Improved DFT from Electrons on a Sphere

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Density functional theory (DFT) is now popular within the chemical physics community, but it still suffers from some serious deficiencies and most of these are now well understood [1]. One of the key goals of modern research, therefore, is to develop new methods that preserve the low cost of DFT calculations while offering significantly enhanced accuracy.

Many of the weaknesses of DFT stem from the fact that most functionals are based on the uniform electron gas, a model consisting of an infinite number of electrons in an infinite volume. Unfortunately, this system does not resemble the electron density in most molecules and one route to the improvement of DFT is to replace this foundation with a new one.

In recent years, there has been growing interest in the quantum mechanics of pairs of confined electrons. The helium atom, of course, has been studied from the early days and the Hooke's Law atom was introduced in the 1960s. But, more recently, accurate solutions have also been found for pairs of electrons trapped inside a ball [2] and on its surface [3–8] and these are now being used for the development of new functionals in density functional theory (DFT).

The electrons-on-a-sphere model is particularly attractive because it is defined by a single parameter (the radius R of the sphere) and varying this takes us from a weakly correlated system (small R) dominated by dynamical correlation, to a strongly correlated system (large R) dominated by static correlation.

I will review this model and show how it can be used as the starting point for a new way of understanding and improving DFT.

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