# Mind the Gap

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Intraband-gap states in conjugated polymers have captivated the chemistry community for the better part of five decades due to their position within the forbidden band gap, between the valence and conduction bands. In a large part, this fascination was (and still is) aided by the quest to find alternative materials that are easily processable compared to their solid-state semiconductor counterpart, which require considerable energy input. The outcome of the polymer story is well-known now, in 1977:[1] "...the dream of combining the processing and mechanical properties of polymers with the electrical and optical properties of metals..." was first realized with the π-conjugated polymer, polyacetylene, or CH_x.[2] There was an additional "surprise" that came out of these materials—the transport properties measured were not consistent with electrons (or holes) being the charge carrier. Polarons, one of the quasiparticles that mediate the intraband-gap states, were implicated, and although being widely studied, there is still uncertainty in fundamental aspects of their nature.

In this month's *ACS Central Science*, Georg Heimel proposes a model that questions the view that photoexcited polarons lead to intragap states without a concomitant disruption in the localized valence and conduction orbitals.[3] Taking into account the Coulomb interactions of the polaron with the surrounding electrons leads to a new band diagram via a re-evaluation of the accessible intragap polaron states. An important outcome of this viewpoint is a reversal in the ionization energy (or electron affinity) trend for the charged polymer, a trend having been observed in photoexcitation spectroscopic measurements.[4] Using density functional theory (DFT), Heimel produces the full density of states (DOS) for a 30mer of the canonical conjugated polymer poly(*para*-phenylene) or PPP to inform this updated view.

> Until recently, density function theory (DFT) was not able to accurately predict the electronic structure of long-range interacting systems like charged polaron states.

Georg Heimel describes coulomb repulsion in polaron gap states of conjugated polymers.
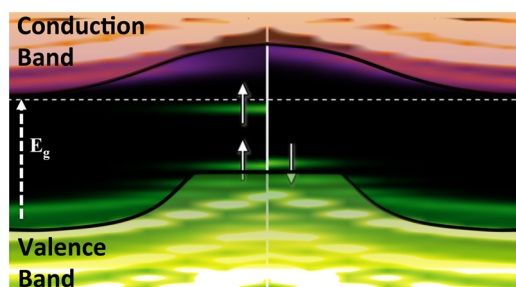
The confluence of polaronic quasiparticles and conjugated polymers has its own varied history and is rooted in concepts developed in the mid-20th century by the many-body electronic structure community to overcome the "band-gap problem". The "band-gap problem" stemmed from the electronic structure models inability to predict the optical gap E_g for many crystalline semiconductors.[5] Quasiparticles, operating within the forbidden band gap, provided a suitable description for the missing physics in the "band-gap problem". A few years later, in CH_x polymers, it was observed that there was a degenerate ground state, and a defect radical, called a soliton, provided the pathway to navigate between the two states.[6] Because the ground-state energy is identical left and right of the soliton, it is delocalized and noninteracting leading to high carrier mobilities.

