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Comments

Comment on the Comment of Dr. W. Gründler on the Paper "Heats of Atomization of Conjugated Hydrocarbons by a New Semiempirical Method"

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In the approach suggested by Dr. Gründler the ground state ψ_S of a conjugated system is represented as a linear combination of closed shell configurations containing atomic orbitals and nonexcited bond orbitals [1]. These configurations are called "significant electron structures" (SES) [1]. The admixture of the energetically higher SES structures is calculated using a simple perturbation expansion [1]. In the MORT-1 approach the ground state ψ_M is an antisymmetrized product of spin-up and spin-down substates ϕ_α and Φ_β, i.e. $\psi = A\phi_\alpha\Phi_\beta$. Both, ϕ_α and Φ_β are represented as a linear combination of determinants containing bond orbitals. SES and MORT structures are hence different, and the MORT-1 state ψ_M is spin-separated, which is not the case with the SES state ψ_S.

Relative merits of the two approaches can be illustrated with few examples. Take e.g. the benzene molecule. In the SES approach the ground state is stabilized by $6/17\beta$ [2–4]. In the MORT-1 approach the ground state is stabilized by 1.2β [5]. This is more than three times as much as in the SES approach. Similarly, in many other cases MORT-1 function ψ_M can be shown to have significantly lower energy than the corresponding SES function ψ_S. The function ψ_M should hence be considered to represent better the "true" ground state. This illustrates a quantitative difference between the two approaches.

Consider now the pentalene molecule. In the SES approach the interaction between the two SES structures vanishes [3]. In the MORT-1 approach the corresponding interaction is different from zero [6]. This leads to the charge polarization and double bond fixation in pentalene [6], the properties which (at least on the comparative level of the sophistication) can not be explained by the

SES approach. This illustrates a qualitative difference between the two approaches.

The basic idea common to both approaches is to use bond orbitals in forming different structures. This idea is however not new, and it is certainly not due to Dr. Gründler. For example, the so called PCILO method developed by Malrieu et al. as early as 1969 [7, 8] uses this idea. In fact, each SES structure containing bond orbitals is *identical* to some PCILO zeroth order wave function which is "a fully localized determinant which represents the wave function according to the chemical formula" [8]. The SES treatment of butadiene [9], methylencyclopropene and fulvene [10], vinylchloride and related compounds [11], etc. is very similar to the PCILO treatment of these molecules. Both approaches use here the same zeroth order wave function, and in addition they both use perturbation expansion in order to include higher structures (PCILO however uses much more elaborate perturbation expansion [7, 8] than SES [1, 2, 9–11]).

The connection between PCILO and MORT approach has been discussed in Ref. [6]. References to many other approaches which also use the chemical bond concept in numerical approximation methods can be found in Ref. [12].

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