Basics of the flexible density

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I. MOTIVATION

In this technical note, we give the essentials of the so-called "flexible density" introduced in Ref. 1. The underlying idea, namely to investigate the effect of the Kato cusp condition [2] first showed up in the DFT literature, so far as we know, in Levy and Ou-Yang [3]. Extending that to densities without a cusp is, we think, original with Ref. 1. The elementary point is that densities both from regularized potentials (e.g. pseudo-potentials) and from expansion in Gaussian basis sets do not obey the Kato condition. Densities expanded in Gaussians also do not have the proper exponential tail. The flexible density provides a tool to explore the implications of such behavior by the most rudimentary route possible, namely an exponent tunable from hydrogenic cusp to Gaussian cusplessness. For an s-like density that is not only easy to do but provides explicit formulae at least for the atomic case.

Remark: SBT remembers that somewhere in J.C. Slater's books there is an example of using a Gaussian orbital as a variational wavefunction for the H atom. We have not gone to the effort to find the specific reference.

II. ATOMIC-LIKE CASE

We define a one-center N_e-electron density in the flexible parametrized form

$$n_f(\mathbf{r}) := A_f \exp(-\lambda r^\gamma) \; , \; 1 \leq \gamma \leq 2 \tag{1}$$

$$A_f \; = \; \frac{N_e \gamma \lambda^{3/\gamma}}{4\pi\Gamma(3/\gamma)} \; , \tag{2}$$

The norm follows from Ref. [4], with the usual Γ function, namely $\Gamma[N] = (N-1)!$ for $N > 0$ and integer. Although there is no strict reason to limit the density to $N_e \leq 2$, the fact that it is of s symmetry makes that limitation physical. For physical realism, we also take

$$\begin{aligned} &1 \leq \gamma \leq 2 \\ &\lambda > 0 \; . \end{aligned} \tag{3}$$

With $\gamma = 1$, $\lambda = 2N_e$, $N_e = 1$, Eq. (1) is the H atom density in the central field approximation. For $\gamma = 2$ it is pure Gaussian.

In some density functional approximations for exchange and correlation (e.g. Ref. 5) and for the so-called Pauli kinetic energy [6, 7], it is common to use the reduced (dimensionless) density gradient defined by

$$s := \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla n|}{n^{4/3}} \equiv \kappa \frac{|\nabla n|}{n^{4/3}} \; . \tag{4}$$

For the flexible density, we have

$$\frac{\partial n_f}{\partial r} := -\lambda\gamma r^{\gamma-1} n_f(r) \tag{5}$$

whence

$$s_f(r) = \lambda\kappa\gamma r^{\gamma-1} n_f^{-1/3}(r) \tag{6}$$

$$p \equiv s^2(r) = \kappa^2\lambda^2\gamma^2 r^{2(\gamma-1)} n_f^{-2/3}(r) \; , \tag{7}$$

Remark: *Beware*! This definition of p is consistent with the general DFT literature, whereas the definition of p in Ref. 1 is *not*. The same is true of q introduced next.

For DFAs containing the density Laplacian (e.g. some KEDFs, de-orbitalized meta-GGA XC DFAs) the reduced density gradient of interest is

$$q := \kappa^2 \frac{\nabla^2 n}{n^{5/3}} \ . \tag{8}$$

For the flexible density atom, the tedious detail is

$$\begin{aligned} \nabla^2 n_f(r) &= r^{-2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial n_f}{\partial r}\right] \\ &= \frac{2}{r}\left[-\lambda\gamma r^{\gamma-1} n_f(r)\right] + \frac{\partial^2 n_f}{\partial r^2} \ . \end{aligned} \tag{9}$$

The radial second derivative is

$$\frac{\partial^2 n_f}{\partial r^2} = \left[-\lambda\gamma(\gamma-1)r^{\gamma-2} + \lambda^2\gamma^2 r^{2(\gamma-1)}\right] n_f(r) \ . \tag{10}$$

