On the gas-phase electronic chemical potential of anions

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In the process of evaluating intrinsic electronic chemical potentials and related properties of anions in the gas phase, positive values for this quantity often arise. We herein examine in detail this result in terms of computational grounds. At a low level of theory, this result is often obtained, but its origin is mainly traced to the fact that the LUMO energy level is not really converged. Therefore, this outcome may be an artifact of the calculation. We establish the minimum basis set analysis that is to be performed before the electronic chemical potential of charged electron donors, in the absence of medium (solvent) effects, may be safely calculated to yield physically meaningful results. The implications that this result may have on the phenomenological chemical reactivity theory are discussed in detail, mainly those related to the definition of the electron-donating (nucleophilicity) ability of anions in the gas phase. The arguments given are illustrated for a large number of