

# Standard grid SG-2 SG-3 for modern density functionals

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Density functional theory is currently the most used ab initio method because of its cost effectiveness. The exchange correlation energy of DFT can be written as

$$E_{xc} = \int dr F[\rho(r)] \quad (1)$$

which becomes an one electron integral, although it arises from the many electron interactions. As the integral is too hard to solve analytically, we are left with the choice of numerical integration only. Several quadrature formulations have been developed to do this efficiently.

$$\int dr F[\rho(r)] \approx \sum_i w_i F[\rho(r_i)] \quad (2)$$

For finite grid we need to define the weights ( $w_i$ ) and points ( $r_i$ ) to obtain the energy precisely. Now the above quadrature can be broken into two pieces, i.e. the radial and the angular parts.

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \sin\theta F(r, \theta, \phi) dr d\theta d\phi \approx \sum_{i=1}^{N^r} w_i^r \sum_{j=1}^{N^\Omega} w_j^\Omega F[\rho(r_i, \theta_j, \phi_j)] \quad (3)$$

Two quadrature schemes are mostly used for Q-Chem package, known as SG-1 and SG-0. The SG-1 grid is a “pruned” version of EML-(50,194) grid (where the EM defines the Euler-Maclaurin quadrature for the radial part, and L stands for angular Lebedev quadrature) having 50 radial and 194 angular points. Whereas SG-0 is much more cost effective using the “MultiExp” radial quadrature, which describes the shell structure of atom quite well, along with Lebedev angular quadrature. These quadrature schemes behave well for the routine purpose, i.e. B3LYP/6-31G\* level of theory. But recently, several anomalies have been observed by using these traditional quadrature schemes. One of those is oscillation of potential energy surfaces of rare gas dimers, where significant inconsistencies have been observed by the use of coarse grid. If the grid becomes finer this oscillation disappears. Another kind of grid error has been observed in case of meta GGA predicted isomerisation energy, by using M06 suite of functionals. From the study done by Wheeler and Houk, it is witnessed that the isomerisation energy is grid dependent and the error will be vanished if we use a more compact grid than SG-1. As DFT scales linearly with respect to the grid size, in order to the accurate energy we need to compromise with the computation time. So we felt the need to develop denser grids, SG-2 and SG-3 which will be the pruned version of (75,302) and (99,590) quadrature scheme respectively.

We have chosen the Double exponential quadrature scheme developed by Mitani and Yoshioka. The radial integral is carried out by combining the double For this grid pruning, we have taken the hydrides of all of the 18 elements and partitioned each atom into several concentric spheres and tried to minimize the error in energy. As an example, for hydrogen molecule, our optimized and pruned SG-2 has Lebedev partition of  $6^{35}110^{12}302^{16}86^726^5$  with error of only 1.6  $\mu$ Hartree in energy. So total number of points for the pruned version of hydrogen is 7094, which is just 31.3% w.r.t the benchmark (22650). Similarly for SG-3 we have found the pruned Lebedev partition (where the base defines number of angular points and the exponents designates number of radial

points) of SG-3 as  $6^{45}110^{16}590^{17}146^{14}50^7$  (with error of  $3 \mu\text{Hartree}$ ) which has 14454 total number of points, which is just 24.7% w.r.t the benchmark (58410). For these calculations we have used  $\omega\text{B97X-V/aug-cc-pVTZ}$  level of theory. Now in order to check the accuracy we did the computation for a handful number of diverse training sets which include the calculation for geometrical parameters, atomisation energy, hyperpolarizability and other non-linear optical properties, vibrational frequencies for small molecules, PES for weak interacting systems. For all of these test sets we have compared the data for benchmarks with the corresponding pruned version. All of the results for the pruned grid are pretty close to corresponding benchmark. So for non-covalent interactions this grids are less error-prone than our traditional SG-1. Furthermore  $\omega\text{B97X-V}$  is a very promising functional, and from our results we can conclude that both SG-2 and SG-3 are more compatible to this functional as well as other meta-GGA or hybrid functionals than SG-1.