Path dependence of the Harbola-Sahni exchange potential

Hui Ou-Yang and Mel Levy
Department of Chemistry and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118
(Received 24 May 1989)

It is shown that the Harbola-Sahni exchange potential w_x is not generally independent of path for nonspherical densities. Requirements for corrections to w_x are put forth.

Consider N interacting electrons in a local-multiplicative spin-independent external potential $v(\mathbf{r})$. The Hamiltonian is

$$\hat{\mathbf{H}}=\sum_{i=1}^{N}-\tfrac{1}{2}\nabla_i^2+\sum_{i=1}^{N}v(\mathbf{r}_i)+\sum_{i<j}^{N}|\mathbf{r}_i-\mathbf{r}_j|^{-1} . \tag{1}$$

According to the Hohenberg-Kohn-Sham theory,[1] the exact ground-state energy may be obtained from

$$E=\min_{\rho}\left[T_s[\rho]+\int v(\mathbf{r})\rho(\mathbf{r})d^3r+\tfrac{1}{2}\int\int\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)|\mathbf{r}_1-\mathbf{r}_2|^{-1}d^3r_1d^3r_2+E_x[\rho]+E_c[\rho]\right] , \tag{2}$$

where $T_s[\rho]$ is the noninteracting kinetic energy, and where $E_x[\rho]$ and $E_c[\rho]$ are the exchange and correlation energies, respectively. The minimizing density $\rho_{\text{g.s.}}$ in Eq. (2) satisfies the Kohn-Sham equations[1] for noninteracting fermions:

$$\left[-\tfrac{1}{2}\nabla^2+v(\mathbf{r})+\int\rho(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-1}d^3r'+v_x([\rho];\mathbf{r})+v_c([\rho];\mathbf{r})\right]\phi_i(\mathbf{r})=\epsilon_i\phi_i(\mathbf{r}) , \tag{3}$$

where

$$v_x([\rho];\mathbf{r})=\frac{\delta E_x[\rho]}{\delta\rho(\mathbf{r})} ,$$

$$v_c([\rho];\mathbf{r})=\frac{\delta E_c[\rho]}{\delta\rho(\mathbf{r})}$$

are, respectively, the exchange and correlation potentials.

Harbola and Sahni[2] have proposed an orbital-generated local exchange potential $w_x(\mathbf{r})$, as an approximation to $v_x([\rho];\mathbf{r})$, and they also provide an interpretation for their potential; it is the work done in bringing an electron from ∞ to $\mathbf{r}$ against the force of an $\boldsymbol{\varepsilon}_x(\mathbf{r})$ electric field. They define $w_x(\mathbf{r})$ as a line integral

$$\mathbf{w}_x(\mathbf{r})=-\int_{\infty}^{\mathbf{r}}\boldsymbol{\varepsilon}_x(\mathbf{r})\cdot d\mathbf{r} , \tag{4}$$

where

$$\boldsymbol{\varepsilon}_x(\mathbf{r})=\int\frac{\rho_x(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d^3r' . \tag{5}$$

The Harbola-Sahni potential has yielded exciting conceptual and numerical results[2-4] for spherical densities and for jellium metal surfaces, and their novel ideas have attracted interest. In fact, Wang *et al.*[5] have recently proved that w_x is exact in the uniform gas limit, and for closed-subshell atoms w_x yields encouraging total energies[3] and highest-occupied orbital energies that are far superior[3] to those given by the local-density approximation.

The exact exchange potential $v_x([\rho];\mathbf{r})$ satisfies the Levy-Perdew[6] relation

$$\langle\Phi[\rho]|\hat{\mathbf{V}}_{ee}|\Phi[\rho]\rangle-U[\rho]=-\int\rho(\mathbf{r})\mathbf{r}\cdot\nabla v_x([\rho];\mathbf{r})d^3r , \tag{6}$$

where for arbitrary ρ, $\Phi[\rho]$ is that single determinant which is composed of the N lowest-occupied orbitals of a local potential and $U[\rho]$ is the classical electron-electron repulsion energy [the third term in Eq. (2)]. Harbola and Sahni have shown that $w_x(\mathbf{r})$ satisfies the Levy-Perdew relation by assuming that

$$\nabla w_x(\mathbf{r})=\boldsymbol{\varepsilon}_x(\mathbf{r}) . \tag{7}$$

This assumption is crucial to their proof and their interpretation of $w_x(\mathbf{r})$.

