

Comment on "Quantum-Mechanical Interpretation of the Exchange-Correlation Potential of Kohn-Sham Density-Functional Theory"

In a recent Letter, Harbola and Sahni¹ (HS) have suggested a procedure for constructing the exchange-correlation potential [which HS call $W_{xc}(\mathbf{r})$] that enters the Kohn-Sham single-particle equations. $W_{xc}(\mathbf{r})$ is given by HS as a path integral [Eq. (5) of HS] of an

$$\rho_x(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \{ f_1(r)^2 f_1(r')^2 + f_2(r)^2 f_2(r')^2 + z^2 f_3(r)^2 f_3(r')^2 z'^2 + 2zz' f_3(r) f_3(r') [f_1(r) f_1(r') + f_2(r) f_2(r')] + 2f_1(r) f_1(r') f_2(r) f_2(r') \} / [2f_1(r)^2 + 2f_2(r)^2 + z^2 f_3(r)^2], \quad (2)$$

where $f_1(r)$ and $f_2(r)$ are the (radial) 1S and 2S wave functions, respectively, and $f_3(r)$ is the radial part of the single 2P wave function. [Of course, the choice of the specific 2P orbital, $z f_3(r)$, is ensured in the usual way by a term of nonspherical symmetry and of magnitude much smaller than all other energy scales of interest. Therefore, the electron density is not spherically symmetrical at the outset and must remain so.] From Eqs. (1) and (2), the components of $\mathcal{E}_x(\mathbf{r})$ and its curl can be explicitly evaluated. For simplicity, first consider large r . The dominant contributions to $\nabla \times \mathcal{E}_x(\mathbf{r})$ in this region of the atom can be isolated. The x component, for example, is given by

$$[\nabla \times \mathcal{E}_x(\mathbf{r})]_x \simeq - \left(\frac{y}{2zr^4} \right) \left(\frac{d}{dr} \frac{f_2(r)}{f_3(r)} \right) \times \int d^3 r' z'^2 f_2(r') f_3(r'), \quad (3)$$

which is not zero. Similar calculations can be made for other regions of the atom. For example, for arbitrary finite x and small y and z , we find $[\nabla \times \mathcal{E}_x(\mathbf{r})]_x = C(x)yz$, where $C(x)$ is again given by a nonzero integral over the wave functions. Of course, these conclusions are an immediate consequence of the fact that

"electric field" $\mathcal{E}_{xc}(\mathbf{r})$ [Eq. (4) of HS], i.e.,

$$\mathcal{E}_{xc}(\mathbf{r}) = \int d^3 r' \rho_{xc}(\mathbf{r}, \mathbf{r}') (\mathbf{r} - \mathbf{r}') / |\mathbf{r} - \mathbf{r}'|^3. \quad (1)$$

However, an inspection of $\mathcal{E}_{xc}(\mathbf{r})$ shows that its curl cannot vanish in general; consequently, $W_{xc}(\mathbf{r})$ depends on the path of integration and has absolutely no meaning as a fundamental potential.

We can see this with an explicit example of a five-electron atom.² The $\rho_{xc}(\mathbf{r}, \mathbf{r}')$ in Eq. (1), in exchange alone, is

$\mathcal{E}_{xc}(\mathbf{r})$ in Eq. (1) cannot, *in general*, be written as the gradient of a scalar function.

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