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Comment on ''Cusp relations for local strongly decaying properties in electronic systems''

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In a recent paper [Phys. Rev. A **52**, 2645 (1995)], Liu *et al.* presented an approach for obtaining physical properties at the nuclear cusps. They compared it with the Hiller-Sucher-Feinberg (HSF) identity [Phys. Rev. A **18**, 2399 (1978)] and found theirs to be superior. It is shown here that this conclusion is based on the comparison on equal footing of different types of identities, namely physical in the case of HSF and mathematical in the case of Liu *et al.*

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Four new expressions have recently been derived [1] which link local properties to their gradients and Laplacians over the whole space

$$F(0) = -\frac{1}{4\pi}\int \frac{\nabla^2 F(\vec{r})}{r}\, d\vec{r}, \tag{1}$$

$$= -\frac{1}{4\pi}\int \frac{\vec{r}\cdot\vec{\nabla}F(\vec{r})}{r^3}\, d\vec{r}, \tag{2}$$

$$= -\frac{1}{4\pi}\int \frac{\exp(-\alpha r)\nabla^2 F(\vec{r})}{r}\, d\vec{r} + \frac{1}{4\pi}\int \frac{\alpha^2 \exp(-\alpha r) F(\vec{r})}{r}\, d\vec{r}, \tag{3}$$

$$= -\frac{1}{4\pi}\int \frac{\exp(-\beta r)\vec{r}\cdot\vec{\nabla}F(\vec{r})}{r^3}\, d\vec{r} + \frac{1}{4\pi}\int \frac{\beta \exp(-\beta r) F(\vec{r})}{r^2}\, d\vec{r}. \tag{4}$$

Liu, Parr, and Nagy (LPN) obtained these relations by invoking Green's theorem and the fast decaying properties of electron charge densities and exchange and correlation potentials. Since there are no other assumptions used in their derivation, these relations are mathematical identities for those physical quantities. On the other hand, the Hiller-Sucher-Feinberg identity [2] (HSF) for the electron charge density at a nucleus

$$\rho(0) = \langle \Psi | \delta(r) | \Psi \rangle \tag{5}$$

$$= \frac{1}{2\pi}\langle \Psi | \frac{\partial v}{\partial r} - \frac{1}{r^3}\hat{x}\mathbf{L}_1^2 | \Psi \rangle \tag{6}$$

was obtained with the assumption that the exact wave function (Ψ) is used. Therefore, for approximate wave functions, Eq. (5) (direct) and Eq. (6) (HSF) do not necessarily yield the same value. Since the global HSF one is expected to be closer to the exact value, one may use it to get a better estimate of local properties than from the traditional direct approach. Note that the HSF identity cannot guarantee such an improvement either. In molecules, for instance, it improves the density at nonhydrogen nuclei greatly, while overestimating the one on hydrogenic centers [3].

LPN used their relations to calculate $\rho(0)$ and $\rho'(0)$ for He to Ar with the Clementi and Roetti (SCF) wave functions [4]. For heavier elements, minute differences among the results are obtained. The authors did not explain the reasons for the latter. In fact, the differences are due to numerical errors in their calculations. Since the four relations used are mathematical identities, they should, in theory, produce identical results for the same wave function. We calculated the same quantities directly and found agreement of better than four decimals with the numerical values employing Eqs. (1)–(4). We believe that the differences for $v_x(0)$ and $v_{xc}(0)$ presented in Ref. [1] are also due to the round-off errors in the numerical integration.

LPN compared their results for $\rho(0)$ and $\rho'(0)$ with the values reported by Porras and Galvez [5,6], which they label ''exact.'' We want to emphasize that these values are just the directly calculated $\rho(0)$ and $\rho'(0)$ from the Clementi-Roetti SCF wave functions. The comparison, therefore, only reflects the limited numerical accuracy of the integration scheme, and cannot be used to infer any superiority of the four formulas (1)–(4) above.

LPN also compared their results with those from the HSF relation and drew the conclusion that their new expressions are superior to the HSF identity. However, the wave functions used by Cioslowski and Challacombe [7] were obtained with a standard unpolarized Gaussian-type orbital basis set, and are of much poorer quality compared to those of Clementi and Roetti from Slater-type orbitals, particularly at the nucleus. The quality difference between the GTO-HSF results and the STO-LPN ones does *not* reflect on the underlying integral formulas, but rather on the basis set.

Furthermore, the new relations presented by LPN cannot be used to improve local properties. They would generate the same results (if there were no significant numerical noise) as the directly calculated ones. The HSF relation, on the other hand, works differently. Take $\rho'(0)$ of Ne as an example. The directly calculated GTO value [7] is 0 with the Gaussian basis sets. The corresponding HSF result is −11 629 a.u., much closer to the (better) Clementi-Roetti value of −12 425 a.u. This improvement is very significant. If we were to apply any one of the four relations in Ref. [1] [Eqs. (1)–(4) above] to the density used in Ref. [7], we would get

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the same values of $\rho'(0)$, still zero. In short, the value of the HSF identity lies in its power to *improve* local values even for mediocre wave functions, a feature that is completely absent in the mathematical identities presented by LPN.

Of course, we will not rule out possible applications of the new relations in other circumstances in order to obtain unavailable local properties. From a pragmatic point of view, they might improve the numerics of the computation of the latter. However, one cannot expect to use them in the same manner as the HSF relation for finding improved local properties such as $\rho(0)$ and $\rho'(0)$. They can at best produce the same value as the directly calculated ones.

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