A necessary and sufficient condition that the line integral in Eq. (4) is independent of path, which guarantees the validity of Eq. (7), is

$$\text{curl}\boldsymbol{\varepsilon}_x(\mathbf{r})\equiv\nabla\times\boldsymbol{\epsilon}_x(\mathbf{r})=\mathbf{0} . \tag{8}$$

Conversely, if the curl of $\boldsymbol{\varepsilon}_x(\mathbf{r})$ is not equal to zero, then (i) the line integral of $w_x(\mathbf{r})$ depends upon path, which implies that $w_x(\mathbf{r})$ cannot be interpreted as work, which must be independent of path, and (ii) Eq. (7) does not hold, and the proof in Ref. 2 is not valid in this situation. [From the development in Ref. 2, it should be clear, however, that w_x always satisfies Eq. (6) for one-dimensional problems.]

Motivated by the above issues, it shall be shown that $\nabla\times\boldsymbol{\varepsilon}_x(\mathbf{r})\neq\mathbf{0}$ for a Kohn-Sham ground-state determinant which yields a *nonspherical* density, but it is noted that w_x is the exact Kohn-Sham exchange potential for one and two electrons, even if the density is nonspherical, so path dependence is obviously no problem for one and two electrons.

To give an example where $\nabla\times\boldsymbol{\varepsilon}_x(\mathbf{r})\neq\mathbf{0}$ for a nonspherical $\rho(\mathbf{r})$, consider a four-electron Kohn-Sham ground state $1s(\uparrow,\downarrow)2p_z(\uparrow,\downarrow)$ where

$$\psi_1=\psi_{1s}=\frac{1}{\pi^{1/2}}z^{3/2}e^{-zr} ,$$

$$\psi_2=\psi_{2p_z}=\frac{1}{4(2\pi)^{1/2}}z^{5/2}e^{-zr/2}r\cos\theta , \tag{9}$$

$$\rho(\mathbf{r})=2\sum_{i=1}^{2}|\psi_i|^2=2\frac{z^3}{\pi}e^{-zr}\left[e^{-zr}+\frac{z^2}{32}r^2\cos^2\theta\right], \quad (10)$$

$$\gamma(\mathbf{r},\mathbf{r}')=2\sum_{i=1}^{2}\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}')$$
$$=2\frac{z^3}{\pi}e^{-z(r+r')/2}\times\left[e^{-z(r+r')/2}+\frac{z^2}{32}rr'\cos\theta\cos\theta'\right], \quad (11)$$

$$\rho_x(\mathbf{r},\mathbf{r}')=\frac{|\gamma(\mathbf{r},\mathbf{r}')|^2}{2\rho(\mathbf{r})}=\frac{z^3}{\pi}e^{-zr'}\frac{\left[e^{-z(r+r')/2}+\frac{z^2}{32}rr'\cos\theta\cos\theta'\right]^2}{\left[e^{-zr}+\frac{z^2}{32}r^2\cos^2\theta\right]}. \quad (12)$$

The curl of $\boldsymbol{\varepsilon}_x(\mathbf{r})$ is

$$\nabla\times\boldsymbol{\epsilon}_x(\mathbf{r})=\nabla\times\int d^3r'\frac{(\mathbf{r}-\mathbf{r}')\rho_x(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}=\nabla\times\int d^3r'\frac{1}{|\mathbf{r}-\mathbf{r}'|}\nabla\rho_x(\mathbf{r},\mathbf{r}'). \quad (13)$$

[Note that $-zr^{-1}$ is the noninteracting Kohn-Sham effective potential for which the density given by Eq. (10) is a ground-state density. This density is simultaneously a ground-state density of some interacting Hamiltonian with a non-Coulomb potential.]

