Electron Localizability

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During the last decade there was a steady increase of the number of studies utilizing the electron localization function (ELF) in the analysis of bonding situation in molecules and solids. These studies were mainly applications of ELF that follow the original definitions as well as the usage guidances of Becke and Edgecombe [1] and of Savin et al. [2], respectively. Considering the impressive number of papers dealing with ELF it should be stressed out that there is an intrinsic arbitrariness in the definition of ELF (an introduction to ELF and a list of references can be found at http://www.cpfs.mpg.de/ELF). Both ELF formulas claim to describe the local effect of the Pauli repulsion – either by the curvature of the Fermi hole (Becke and Edgecombe) or by the Pauli kinetic energy density (Savin et al.). But all the information, as supplied by ELF, seemingly emerge only with the uniform electron gas as the (arbitrarily chosen) reference. This leads to some confusion about the meaning of the ELF values [3].

There is another possibility to treat the localizability of an electron [4]. It follows a suggestion, based on the pair density, that the localizability of an electron can be described by means of the correlation of motion of same-spin electrons [5]. The integral of the same-spin pair density over a certain region Ω yields the number of same-spin electron pairs in that region. Under the restriction that all regions contain the same charge (fixed-charge condition) the above integral is proportional to the correlation of the electronic motion. Of course such a division implies a finite number of regions (and localizability values) for any choice of the fixed charge (for a system of N electrons and a fixed charge q there will be N/q such regions).

Using the fixed-charge condition and assuming a compact shape of the (non-overlapping) regions the integral of the same-spin pair density is a discrete function termed the q-restricted pair population ζ_q. The motion of the same-spin electrons is maximally correlated (with respect to Fermi correlation) in a region where ζ_q attains zero. It can be shown that in this case the charge in such a region originates from one electron only. Thus, the localizability is

understood to be maximal. The inverse relation between the electron localizability and ζ_q was removed applying an appropriate scaling. We define an electron localizability indicator (ELI):

$$\Upsilon_q = 1 \,/\, [1 + (c_q \; \zeta_q)^2]$$

The factor c_q compensates the charge dependency of ζ_q. Principally, ELI is defined at any level of theory (Hartree-Fock as well as for correlated wavefunction from a configuration interaction calculation) as long as the same-spin pair density is accessible.

In the Hartree-Fock approximation the expression for the q-restricted pair population ζ_q is especially simple. For each region Ω it is given by the sum of squared overlap integrals $S_{k,l}(\Omega)$:

$$\zeta_q \;=\; 1/2 \,[q^2 - S_{k,l}(\Omega)]$$

Figure 1 shows ELI for the Hartree-Fock calculation of the Ne atom using the fixed charge $q = 10^{-5}$ electrons and the factor $\zeta_q = 6 \,/\, b_F \, q^{8/3}$ to compensate the charge dependence (cf. the following derivation; the dimensionless constant b_F has the same numerical value as the Fermi constant c_F). These data nicely fit the curve given by the ELF formula:

$$\eta = 1 \,/\, [1 + (t_P \,/\; c_F \rho^{5/3})^2]$$

with the Pauli kinetic energy density t_P . The small deviations at larger distances from the nucleus are due to the numerical inaccuracy in the determination of the region Ω as well as the calculation of the overlap integrals T.

It is a ponderous task to compute ELI for a very small fixed charge q (for instance the above used 10^{-5} electrons – to get detailed information about the localizability) on the basis of the pair density integral, i.e., first to determine the regions containing the fixed charge and then to integrate the pair density within this regions. Instead, the pair density can be approximated by a Taylor expansion. At the Hartree-Fock level of calculation this expansion leads to a formula for ζ_q that is dependent on pow-
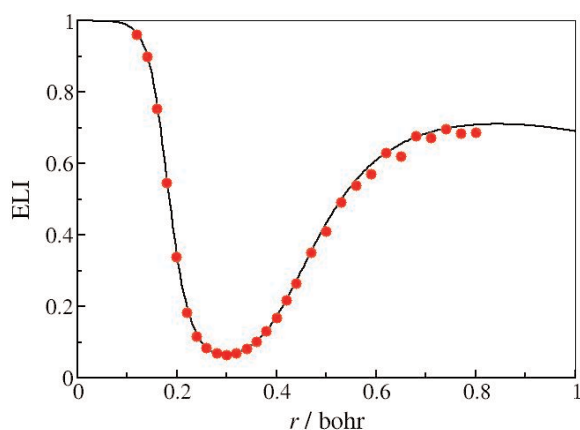
Fig. 1: The ELI for the Hartree-Fock calculation of the Ne atom. The red circles represent data computed from the overlap integrals. The solid line shows ELF.

ers of the volume V of the examined region. Considering that the volume V of the region is controlled by the fixed charge q and the electron density ρ by the approximate relation $V = q/\rho$, then the q-restricted pair population is dependent on powers of the fixed charge q. For small enough q only the term with the lowest power of q remains yielding $1/6 \, q^{8/3} \, \tilde{t}_P \, / \, \rho^{5/3}$ (the term $\tilde{t}_P$ resembles, except for the dimension, the Pauli kinetic energy density).

Using this expression in the ELI formula (with $c_q = 6 \, / \, b_F \, q^{8/3}$; the dimensionless constant b_F has the same numerical value as the Fermi constant) recovers the ELF formulas of Becke and Edgecombe, and Savin et al., respectively, as an approximation to ELI. Nevertheless, this equivalence between ELF and ELI is valid only at the Hartree-Fock level of theory. Moreover, in our approach the $\rho^{5/3}$ term does not refer to the kinetic energy density $c_F \rho^{5/3}$ of the uniform electron gas, but is a consequence of the Taylor expansion of the pair density. The electron localizability index suggests a theoretical background for (yet unknown) relations between ELI and physically relevant quantities.

References

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