

Electron Localisation Descriptors

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ONETEP now has the electron localisation descriptors:

- Electron Localisation Function (ELF) [1]
- Localised Orbital Locator (LOL) [2]

These descriptors provide a visualisation tool for indicating the location of electron pairs, including bonding and lone pairs, and distinguishing between σ and π bonds. It is a dimensionless quantity in the range of 0 and 1. The plots can be output in *.cube* or *.dx* format for visualisation as isosurfaces or volume slices.

The ELF was first introduced by Edgecombe and Becke in 1990 for Hartree-Fock Theory, and later updated for Density Functional Theory by Savin *et al.*. [1, 2, 3] It is based on the Hartree Fock probability of finding two particles of the same spin σ at two different positions of a multielectron system. From this, Edgecombe and Becke used the spherically averaged same-spin conditional pair probability, as a basis for a non-negative density for describing electron localisation. The smaller the probability, the increased likelihood that the reference electron is localised, provided both the electrons are of the same spin. This probability vanishes to zero when the two electrons have the same position, in agreement with the Pauli principle.

This probability is not upper-bounded and so for more convenient graphical interpretation, it is inverted, therefore the ELF represents localisation at unity. Details are below.

The LOL is similar to the ELF, but with a simpler representation, and produces cleaner plots in some cases. [4]

The ELF provides quantum Valence Shell Electron Pair Repulsion (VSEPR) representation of coordination compounds, and the identification of covalent bonding across crystalline solids and surfaces. This provides a useful tool for the main applications of ONETEP; biomolecular simulations, catalysis, and the design of nanostructured materials.

Electron Localisation Function

Becke introduced the ELF formula as the leading two terms of the Taylor series expansion of the spherically averaged same-spin conditional pair probability;

$$\tau_\sigma^P = \sum_i^{n_\sigma} |\nabla\psi_{i\sigma}|^2 - \frac{1}{4} \frac{|\nabla n_\sigma|^2}{n_\sigma}. \quad (1)$$

where $n_\sigma(\mathbf{r})$ is the charge density for each spin σ , and $\nabla n_\sigma(\mathbf{r})$ is its gradient. τ_σ^P is named the Pauli kinetic energy density since when multiplied by $\frac{1}{2}$, we have the physical interpretation as the excess of kinetic energy density due to Pauli repulsion:

$$\frac{1}{2}\tau_\sigma^P = \frac{1}{2} \sum_i^{n_\sigma} |\nabla\psi_{i\sigma}|^2 - \frac{1}{8} \frac{|\nabla n_\sigma|^2}{n_\sigma} = \tau_\sigma - \tau_\sigma^W \quad (2)$$

where the von Weiszäcker kinetic energy density,

$$\tau_\sigma^W = \frac{1}{8} \frac{|\nabla n_\sigma|^2}{n_\sigma} \quad (3)$$

We use the kinetic energy density as defined in ONETEP for τ_σ^P [5]:

$$\tau_\sigma(\mathbf{r}) = \frac{1}{2} \sum_\alpha \tau(\mathbf{r}; \alpha), \quad (4)$$

where the "per-NGWF" contributions are

$$\tau(\mathbf{r}; \alpha) = (\nabla\psi_\alpha(\mathbf{r})) \cdot \left(\nabla \sum_\beta K^{\alpha\beta} \psi_\beta(\mathbf{r}) \right) \quad (5)$$

where ψ_β are all NGWFs which overlap with ψ_α NGWFs.

τ_σ^P is compared with the kinetic energy density of the uniform electron gas as a reference:

$$\chi_\sigma = \frac{\tau_\sigma^P}{\tau_\sigma^{LSDA}} \text{ where } \tau_\sigma^{LSDA} = \frac{3}{5} (6\pi^2)^{\frac{2}{3}} n_\sigma^{\frac{5}{3}} \text{ or } 2^{\frac{5}{3}} c_F n_\sigma^{\frac{5}{3}}, \quad (6)$$

for a physical interpretation using the Fermi constant, c_F . The charge density is the local value of $n_\sigma(\mathbf{r})$ here.

