GGA's role in electronic correlation in two-electron harmonium atom and a new electron correlation tool.

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Due to its very favorable efficiency-cost ratio, density functional theory (DFT) is one of the most utilized methodologies in modern quantum and computational chemistry. Nevertheless, the exact density functionals for exchange and correlation (E_{xc}) are still unknown for the vast majority of systems. Some of the failures of current functionals are known and well documented[1]. New DFT E_{xc} functionals may be built using different starting points from the Homegenous Electron Gas (HEG). For example, using a more realistic model like the Harmonium Atom (HA), where the Coulomb electron-nucleus potential is replaced by a parabolic potential ($-Z/r_i \rightarrow 1/2\omega^2 r_i^2$, where ω is known as the confinement strength; which plays a crucial role in correlation) and where the actual Coulomb electron-electron potential is kept unchanged ($1/r_{ij}$). This model is specially fascinating due to the presence of analytic solutions[2] for the two-electron case and several values of ω.
In the present talk, following previous studies (HA and B3LYP[3] functional),[4] we unveil the role of the GGA exchange in B3LYP (B88[5]) in the description of the HA. We also introduce a well known quantity from classical mechanics that finds here a new application as indicator of electronic correlation. Finally, with this new ingredient we show a simple link between two-electron HA and He-like atoms ($Z = 2$).

$$\begin{array}{c} \omega \\ \downarrow\uparrow \end{array}$$

$$I = \begin{pmatrix} \int \rho(\mathbf{r})(y^2+z^2)d^3\mathbf{r} & -\int \rho(\mathbf{r})xyd^3\mathbf{r} & -\int \rho(\mathbf{r})xzd^3\mathbf{r} \\ -\int \rho(\mathbf{r})xyd^3\mathbf{r} & \int \rho(\mathbf{r})(x^2+z^2)d^3\mathbf{r} & -\int \rho(\mathbf{r})yzd^3\mathbf{r} \\ -\int \rho(\mathbf{r})xzd^3\mathbf{r} & -\int \rho(\mathbf{r})yzd^3\mathbf{r} & \int \rho(\mathbf{r})(x^2+y^2)d^3\mathbf{r} \end{pmatrix}$$

$$\begin{array}{c} \downarrow\uparrow \\ Z \end{array}$$

Can you guess what the above matrix is?

[1] M. Swart. *Int. J. Quant. Chem.*, 113:2, 2013.
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[5] A. D. Becke. *J. Chem. Phys.*, 98:1372, 1993.