On the other hand, polymers like PPP do not have degenerate ground states, instead having bound defect pairs that lead to *localized* deformations or polarons.[7] The Su−Schrieffer−Heeger (SSH) model was successfully used to describe solitons and polarons; being based on a tight-binding description it did not include Coulomb interactions.[6] The band diagrams that came out of these models described polaron states as emanating out of the valence and conduction bands without a concomitant change in the local band structure. This is because they are based on one-
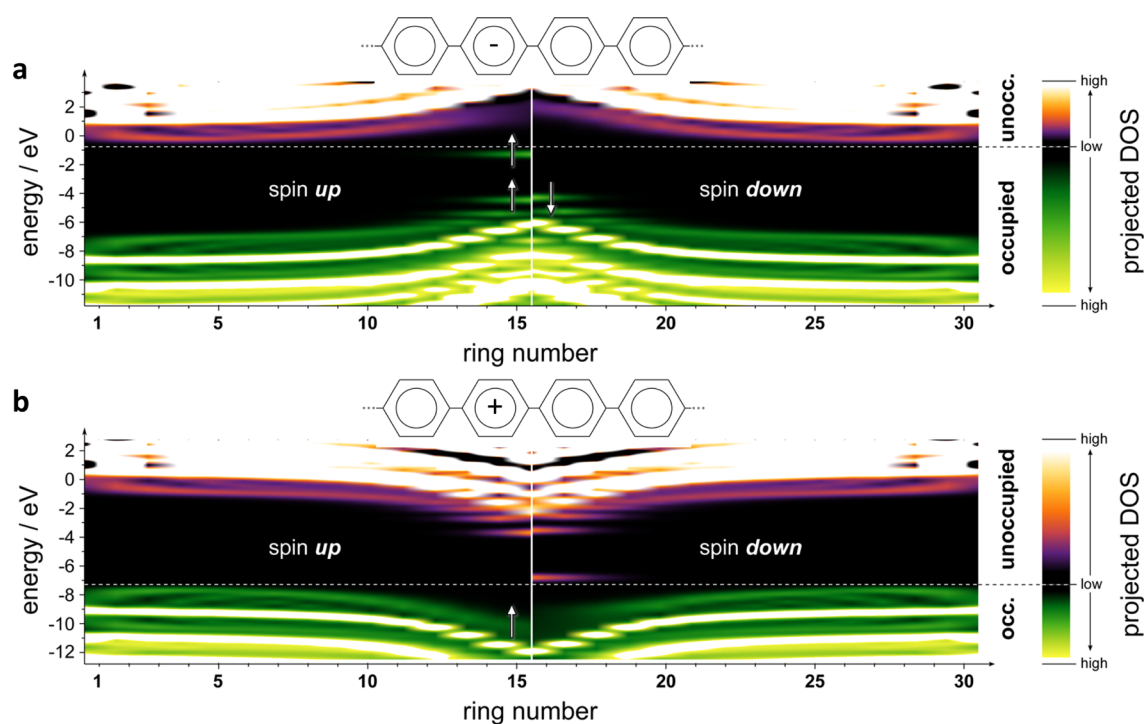
Figure 1. Electronic density of states in a ionized PPP 30mer oligomer. (a) Calculated density of states (DOS) for the radical anion, projected onto individual rings. The spin-up channel is shown for rings 1 through 15 and the spin-down channel for rings 16 through 30. The respective other half of the oligomer is symmetry equivalent. The color scheme indicates the magnitude of the projected DOS from low (black) to high (white) as well as its occupation (green and violet tones for occupied and unoccupied, respectively). The horizontal, white, dashed line marks the boundary between the occupied and the unoccupied states. The white arrows indicate electrons with according spin. (b) Same as (a) for the radical cation.
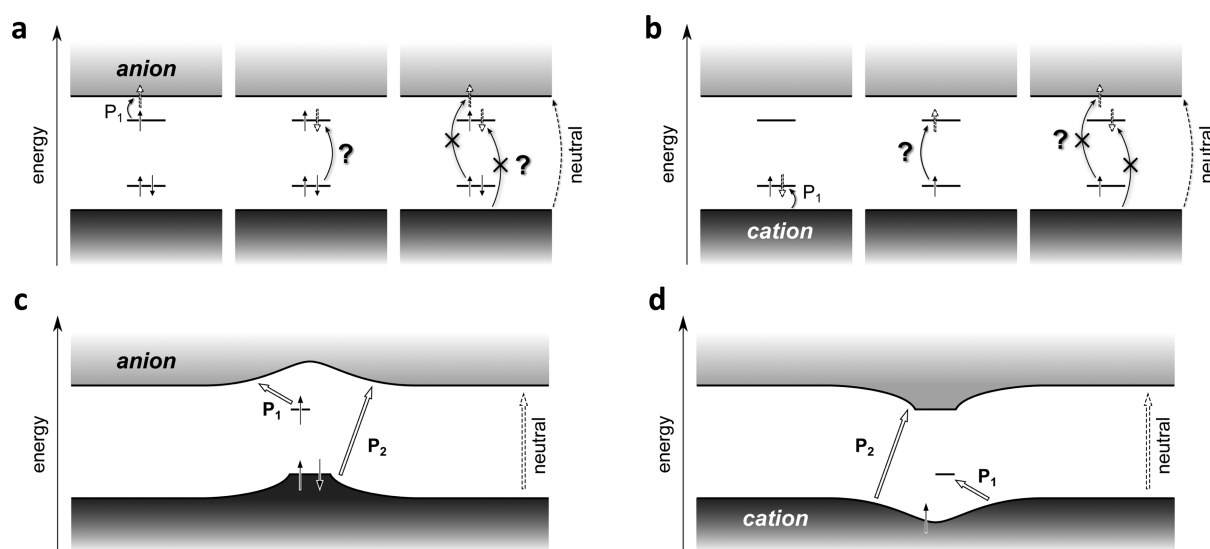

