

## Comparison of Dyson, Hartree-Fock, Kohn-Sham, natural, and natural-bond orbitals: electron momentum spectroscopy of CH<sub>4</sub>

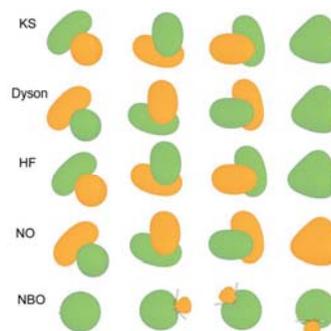
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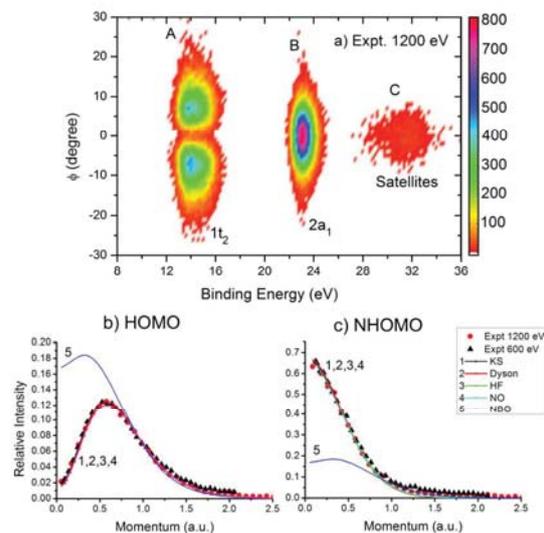
**Synopsis** The Dyson, Hartree-Fock, Kohn-Sham, natural, and natural-bond orbitals of methane (CH<sub>4</sub>) were compared with the experimental electron momentum distributions. The Dyson, Hartree-Fock, Kohn-Sham theories can present a direct concise interpretation and well reproduce the experimental results, but the natural-bond orbital cannot.

Recently, an intensive controversy has been aroused by Grushow's paper "Is It Time To Retire the Hybrid Atomic Orbital?" [1]. We try to discuss it from an experimental view. With appropriate approximations, the delocalized Dyson, Hartree-Fock (HF), Kohn-Sham (KS) orbitals can give a concise explanation of (e,2e) experiment, but the localized natural-bond orbital (NBO) cannot. Although those delocalized orbitals and localized orbitals are equivalent for describing the total electronic wavefunction of molecule, they are not equivalent on explaining physical progresses related to ionization, excitation, and charge transfer.

Figure 1 plots Dyson, HF, KS, natural orbital, NBO of CH<sub>4</sub> for illustrating their difference. It can be seen that those delocalized orbitals are similar, but they are remarkably different from the localized NBO. The delocalized orbitals have two types: one is similar to the p-type orbital, the other is similar to the s-type orbital. The four localized NBOs are corresponding with the classical concept sp<sup>3</sup> hybridization. Figure 2a) is the measured (e, 2e) density map for CH<sub>4</sub>. Three distinct features can be seen in the map. Feature A located at 14.2 eV has a minimum intensity at the azimuthal angle  $\phi=0^\circ$ , while feature B (23.2 eV) has a maximum intensity at  $\phi=0^\circ$ . Figure 2b) and c) compare the spherically averaged electron momentum distributions of each orbital with the experimental results. The delocalized Dyson, HF, KS, and natural orbitals (NO) can well reproduce the experimental electron momentum distributions, but the localized NBOs cannot. Within the picture of the molecular orbital, the binding energies for features A and B are approximately equal to the negative orbital energies of HF or KS, but there is no such a simple relation for NO and NBO. It should be noted that the natural orbital cannot describe experimental distributions of molecular orbitals for most molecules, although it can for CH<sub>4</sub>.



**Figure 1.** Molecular orbitals generated using different models (Contour value 0.05). KS was generated using B3LYP functional, and Dyson using SAC-CI theory. The Aug-cc-pVTZ basis set was used for all calculations.



**Figure 2.** a) Experimental (e, 2e) density map at the impact energy of 1200 eV and electron momentum distributions for b) the highest occupied molecular orbital (HOMO, feature A) and c) the next HOMO (NHOMO, feature B). The experimental momentum was determined through the azimuthal angle  $\phi$ .

### References

- [1] A Grushow 2011 *J. Chem. Educ.*, **88** 860

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