We assign $[\nabla\times\boldsymbol{\epsilon}_x(\mathbf{r})]_{\hat{\mathbf{r}}}$, $[\nabla\times\boldsymbol{\epsilon}_x(\mathbf{r})]_{\hat{\theta}}$, and $[\nabla\times\boldsymbol{\epsilon}_x(\mathbf{r})]_{\hat{\phi}}$ to represent three components of $\nabla\times\boldsymbol{\epsilon}_x(\mathbf{r})$. For this particular case $\rho_x(\mathbf{r},\mathbf{r}')$ does not depend upon ϕ and ϕ', and it is readily obtained that $[\nabla\times\boldsymbol{\epsilon}_x(\mathbf{r})]_{\hat{\mathbf{r}}}=[\nabla\times\boldsymbol{\epsilon}_x(\mathbf{r})]_{\hat{\theta}}=0$. Equation (13) becomes

$$\nabla\times\boldsymbol{\varepsilon}_x(\mathbf{r})=\hat{\boldsymbol{\phi}}\frac{1}{r}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{-4\pi}{2l+1}\left[\left[\frac{\partial}{\partial r}\int_0^\infty\frac{r_<^l}{r_>^{l+1}}r'^2dr'\right]Y_{lm}(\theta,\phi)\frac{\partial}{\partial\theta}\int d\Omega'\rho_x(\mathbf{r},\mathbf{r}')Y_{lm}^*(\theta',\phi')\right.$$
$$\left.-\int_0^\infty\frac{r_<^l}{r_>^{l+1}}r'^2dr'\left[\frac{\partial}{\partial\theta}Y_{lm}(\theta,\phi)\right]\frac{\partial}{\partial r}\int d\Omega'\rho_x(\mathbf{r},\mathbf{r}')Y_{lm}^*(\theta';\phi')\right]. \quad (14)$$

In order to calculate $[\nabla\times\boldsymbol{\varepsilon}_x(\mathbf{r})]$, we first deal with the integral $\int d\Omega'\rho_x(\mathbf{r},\mathbf{r}')Y_{lm}^*(\theta',\phi')$:

$$\int d\Omega'\rho_x(\mathbf{r},\mathbf{r}')Y_{lm}^*(\theta',\phi')=\frac{z^3}{\pi}\frac{e^{-zr'}}{\left[e^{-zr}+\frac{z^2}{32}r^2\cos^2\theta\right]}\int d\Omega'\left[e^{-z(r+r')/2}+\frac{z^2}{32}rr'\cos\theta\cos\theta'\right]^2Y_{lm}^*(\theta',\phi')$$
$$=\frac{z^3}{\pi}\frac{e^{-zr'}}{\left[e^{-zr}+\frac{z^2}{32}r^2\cos^2\theta\right]}\left\{\sqrt{4\pi}e^{-z(r+r')}\delta_{l0}\delta_{m0}+\frac{z^2}{16}(\cos\theta)rr'e^{-z(r+r')/2}\left[\frac{4\pi}{3}\right]^{1/2}\delta_{l1}\delta_{m0}\right.$$
$$\left.+\left[\frac{z^2}{32}\right]^2r^2r'^2(\cos^2\theta)\left[\frac{2}{3}\left[\frac{4\pi}{5}\right]^{1/2}\delta_{l2}\delta_{m0}+\tfrac{1}{3}\sqrt{4\pi}\delta_{l0}\delta_{m0}\right]\right\}. \quad (15)$$

The first term in Eq. (14) then becomes

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{-4\pi}{2l+1}\left[\left[\frac{\partial}{\partial r}\int_0^\infty\frac{r_<^l}{r_>^{l+1}}r'^2dr'\right]Y_{lm}(\theta,\phi)\frac{\partial}{\partial\theta}\int d\Omega'\rho_x(\mathbf{r},\mathbf{r}')Y_{lm}^*(\theta',\phi')\right]$$
$$=-4z^3e^{-zr}\left[\frac{\partial}{\partial r}\int_0^\infty\frac{r'^2}{r_>}e^{-2zr'}dr'\right]\frac{\partial}{\partial\theta}\left[\frac{1}{e^{-zr}+\frac{z^2}{32}r^2\cos^2\theta}\right]$$
$$-\frac{4}{3}\frac{z^5}{16}re^{-zr/2}\cos\theta\left[\frac{\partial}{\partial r}\int_0^\infty\frac{r_<}{r_>^2}r'^3e^{-(3/2)zr'}dr'\right]\frac{\partial}{\partial\theta}\left[\frac{\cos\theta}{e^{-zr}+\frac{z^2}{32}r^2\cos^2\theta}\right]$$
$$-\left[\frac{4}{5}z^3\left[\frac{z^2}{32}\right]^2r^2(\cos^2\theta-\tfrac{1}{3})\left[\frac{\partial}{\partial r}\int_0^\infty\frac{r_<^2}{r_>^3}r'^4e^{-zr'}dr'\right]\right.$$