Figure 2. Historical and revised assignment of charge-induced optical transitions in conjugated polymers. (a) Dark- and light-gray shaded boxes indicate the valence and conduction bands, respectively. Straight, solid, and vertical arrows signify electrons with according spin. Straight, dashed, and empty arrows highlight where electrons are promoted to following the optical excitations indicated by curved arrows. The lowest-energy absorption is labeled P1, question marks near optical transitions underline that they are no longer possible in the revised picture based on Figure 1. (b) Same as (a) for cations. (c) Schematic of the charged-induced energy levels and resulting optical transitions in polymer anions according to the revised picture proposed in the present work. (d) Same as (c) for cations.

electron energy levels and by definition do not include the Coulomb repulsion of the surrounding electrons. Yet, for historical reasons, this qualitative picture has been unchallenged.

"The Optical Signature of Charges in Conjugated Polymers" by Georg Heimel challenges this picture.[3] Until

recently, DFT was not able to accurately predict the electronic structure of long-range interacting systems like charged polaron states. Through the use of properly tuned DFT calculations, the author calculates the DOS for both a cationic and anionic polaron state in PPP and finds distorted

frontier orbitals at the band edge where the polaron resides (Figure 1a,b). Additionally, the DOS shows fewer states available than the traditional single electron picture predicted, meaning that upon further reduction or oxidation the electron must be excited from a different energy level. For example, in the anionic polaron state, upon bringing another electron to the system, the missing DOS in the spin down monomer in the state, just below the conduction band, implies that the electron affinity decreases with respect to the neutral polymer (Figure 1a). This is in opposition to the traditional viewpoint that keeps a spin down state present leading to a larger electron affinity with respect to the neutral polymer.

> Using the metaphor of DFT being a hammer is apt here, since a broader look at other polymers (nails) with different bond reorganization energies will help as a comparative study.

Spectroscopic measurements will be key in determining the importance of Coulomb repulsion in this model.[8] Disorder and interchain effects still cloud the spectroscopic picture,[9] but single chain measurements are clarifying the contributions.[10] Indeed, many doped polymers are in solution with counterions that screen the electron repulsion and stabilize the often sought after doubly excited, spinless bipolarons. The optical spectra that are incongruent with the traditional model are often attributed to bipolaron formation (Figure 2). Are we misattributing those measurements? This work points toward yes, but much work still needs to be done to disentangle bipolaron formation from two interacting polarons. Using the metaphor of DFT being a hammer is apt here, since a broader look at other polymers (nails) with different bond reorganization energies will help as a comparative study. Alternatively, refinement of the SSH model with Coulomb repulsion has been available in the form of the SSH-Hubbard model for many years, but analytical solutions are no longer easily obtained when the two models are combined making intuitive conclusions challenging. The lack of analytic treatment has opened the door for DFT calculations, and this work leverages DFT toward getting a more refined picture of polaronic behavior in conjugated polymers. Using the metaphor of DFT being a hammer is apt here, since a broader look at other polymers (nails) with different bond reorganization energies will help as a comparative study.

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