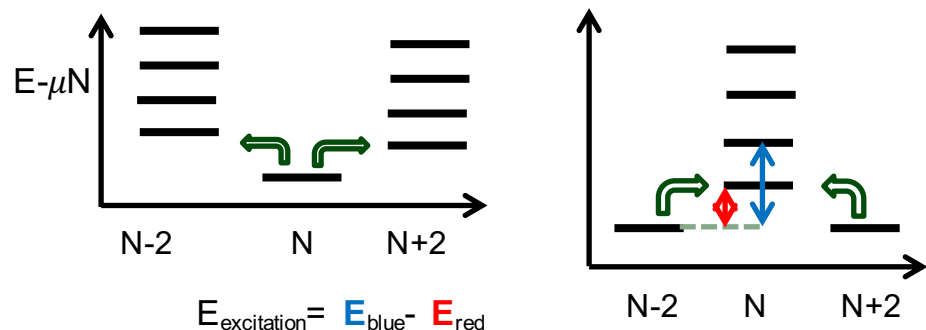
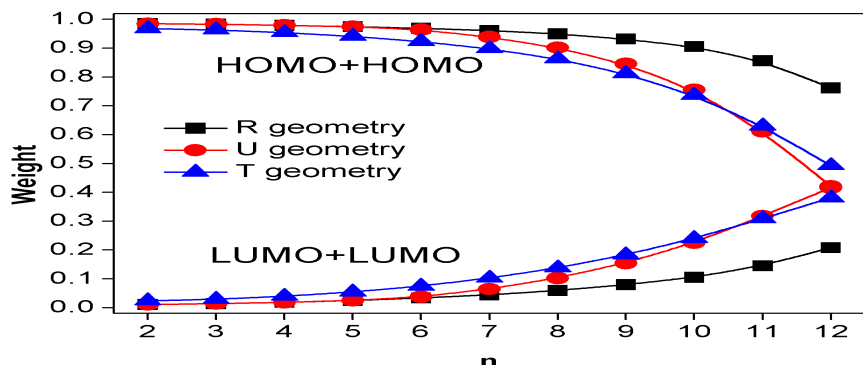


# Nature of ground and electronic excited states of higher acenes from pp-RPA



Excitation energy (in eV) of  ${}^3B_{2u}$  state

Acene	2	3	4	5	6	7	8	9	10	11	12
pp-RPA	2.87	1.98	1.39	0.98	0.70	0.51	0.37	0.28	0.22	0.18	0.16
Expt.	2.65	1.87	1.27	0.86							



**Top:** Structure of acenes in one Kekule resonance form; **2nd left:** Two-electron removal and addition in pp-RPA, **2nd right:** Obtaining excitation energies; **3rd:** Singlet-triplet gaps; **Bottom:** First (HOMO and HOMO) and second (LUMO and LUMO) dominant configurations of the ground state.

Y. Yang, E. R. Davidson, W. Yang *PNAS* (2016) DOI:10.1073/pnas.1606021113  
Work performed at Duke University

## Scientific Achievement

Higher acenes have versatile electronic properties. We developed and employed particle-particle random phase approximation (pp-RPA) to unveil the nature of their ground and electronic excited states. The excitation energies are presented, along with a detailed description of the bonding nature, which switches from regular molecules to full diradicals, and then even to polyradicals.

## Significance and Impact

A better understanding of acenes ground and electronic excited states will benefit further molecular design and future applications. However, their instability and multi-reference character impeded experimental and theoretical studies. pp-RPA we developed made this possible and should lead to much broader applications.

## Research Details

The  ${}^1A_g$  ground states of acenes up to decacene are closed-shell, while the ground state of undecacene and dodecacene tilts more to the open-shell. The lowest triplet state  ${}^3B_{2u}$  is always above the singlet ground state even though the energy gap could be vanishingly small in the polyacene limit.

Supported as part of the Center for the Computational Design of Functional Layered Materials, an Energy Frontier Research Center funded by DOE BES under Award # DE-SC0012575.



U.S. DEPARTMENT OF  
**ENERGY**

Office of  
Science



TEMPLE  
UNIVERSITY