Documentation of the algorithms implemented in amolqc

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1 Determinantal part

TODO (MOs as in Gaussian, Gamess)

2 Jastrow correlation factors

Jastrow factor $J = e^U$ where U is expanded into many-particle terms: ee, en, een, eee, enn, eenn, ... (e=electron, n=nucleus)

$$U = U^{ee} + U^{en} + U^{een} + \dots \tag{1}$$

Each term is expanded into distance-dependent terms

$$U^{ee} = \sum_{i<j}^{n_{elec}} U^{ee}_{ij}(r_{ij}) \tag{2}$$

$$U^{en} = \sum_{a=1}^{n_{nuc}} \sum_{i}^{n_{elec}} U^{en}_{ai}(r_{ai}) \tag{3}$$

$$U^{een} = \sum_{a=1}^{n_{nuc}} \sum_{i<j}^{n_{elec}} U^{een}_{aij}(r_{ai}, r_{aj}, r_{ij}) \tag{4}$$

2.1 Schmidt-Moskowitz-stype Jastrow (sm)

The U-terms are expanded into scaled distanceswith the scaled distances

$$\bar{r}_{ij} := \frac{a r_{ij}}{1 + a r_{ij}}, \qquad \bar{r}_{ai} := \frac{b_a r_{ai}}{1 + b_a r_{ai}} \tag{5}$$

with individual parameter b_a for each nucleus a.

$$U^{ee}_{ij} = \sum_{k=1}^{k_{max}} c^{ee}_k \bar{r}^k_{ij}$$

where $c^{ee}_1 = \frac{1}{2a}$ (ee cusp). It is possible (with type "7") to satisfy like-spin cusp with $c^{ee}_1 = \frac{1}{4a}$.

$$U^{en}_{ai} = (n-1) \sum_{m=1}^{m_{max}} c^{en}_m \bar{r}^m_{ai}$$

please note the factor $n-1$ that makes the coefficients identical to the coefficients in the original paper by Schmidt and Moskowitz.

The een terms are restricted to $\bar{r}^k_{ij} \cdot (\bar{r}^m_{ai} + \bar{r}^m_{aj})$ and $\bar{r}^m_{ai} \bar{r}^m_{aj}$.

2.1.1 sm1

This is $k_{max} = 2$, $m_{max} = 2$, no een terms. The first terms are fixed for cusp conditions, $c_1^{ee} = \frac{1}{2}$, $c_1^{en} = 0$. Therefore, sm1 has one ee parameter, and one en parameter for each "symmetry equivalent" nucleus. Default behavior is to use the same parameters for the same nucleus. The order of the parameters is taken from the order in the geometry. Different parameters for identical nuclei can be obtained by adding a "sa" entry in the geometry (see user manual).

CH_4 and C_2H_6 and all hydrocarbons have thus three parameters: c_2^{ee}, c_2^{en}(C), c_2^{en}(H) in this order.

2.1.2 sm2

Like sm1 with $k_{max} = 4$, $m_{max} = 4$, i.e. three parameters for ee and three parameters for each nucleus.

2.1.3 sm3

Like sm2 with additional two een terms: $\bar{r}_{ij}^2 \cdot (\bar{r}_{ai}^2 + \bar{r}_{aj}^2)$ and $\bar{r}_{ai}^2 \bar{r}_{aj}^2$ for each nucleus. The order is ee, en(nuc1) een(nuc1), en(nuc2), een(nuc2), ... The number of parameters is $3 + 5n_{nuc}$.

2.2 Drummond-Towler-Needs Jastrow (dtn)

2.3 Generic Jastrow (ic)

This Jastrow factor implements a generic power series with U_{ij}^{ee} as in Schmidt-Moskowitz and

$$U_{ai}^{en} = \sum_{m=1}^{m_{max}} c_m^{en} \bar{r}_{ai}^m$$

(note the missing factor $(n-1)$ in comparison with Schmidt-Moskowitz).

The form of the een terms is described in the report on Jastrow factors.

2.3.1 Schmidt-Moskowitz-like form

$\bar{r}$ is defined as in Schmidt-Moskowitz

2.3.2 double exponential form

$\bar{r}$ is defined as $\bar{r} = 1 - \exp(-a \cdot r)$.

3 Parameter optimization routines

TODO