Nuclear Site Singularity in the Functional Derivative of the von Weizsäcker KE

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The functional derivative of the von Weizsäcker KE has a singularity at the nuclear site for an atomic density consistent with the Kato cusp condition.

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In our (Karasiev, Jones, Trickey, and Harris) orbital-free KE paper [1], we mention the nuclear-site singularity in the potential v_W which is the functional derivative of the von Weizsäcker KE [2]

$$T_W[n] = \frac{1}{8}\int d\mathbf{r}\frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})} \equiv \int d\mathbf{r} t_W[n(\mathbf{r})]\,. \tag{1}$$

The singularity is made evident by use of a model atomic density which obeys the Kato cusp condition [3–6] near the nucleus,

$$n_H(\mathbf{r}) = C_H \exp(-2Z|\mathbf{r}|)\ . \tag{2}$$

or, alternatively,

$$n_K(\mathbf{r}) = C_K(1 - 2Z|\mathbf{r}| + \ldots)\ . \tag{3}$$

The forms in Eq. (3) and (2) are the same as Eqs. (27) and (26) respectively of Ref. [1]. Unfortunately, the sign we give in Eq. (32) of Ref. [1] is wrong. Though of less consequence, the coefficient is wrong too. The proper values are obtained here.

From the definition above

$$\begin{aligned} v_W &= \frac{\delta T_W}{\delta n} = \frac{\partial t_W}{\partial n} - \nabla\cdot\frac{\partial t_W}{\partial \nabla n} \\ &= -\frac{1}{8}\left(\frac{2\nabla^2 n}{n} - \frac{|\nabla n|^2}{n^2}\right) \end{aligned} \tag{4}$$

For a density of the form (2), we have

$$\frac{|\nabla n_H|^2}{n_H^2} = 4Z^2 \tag{5}$$

and

$$\begin{aligned} \nabla^2 n_H &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial n_H}{\partial r}\right) \\ &= \frac{n_H}{r}\left(-4Zr + Z^2r^2\right) \\ \Rightarrow \frac{\nabla^2 n_H}{n_H} &= -\frac{4Z}{r} + 4Z^2 \end{aligned} \tag{6}$$

Insertion of these results in Eq. (4) gives

$$v_{wH} = \frac{Z}{r} - \frac{Z^2}{2}\ . \tag{7}$$

Similarly, for a density of the form (3), we have

$$\frac{|\nabla n_K|^2}{n_K^2} = \frac{4Z^2}{(1-2Zr)^2} \tag{8}$$

and

$$\begin{aligned} \nabla^2 n_K &= -\frac{4ZA}{r} \\ \Rightarrow \frac{\nabla^2 n_K}{n_K} &= -\frac{4Z}{r(1-2Zr)} \end{aligned} \tag{9}$$

Insertion of these results in Eq. (4) gives

$$v_{wK} = \frac{1}{8}\left[\frac{8Z}{r(1-2Zr)} + \frac{4Z^2}{(1-2Zr)^2}\right] \tag{10}$$

As $r \to 0$ this becomes

$$v_{wK} = \frac{Z}{r} + \frac{5}{2}Z^2 + \ldots\ . \tag{11}$$

Unsurprisingly, this is the same behavior as already found.

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