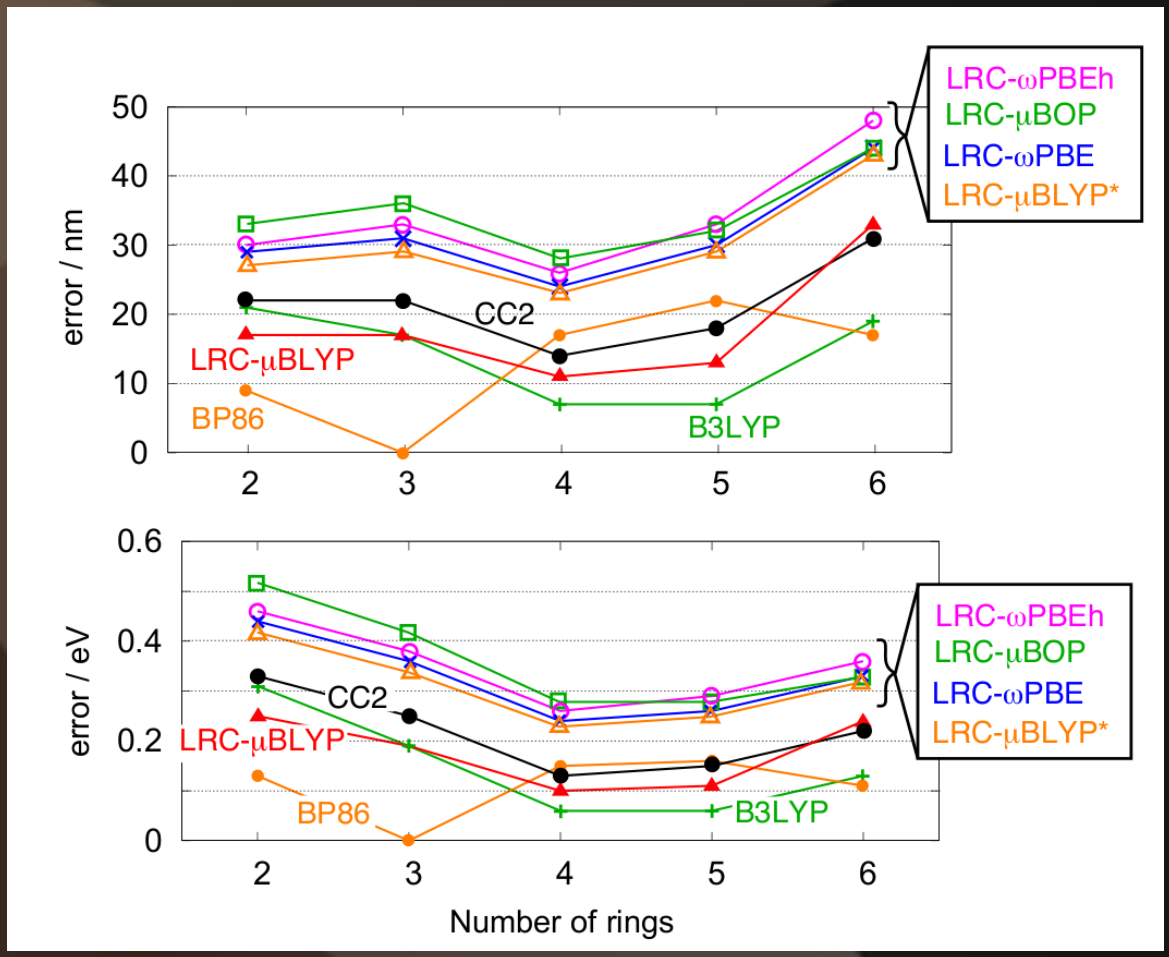
- L_a State:
  - Nodes on bonds
  - Transition dipole along short axis