$$-\frac{4}{3}z^3\left[\frac{z^2}{32}\right]^3\left[\frac{\partial}{\partial r}\int_0^\infty \frac{r'^4}{r_>}e^{-zr'}dr'\right]\Bigg]\frac{\partial}{\partial\theta}\left[\frac{\cos^2\theta}{e^{-zr}+\frac{z^2}{32}r^2\cos\theta}\right]$$

$$=\frac{2(\frac{2}{3})^5\sin(2\theta)e^{-zr/2}[e^{-zr}-(z^2r^2/32)\cos^2\theta]}{r^2\left[e^{-zr}+\frac{z^2r^2}{32}\cos^2\theta\right]^2}+(\text{nonzero terms})\ . \tag{16}$$

To calculate the second term in Eq. (14), we start with

$$\frac{\partial}{\partial\theta}Y_{lm}(\theta,\phi)\frac{\partial}{\partial r}\int d\Omega'\rho_x(\mathbf{r},\mathbf{r}')Y^*_{lm}(\theta'\phi')=-\sin\theta\frac{\partial}{\partial r}\left[\frac{z^3}{\pi}\left[\frac{(\cos\theta)e^{-zr'}}{\left[e^{-zr}+\frac{z^2}{32}r^2\cos^2\theta\right]}\right]\frac{z^2}{16}rr'e^{-z(r+r')/2}\right]\delta_{l1}\delta_{m0}$$

$$-\frac{z^3}{\pi}\left[\frac{z^2}{32}\right]^2\sin(2\theta)\frac{\partial}{\partial r}\left[\frac{r^2r'^2(\cos^2\theta)e^{-zr'}}{\left[e^{-zr}+\frac{z^2}{32}r^2\cos^2\theta\right]}\right]\delta_{l2}\delta_{m0}\ , \tag{17}$$

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{2l+1}\int_0^\infty\frac{r_<^l}{r_>^{l+1}}r'^2dr'\left[\frac{\partial}{\partial\theta}Y_{lm}(\theta,\phi)\right]\frac{\partial}{\partial r}\int d\Omega'\rho_x(\mathbf{r},\mathbf{r}')Y^*_{lm}(\theta',\phi')$$

$$=-\frac{4\pi}{3}\int_0^\infty\frac{r_<}{r_>^2}r'^2dr'\sin\theta\frac{\partial}{\partial r}\left[\frac{z^3}{\pi}\frac{(\cos\theta)e^{-zr'}}{\left[e^{-zr}+\frac{z^2}{32}r^2\cos^2\theta\right]}\left[\frac{z^2}{16}rr'e^{-z(r+r')/2}\right]\right]$$

$$+\frac{4\pi}{5}\left[\frac{z^3}{\pi}\right]\left[\frac{z^2}{32}\right]^2\int_0^\infty\frac{r_<^2}{r_>^3}r'^2dr'\sin(2\theta)\frac{\partial}{\partial r}\left[\frac{e^{-zr'}r^2r'^2\cos^2\theta}{e^{-zr}+\frac{z^2}{32}r^2\cos^2\theta}\right]$$

$$=\left[\frac{z^5}{24}\right]\frac{\sin(2\theta)\left[1+\frac{zr}{2}\right]e^{-zr/2}}{\left[e^{-zr}+\frac{z^2}{32}r^2\cos^2\theta\right]^2}\left[e^{-zr}-\frac{z^2r^2}{32}\cos^2\theta\right]\int_0^\infty\frac{r_<}{r_>^2}r'^3e^{-3zr'/2}dr'$$