Therefore

$$\nabla^2 n_f(r) = \left[(-\lambda\gamma)(\gamma+1)r^{\gamma-2} + \lambda^2\gamma^2 r^{2(\gamma-1)}\right] n_f(r) \tag{11}$$

and therefore

$$\begin{aligned} q_f(r) &= \kappa^2 \left[-\lambda\gamma(\gamma+1)r^{\gamma-2} + \lambda^2\gamma^2 r^{2(\gamma-1)}\right] n_f^{-2/3}(r) \\ &= \kappa^2 \lambda\gamma r^{\gamma-2}[\lambda\gamma r^{\gamma} - (\gamma+1)] n_f^{-2/3}(r) \ . \end{aligned} \tag{12}$$

Another reduced density derivative (again with *different* notation from that in Ref. 1) is

$$\tilde{q} := \kappa^4 \frac{\nabla n \cdot (\nabla\nabla n) \cdot \nabla n}{n^{13/3}} \ . \tag{13}$$

Evaluated for the atomic flexible density this becomes

$$\tilde{q}_f(r) = \kappa^4 \lambda^3 \gamma^3 r^{3\gamma-4}[\lambda\gamma r^{\gamma} - (\gamma-1)] n_f^{-4/3}(r) \ . \tag{14}$$

As an example of use of these forms, the von Weizsäcker potential is

$$v_W = \frac{\delta T_W}{\delta n} = \frac{\lambda\gamma}{8} r^{\gamma-2}[2(\gamma+1) - \lambda\gamma r^{\gamma}] \ . \tag{15}$$

III. ARTIFICIAL MOLECULE

For the case $N_e = 1$ for the atomic-like density, it is straightforward to construct the density for a closed shell homonuclear diatomic molecule that is the counterpart of H_2. Let the bond length be R, then

$$n_2(\mathbf{r}|\mathbf{R}) := A_f \left[\exp(-\lambda|\mathbf{r} - \mathbf{R}/2|^{\gamma}) + \exp(-\lambda|\mathbf{r} + \mathbf{R}/2|^{\gamma})\right] \ . \tag{16}$$

Obviously this density is symmetric with respect to interchange of the two centers. For practicality in doing the needed spatial derivatives, it is convenient to rewrite in Cartesian coordinates, with the bond along x:

$$n_2(\mathbf{r}|R\hat{\mathbf{e}}_1) = A_f \left\{ \exp(-\lambda[\sqrt{(x-R/2)^2 + y^2 + z^2}]^{\gamma} + \exp(-\lambda[\sqrt{(x+R/2)^2 + y^2 + z^2}]^{\gamma} \right\} \ . \tag{17}$$

$$\equiv A_f \left\{ \exp -\lambda[(x-R/2)^2 + y^2 + z^2]^{\gamma/2} + \exp -\lambda[(x+R/2)^2 + y^2 + z^2]^{\gamma/2} \right\} \ . \tag{18}$$

The unit vector along x is $\hat{\mathbf{e}}_1$.

The gradient and Laplacian of this density are needed for the dimensionless variables s and q introduced above. In principle, these can be done by hand but doing so is quite tedious.

Here are the Cartesian components of the gradient.

$$\begin{aligned}\frac{\partial n_2}{\partial x} &= -A_f\lambda\gamma\Big\{\left[(x-R/2)^2+y^2+z^2\right]^{(\gamma/2-1)}(x-R/2)\exp -\lambda[(x-R/2)^2+y^2+z^2]^{\gamma/2} \\ &\quad + \left[(x+R/2)^2+y^2+z^2\right]^{(\gamma/2-1)}(x+R/2)\exp -\lambda[(x+R/2)^2+y^2+z^2]^{\gamma/2}\Big\}\end{aligned} \tag{19}$$

$$\begin{aligned}\frac{\partial n_2}{\partial y} &= -A_f\lambda\gamma\Big\{\left[(x-R/2)^2+y^2+z^2\right]^{(\gamma/2-1)}(y)\exp -\lambda[(x-R/2)^2+y^2+z^2]^{\gamma/2} \\ &\quad + \left[(x+R/2)^2+y^2+z^2\right]^{(\gamma/2-1)}(y)\exp -\lambda[(x+R/2)^2+y^2+z^2]^{\gamma/2}\Big\}\end{aligned} \tag{20}$$

For the z component replace the one factor written (y) in Eq. (20) with (z).

