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Perspective

Perspective on "MO approach to electronic spectra of radicals" Čársky P, Zahradník R (1973) Top Curr Chem 43: 1

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Abstract. The development of open-shell molecular orbital theory provided a tool for understanding the observed electronic spectra of radicals and radical ions. This then permitted chemists to understand the origin of the color of many radical ions and to explain in detail the photochemistry and reactivity of radicals and radical ions.

Key words: Open–shell MO methods –
Electronic spectra of radicals

In this review we summarized our experience with the development and applications of semiempirical Pariser–Parr–Pople (PPP)-type and all-valence-electron methods to electronic spectra of radicals. After the era of PPP calculations on closed-shell molecules and the advent of semiempirical all-valence-electron methods, the electronic spectra of radicals represented a new challenge for molecular orbital (MO) theory. It was a time when progress in experimental techniques resulted in accumulation of a vast amount of data on the electronic spectra of radicals of various structural types. Compared to closed-shell molecules, the electronic spectra of some radicals exhibited peculiar features: bands in the near infrared, many transitions in the whole UV/vis region, and some bands of extraordinary intensity. Clearly, without the help of MO theory, their interpretation seemed even harder than with closed-shell molecules.

There was a rich choice of available open-shell methods in the early 1960s [1] but their applications were rare and the results met with a differing degree of success. Obviously, a systematic examination was lacking. We decided to undertake this with the aim of formulating a generally applicable computational scheme for radicals which would be a natural extension of the PPP and semiempirical all-valence-electron methods for closed-shell molecules. We used for this purpose the self-consistent-field open-shell methods of Longuet-Higgins and Pople [2] and of Roothaan [3], we derived all expressions necessary for CI-S calculations [4, 5], and we tested the semiempirical open-shell PPP-type and INDO/S calculations systematically for various classes of radicals.

Needless to say that after 30 years or so, this type of calculation, as all other semiempirical calculations, lost much of its importance. By means of highly sophisticated ab initio methods, such as SAC-CI [6] and CASPT2 [7], it is now possible to treat rather extensive open-shell systems and with remarkable accuracy. Still, we believe that for large conjugated hydrocarbon radicals, the open-shell PPP-type approach remains a method of choice. To document this we present a figure (Fig. 1) from our review on the radical anions of α, ω-diphenylpolyenes.

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Fig. 1. Absorption spectra of anions of α,ω-diphenylpolyenes [8] and results of open-shell Pariser–Parr–Pople-type calculations. The *wavy lines* with *arrows* represent forbidden transitions