Hence, the measure of electron localisation has now become dimensionless. χ_σ is then reformulated to avoid the open bounds of the above formula, limiting the ELF to a more desirable finite range of values of 0 to 1 for visual representation:

$$ELF_\sigma = \frac{1}{1 + \chi_\sigma^2} \quad (7)$$

In the spin unpolarised case, the up and down spin densities are equivalent to half of the total charge density; $n_{\uparrow} = n_{\downarrow} = \frac{1}{2}n$. Substituting this into χ :

$$\chi = \frac{\frac{1}{2}\tau - \frac{1}{2}\tau^W}{2^{\frac{2}{3}}c_F(\frac{1}{2}n)^{\frac{5}{3}}} = \frac{\frac{1}{2}(\tau - \tau^W)}{2^{-\frac{5}{3}}2^{\frac{2}{3}}c_F n^{\frac{5}{3}}} = \frac{\tau - \tau^W}{c_F n^{\frac{5}{3}}} = \frac{\frac{1}{2}\tau^P}{2^{-\frac{5}{3}}\tau^{LSDA}} = \frac{\tau^P}{2^{-\frac{2}{3}}\tau^{LSDA}} \quad (8)$$

and

$$ELF = \frac{1}{1 + \chi^2}. \quad (9)$$

Localised Orbital Locator

The LOL is similar to the ELF, only simpler:

$$LOL_{\sigma} = \frac{1}{1 + \frac{\tau_{\sigma}}{\tau_{\sigma}^{LSDA}}} \quad (10)$$

without the need for the von Weiszäcker kinetic energy density term, τ_{σ}^W .

For the spin unpolarised case:

$$LOL = \frac{1}{1 + \frac{\tau}{c_F n^{\frac{5}{3}}}} = \frac{1}{1 + \frac{\tau}{2^{-\frac{2}{3}}\tau^{LSDA}}} \quad (11)$$

How to use

Keywords

The keywords related to the implementation of the electron localisation descriptors are as follows:

Keyword:	Options (default):
<code>eld_calculate</code>	T/F (F)
<code>eld_function</code>	ELF/LOL (ELF)
<code>ke_density_calculate</code>	T/F (F)
<code>do_properties</code>	T/F (F)
<code>cube_format</code>	T/F (T)
<code>dx_format</code>	T/F (F)

- Setting `eld_calculate` to true turns on the calculation. The calculation will not proceed if this keyword is missing or if it set to false.
- The keyword `eld_function` determines which of the ELF or LOL ONETEP is to calculate, by specifying either string. The default here is the ELF, provided the keyword `eld_calculate` has been specified.

- As part of this implementation, the kinetic energy density can now also be output, using the logical keyword *ke_density_calculate*. This does not automatically output with *eld_calculate*.
- Electron localisation descriptors and kinetic energy density are available in the formats of *.cube* or *.dx* files.
- For spin polarised systems, there will be an ELF output for each spin individually, showing the electron localisation for one of the spins.

In order to use any of the above keywords, ONETEP's properties calculation must be enabled, using *do_properties* or setting the task to *properties*, if reading in density results of an energy minimisation calculation. To produce the density plot during the original energy calculation, the input should include:

```
task                singlepoint
write_density_plot  T
```

Example input file

Below is an example input for using the ELF, for the water molecule:

```
1 task                singlepoint
2 cutoff_energy      900.0 eV
3 maxit_ngwf_cg      100
4 output_detail      verbose
5 do_properties      T
6 cube_format        T
7 dx_format          F
8 grd_format         F
9 eld_calculate      T
10 eld_function       ELF
11
12 %block lattice_cart
13 40.000000000000    0.000000000000    0.000000000000
14 0.000000000000    40.000000000000    0.000000000000
15 0.000000000000    0.000000000000    40.000000000000
16 %endblock lattice_cart
17
18 %block positions_abs
19 O 20.000000000    20.000000000    20.000000000
20 H 18.565580829    18.889354011    20.000000000
21 H 21.434419171    18.889354011    20.000000000
22 %endblock positions_abs
23
24 %block species
25 O O 8 4 8.0
26 H H 1 1 8.0
```

```
27 |%endblock species
28 |
29 |%block species_pot
30 |O <path to oxygen.recpot>
31 |H <path to hydrogen.recpot>
32 |%endblock species_pot
```

References

- [1] A. D. Becke and K. E. Edgecombe. A simple measure of electron localization in atomic and molecular systems. *J. Chem. Phys.*, 92(9):5397–5403, 1990.
- [2] A. D. Becke and H. L. Schmider. Chemical content of the kinetic energy density. *Journal of Molecular Structure (Theochem)*, 527:51–61, 2000.
- [3] A. Savin, O. Jepsen, J. Flad, O. K. Andersen, H. Preuss, and H. G. von Schnering. Electron localization in solid-state structures of the elements: the diamond structure. *Angewandte Chemie International Edition in English*, 31(2):187–188, 1992.
- [4] H. Schmider and A. Becke. Chemical content of the kinetic energy density. *Journal of Molecular Structure (Theochem)*, 527(1):51 – 61, 2000.
- [5] J. C. Womack, N. Mardirossian, M. Head-Gordon, and C.-K. Skylaris. Self-consistent implementation of meta-gga functionals for the onetep linear-scaling electronic structure package. *The Journal of Chemical Physics*, 145(20):204114, 2016.