Then the reduced density gradient s needs

$$|\nabla n| = \sqrt{\left(\frac{\partial n_2}{\partial x}\right)^2+\left(\frac{\partial n_2}{\partial y}\right)^2+\left(\frac{\partial n_2}{\partial z}\right)^2} \tag{21}$$

with the positive square root taken. Again, calculating that is messy but straightforward.

The same is true of the reduced Laplacian. It simply requires the second partial derivatives, $\partial^2 n/\partial x^2$ etc. i.e. the corresponding first partial derivatives of the three gradient terms.

The expressions obtained from Mathematica are as follows.

$$\begin{aligned}|\nabla n_2| = \Bigg\{\Bigg[\Bigg(&-\lambda\gamma e^{-\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda}\left(-\frac{R}{2}+x\right)\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-1+\frac{\gamma}{2}} \\ &-e^{-\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda}\left(\frac{R}{2}+x\right)\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-1+\frac{\gamma}{2}}\gamma\lambda\Bigg]^2 A_f^2 \\ &+\Bigg[-e^{-\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda}y\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-1+\frac{\gamma}{2}}\gamma\lambda \\ &-e^{-\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda}y\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-1+\frac{\gamma}{2}}\gamma\lambda\Bigg]^2 A_f^2 \\ &+\Bigg[-e^{-\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda}z\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-1+\frac{\gamma}{2}}\gamma\lambda \\ &-e^{-\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda}z\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-1+\frac{\gamma}{2}}\gamma\lambda\Bigg)^2 A_f^2\Bigg]\Bigg\}^{1/2}\end{aligned} \tag{22}$$

$$
\begin{aligned}
\nabla^2 n_f = A_f \Bigg[& -\exp^{-\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} \left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-1+\frac{\gamma}{2}} \gamma\lambda \\
& -\exp^{-\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} \left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-1+\frac{\gamma}{2}} \gamma\lambda \\
& -2\exp^{-\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} \left(-\frac{R}{2}+x\right)^2 \left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-2+\frac{\gamma}{2}} \left(-1+\frac{\gamma}{2}\right)\gamma\lambda \\
& -2\exp^{-\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} \left(\frac{R}{2}+x\right)^2 \left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-2+\frac{\gamma}{2}} \left(-1+\frac{\gamma}{2}\right)\gamma\lambda \\
& +\exp^{-\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} \left(-\frac{R}{2}+x\right)^2 \left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-2+\gamma} \gamma^2\lambda^2 \\
& +\exp^{-\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} \left(\frac{R}{2}+x\right)^2 \left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-2+\gamma} \gamma^2\lambda^2 \Bigg] \\
+A_f \Bigg[& -\exp^{-\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} \left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-1+\frac{\gamma}{2}} \gamma\lambda \\
& -\exp^{-\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} \left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-1+\frac{\gamma}{2}} \gamma\lambda \\
& -2\exp^{-\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} y^2 \left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-2+\frac{\gamma}{2}} \left(-1+\frac{\gamma}{2}\right)\gamma\lambda \\
& -2\exp^{-\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} y^2 \left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-2+\frac{\gamma}{2}} \left(-1+\frac{\gamma}{2}\right)\gamma\lambda \\
& +\exp^{-\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} y^2 \left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-2+\gamma} \gamma^2\lambda^2 \\
& +\exp^{-\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} y^2 \left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-2+\gamma} \gamma^2\lambda^2 \Bigg] \\
+A_f \Bigg[& -\exp^{-\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} \left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-1+\frac{\gamma}{2}} \gamma\lambda \\
& -\exp^{-\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} \left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-1+\frac{\gamma}{2}} \gamma\lambda \\
& -2\exp^{-\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} z^2 \left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-2+\frac{\gamma}{2}} \left(-1+\frac{\gamma}{2}\right)\gamma\lambda \\
& -2\exp^{-\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} z^2 \left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-2+\frac{\gamma}{2}} \left(-1+\frac{\gamma}{2}\right)\gamma\lambda \\
& +\exp^{-\left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} z^2 \left(\left(-\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-2+\gamma} \gamma^2\lambda^2 \\
& +\exp^{-\left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{\gamma/2}\lambda} z^2 \left(\left(\frac{R}{2}+x\right)^2+y^2+z^2\right)^{-2+\gamma} \gamma^2\lambda^2 \Bigg] .
\end{aligned}
\tag{23}
$$

