

Reply to the comments by Burrow & Gallup on our earlier publication in *New. J. Phys.* 15, 013019, 2013

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Abstract.

We discuss in some detail the implications of the suggestion made by P.D. Burrow and G.A. Gallup on the physics of anion formation and of resonant electron attachment in gas-phase anthracene molecules.

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The Comment by P.D. Burrow and G.A. Gallup (to be named, from now on: B&G) on our earlier calculations of the resonant lowest metastable anions in anthracene is linked to three different aspects of the problem that we wish to analyze below:

- (i) the largely empirical nature of their scaling procedure,
- (ii) the specific physical features of anion formation in linear acenes,
- (iii) the physical basis of the interaction forces in our scattering model.

We would therefore like to examine all three aspects in our present discussion in order to better understand the physics of the processes involved in the light of the empirically-based suggestion made by B&G.

1. The comment by B&G, while raising an interesting possibility, is however not providing any physical reason as to why one should believe the findings of an empirical scaling of some Virtual Molecular Orbitals (VOs) that originate from rather low-level quantum calculations. While, in fact, scattering calculations of resonances have been routinely linked to the VOs generated by Minimal Basis Set (MBS) calculations, and we also indeed use such a scheme in our present work of [1], the connection has always been a purely qualitative one, chiefly based on symmetry comparisons between Molecular Orbitals (MOs) and scattering resonances, i.e. without really taking into consideration the usually incorrect energy location of such resonance estimates with respect to the scattering resonance positions. Additionally, such empirical estimates tell us nothing about the lifetimes of the metastable anionic states, an important link to the experiments which can only come from our scattering calculation.

The authors of the Comment basically modify these rather approximate estimates by using an entirely empirical series of scaling parameters, a pragmatic procedure which however does not advance our understanding of the real physical process even if it may turn out to fit the experimentally determined Electron Transmission Spectroscopy (ETS) spectra. Furthermore the latter spectra do not give any indication on the possible existence of anionic bound states nor provide indications on the symmetry features of the transmission's second-derivative changes which are being measured [2]. Hence, to match experimental data that are blind to symmetry considerations with empirical scalings that have the wrong initial energy estimates, albeit perhaps useful, does not seem to us to help, in the end, our physical understanding of the process at hand.

2. On the other hand, several recent studies on the electronic nature of linear acenes containing more than one aromatic ring, e.g. naphthalene ($n=2$, n being the number of aromatic rings), anthracene ($n=3$) up to heptacene ($n=7$), have pointed [3,4] out the diradical nature of such systems where the singlet-triplet structures are nearly degenerate. Such findings bear directly on the present problem, where an extra electron is being attached to the $n=3$ system, since it is well known that the corresponding electron affinity (EA) values are negative and large for the $n=1$ case (benzene), are still negative and small for the $n=2$ case (naphthalene) and only become positive (+0.53 eV) for the present case of $n=3$, i.e. for anthracene [5]. Thus we see that the present system may require a particularly delicate interplay between attractive and repulsive interaction forces between the target's diradical structures and the impinging electron

in order to provide the correct EA value, from both quantum chemical and scattering treatments, an aspect of the present issue that we shall further discuss below.

3. We further wish to remind readers that the scattering calculations we have reported in [1] employ the ab initio evaluation of the static interaction of the molecular target with the impinging electron, plus a DFT modeling of correlation-polarization forces [6] and also a local model for the bound-continuum exchange interaction [7]. The latter assembly of the interaction potential in low-energy electron-molecule scattering has been tested by us over many years for several systems, providing results which turned out to be in agreement both with experiments and with more accurate treatments. Recent examples are: comparisons of different molecules with the R-matrix approach [8,9] or with a more accurate form of exchange potential [10]. Even the treatment of single-ring acenes like benzene was found to produce [11] better accord with experiments than the results from other scattering methods [12]. We have therefore employed this approach also in the present linear acene, the first of this class of molecules that we have analyzed. In order to check on possible numerical errors we have now repeated the calculations already reported in [1] and found no numerical or computational errors in our results, thus confirming that the data reported in that paper are, within the model employed, numerically correct and reproducible.

In any event, in order to further investigate the suggestion in the above Comment, we have however carried out a fairly extensive ensemble of quantum chemical calculations at various levels of basis set expansion and of correlation correction, always finding negative EA values, both vertical and adiabatic: we shall report elsewhere the actual results of this analysis. It is however relevant to report here that the use of the cc-pVTZ expansion within a DFT approach (the B3LYP formulation of correlation/exchange), yielded finally a positive EA of +0.42 eV at the vertical level, and of + 0.50 eV at the adiabatic level. The bound anionic state was of ${}^2B_{3u}$ symmetry, like our resonant anionic state, in agreement with earlier calculations for the bound anion[13]. This result does indicate the crucial role of correlation corrections for EA evaluation when using quantum chemical methods for linear acenes, as discussed before.

To further stress this point, in the two panels of Figure 1 below we show the spatial maps of the scattering electron wavefunction obtained for the b_{3u} resonant electron in our earlier calculations (left side) and the corresponding singly-occupied-molecular-orbital (SOMO) obtained from the quantum chemical calculations at the DFT level mentioned above (right side).

One clearly sees there the essentially identical wavefunctions produced by the two sets of calculations for the added electron. The implication would therefore be that, due to the special physical nature of the bound electrons in the linear acenes with more than one ring, the extra electron interaction which one should employ to describe the scattering resonances would require a different interaction potential model from the one which we have employed successfully over the years for many other molecular systems with different character, so that the positive-energy, near-threshold B_{3u} resonance might become a negative-energy, weakly bound anionic state, as suggested by quantum

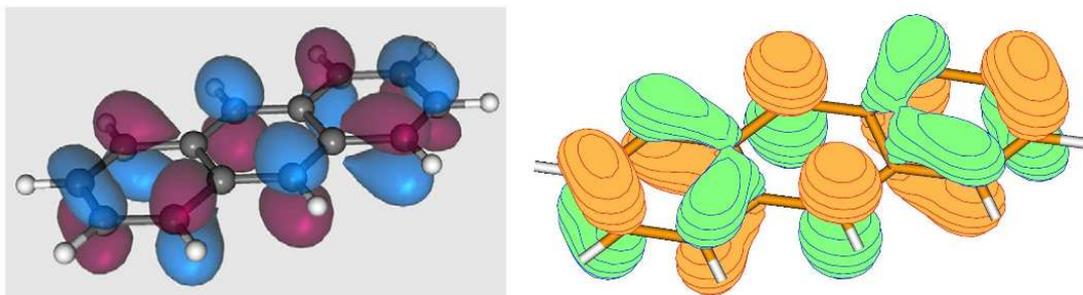


Figure 1. Computed spatial distributions of the scattering electron wavefunction (left) and of the bound singly-occupied orbital from the DFT calculations,(right). See main text for further details.

chemical calculations. We therefore plan to further investigate this aspect of the calculations in a later analysis of the resonances in the anthracene and further extend it to the multi-ring linear acenes like naphthalene and tetracene, employing different DFT models for dynamical correlation effects and for bound-continuum exchange contributions. Such further study will be hopefully able to provide more specific physical reasons about the possible formation of a bound anthracene anion of ${}^2B_{3u}$ electronic structure as well as for better understanding the general anions' features in this special class of linear acenes.

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