Localized orbital scaling correction functional ushering DFT to a new level of accuracy
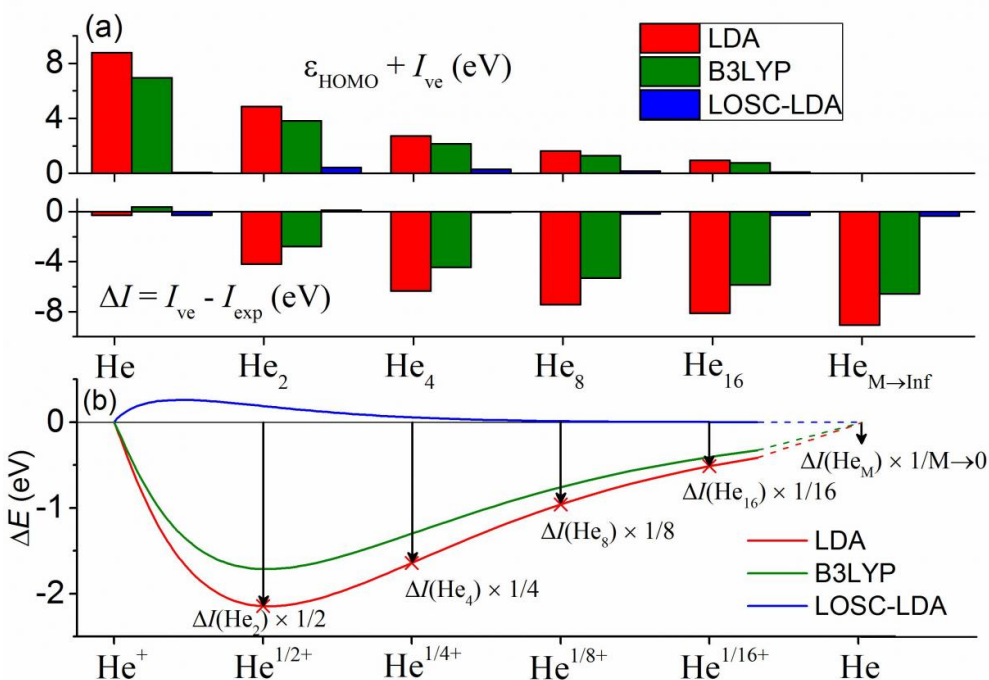
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(a) Deviations between the calculated ϵHOMO and -Ive and between Ive and Iexp for a series of HeM clusters. In each cluster all the He atoms are chemically equivalent. The nearest neighboring atoms are separated by 10Å, and the Iexp of HeM is well approximated by Iexp of a He atom. (b) Calculated total energy deviation from the linearity condition of a fractionally charged He atom as a function of the fractional charge δ. Here $\Delta E(He^{\delta+}) =$

E(Heδ+)-δE(He+)-(1-δ)E(He), and the δ values have been scaled in the figure for a direct comparison with (a). Credit: ©Science China Press

Kohn-Sham density functional theory is one of the most successful theories in chemistry. It is formally rigorous; its relatively low computational cost and competitive accuracy in small and medium-sized systems make it one of the most popular methods in electronic structure calculations, and perhaps the only choice for modeling quantum effects of electrons in large chemical and biological systems. Nevertheless, the exact functional is not explicitly known and the state-of-the-art density functional approximations (DFAs) suffer from systematic errors. One of the dominant errors in DFAs is the delocalization error, which is ubiquitous and manifested in various ways. This has been a challenging open problem for decades. Recently, Chen Li, Neil Qiang Su and Weitao Yang from Duke University and Xiao Zheng from the University of Science and Technology of China developed a novel localized orbital scaling correction (LOSC) framework that demonstrates systematic elimination of the delocalization error.

The major consequences of delocalization errors in DFAs can be categorized in two aspects: (1) Kohn-Sham (KS) orbital energy error and (2) total energy error. The delocalization error leads to important failures in practical applications such as the unphysical underestimation of band gaps, the excessively delocalized electron distributions and wrong charge transfers. Regarding these two aspects of errors, both are manifested in a size-dependent manner. In particular, among the KS orbital energies, the highest occupied molecular orbital (HOMO) energy, ε_{HOMO}, is supposed to agree with the (negative) vertical ionization potential ($-I_{ve}$), as required by the exact functional. Furthermore, the I_{ve} as calculated by DFAs are supposed to agree with the experimental value, I_{exp}.

For commonly used DFAs, the two conditions are not satisfied. As shown by the helium cluster calculations in the subfigure (a), the HOMO energy by the local density approximation (LDA) shows a positive error compared to -Ive while Ive exhibits a negative error, and the two errors are displayed in a size-dependent manner, suggesting that the delocalization error of DFAs has to show up in one way or the other, or both, while the sum of the magnitudes remains unchanged. Moreover, this is prevalent in all kinds of DFAs, including the most popular B3LYP functional, as shown in green.

To understand these errors, chemists can map them into the errors of a fractionally charged He atom, as illustrated in the subfigure (b). The fractional system energies are supposed to scale linearly with the fractional electron number n (0?n