Remarks: (i) Obviously we haven't simplified the Mathematica expressions!

(ii) This little exercise is a reminder of why Slater-type orbitals (essentially $\gamma = 1$) never have seen widespread use as molecular basis functions. It is tedious enough to work with $\gamma = 2$ (especially for integrals, which haven't been mentioned here) but almost prohibitively difficult for $\gamma = 1$.

We give one example of the artificial H_2. One flexible density each was placed at $-R/2$ and at $R/2$, with $R = 1.4036$ au, which is the equilibrium H_2 molecular bond length. $N_e = 1$ was used for each atomic flexible density, thus $N_{e,total} = 2$. Fig. 1 shows the molecular density plotted along the bond axis for the cases $\gamma = 1$ and $\gamma = 2$.

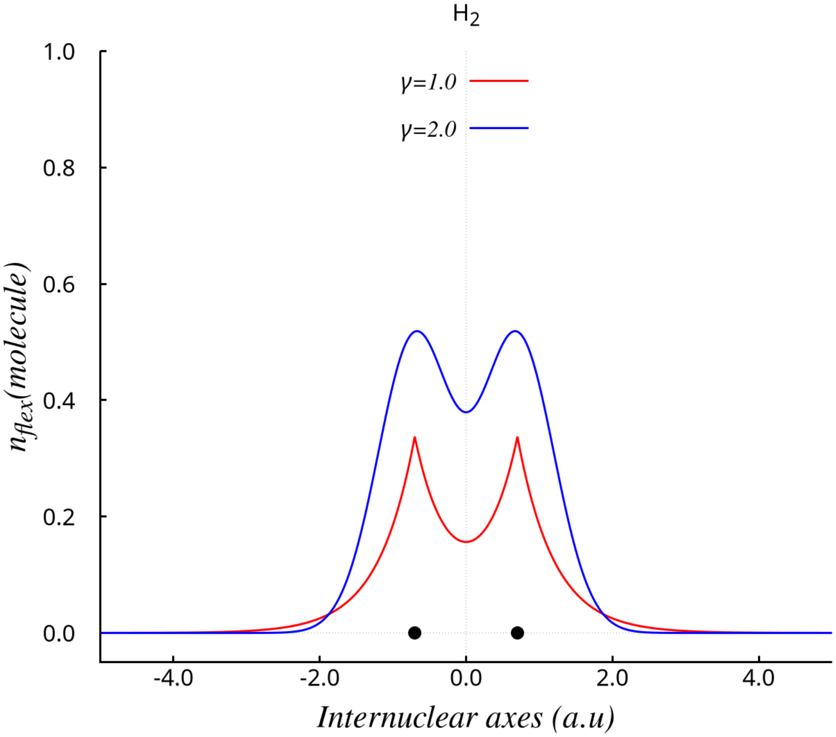

FIG. 1. Density of the artificial H_2 molecule for two cases $\gamma = 1$ and $\gamma = 2$. The dots on the axis indicate the nuclear sites. This plot is representative of a bond in an artificial molecule.

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