- L_b State:
  - Nodes on atoms
  - Transition dipole along long axis

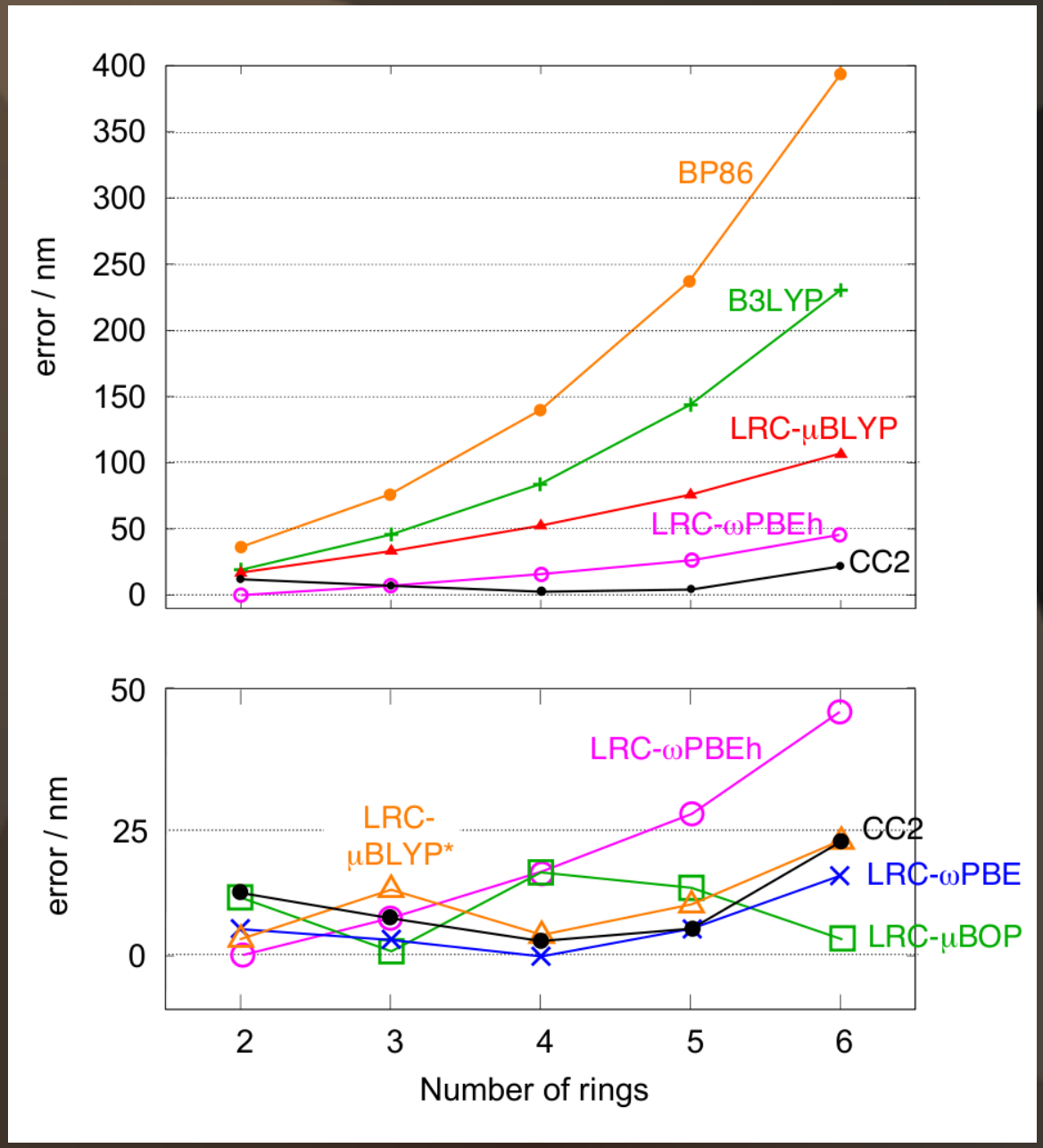


L_b State of PAHs

- L_b state does not pose problems to non-LRC-TD-DFT
- All methods tend to be of comprable errors



L_a State of PAHs



L_a and L_b States of PAHs

- LRC-TD-DFT correctly fixes N dependence of energy
- Ground state and L_a state have no permanent dipole moment
  - Excludes a Zwitterionic picture of L_a state
- Tozer et al.'s overlap metric is inconclusive

$$O_{i,a} = \langle |\phi_i| \mid |\phi_a| \rangle$$

$$\kappa_{i,a} = X_{i,a} + Y_{i,a}$$

$$\Lambda = \frac{\sum_{i,a} \kappa_{ia}^2 O_{ia}}{\sum_{ia} \kappa_{ia}^2}$$

Conclusions

- Looked at properties of systems that depend on the correct asymptotic dependence of the XC potential
- DNA
  - Exciton length
  - Further study required to determine cut-off values
- LCA
  - L_a state appears to have hidden CT character
  - Important for all polycyclic aromatic hydrocarbons, and the amino-acid tryptophan

Acknowledgements

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