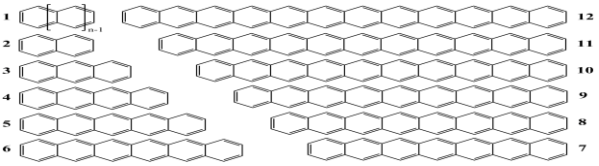
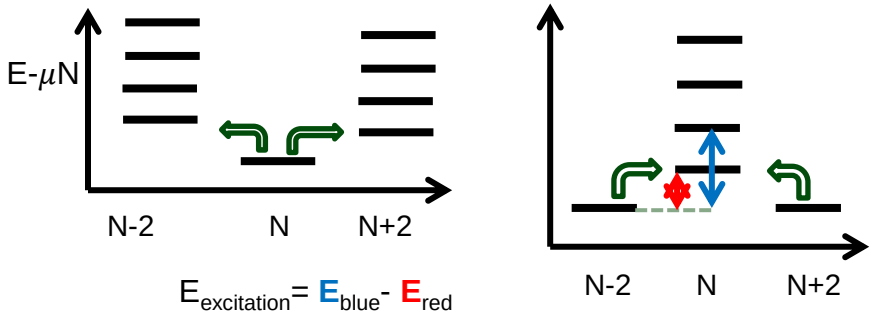
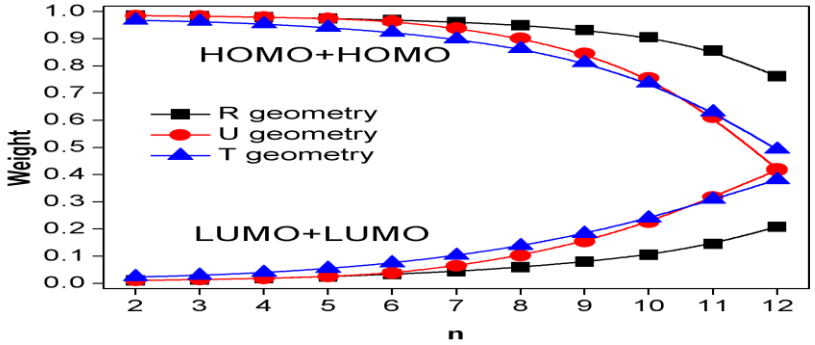
Nature of ground and electronic excited states of higher acenes from pp-RPA





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.

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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.

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