$$+\frac{4}{5}\frac{z^3\left[\frac{z^2}{32}\right]^2\sin(2\theta)(\cos^2\theta)e^{-zr}}{\left[e^{-zr}+\frac{z^2}{32}r^2\cos^2\theta\right]^2}(zr^2+2r)\int_0^\infty\frac{r_<^2}{r_>^3}r'^4e^{-zr'}dr'$$

$$=\left[\frac{2}{3}\right]^5\frac{\sin(2\theta)\left[1+\frac{zr}{2}\right]e^{-zr/2}\left[e^{-zr}-\left[\frac{z^2r^2}{32}\right]\cos^2\theta\right]}{r^2\left[e^{-zr}+\frac{z^2r^2}{32}\cos^2\theta\right]^2}+(\text{nonzero terms})\ . \tag{18}$$

Subtraction of Eq. (18) [its rhs denoted by $\mathcal{R}(18)$] from Eq. (16) [denoted by $\mathcal{R}(16)$] yields the curl of $\boldsymbol{\varepsilon}_x(\mathbf{r})$:

$$\nabla\times\boldsymbol{\varepsilon}_x(\mathbf{r})=\frac{1}{r}[\mathcal{R}(16)-\mathcal{R}(18)]\hat{\boldsymbol{\phi}}=\left[\frac{2}{3}\right]^5\frac{\sin(2\theta)e^{-zr/2}\left[e^{-zr}-\frac{z^2r^2}{32}\cos^2\theta\right]}{r^3\left[e^{-zr}+\frac{z^2r^2}{32}\cos^2\theta\right]^2}\left[1-\frac{zr}{2}\right]\hat{\boldsymbol{\phi}}+(\text{nonzero terms})\ . \tag{19}$$

Note that the first term in Eq. (19) cannot be canceled out by any other terms and we therefore arrive at

$$\nabla\times\boldsymbol{\varepsilon}_x(\mathbf{r})\neq\mathbf{0}\ . \tag{20}$$

This simple example illustrates a case where $\nabla w_x(\mathbf{r})\neq\boldsymbol{\varepsilon}_x(\mathbf{r})$ for a nonspherical density, and thus $w_x(\mathbf{r})$ and its interpretation should be reexamined and modified for nonspherical densities.

Requirements for a modified Harbola-Sahni potential $w_x'(\mathbf{r})$ are now asserted:

$$w_x'(\mathbf{r})=-\int_{\infty}^{\mathbf{r}}[\boldsymbol{\varepsilon}_x(\mathbf{r})+\mathbf{Y}(\mathbf{r})]\cdot\mathbf{d}\ , \tag{21}$$

where

$$\nabla\times[\boldsymbol{\varepsilon}_x(\mathbf{r})+\mathbf{Y}(\mathbf{r})]=0\ . \tag{22}$$

It is obvious, from Eqs. (8)–(10) of Harbola and Sahni,[2] that $w_x'(\mathbf{r})$ satisfies the Levy-Perdew relation if $Y(\mathbf{r})$ satisfies

$$\int\rho(\mathbf{r})\mathbf{r}\cdot\mathbf{Y}(\mathbf{r})d^3r=0\ . \tag{23}$$

Along with other constraints on $\mathbf{Y}(\mathbf{r})$, the solution to Eqs. (22) and (23) yields $\mathbf{Y}(\mathbf{r})$, from which one can calculate $w_x'(\mathbf{r})$.

It is obvious from Ref. 2 that for one and two particles, $w_x(\mathbf{r})$ is the exact Kohn-Sham exchange potential v_x. This arises from the fact that w_x is v_x for a system with N particles occupying just one orbital, as implied in Ref. 2. If N particles are in the same orbital, the exchange hole takes on a very simple form,

$$\rho_x(\mathbf{r}'\mathbf{r}'')=-\frac{N}{2}\rho(\mathbf{r}'')\ . \tag{24}$$

Then $\boldsymbol{\varepsilon}_x(\mathbf{r}')$ becomes

$$\epsilon_x(\mathbf{r}')=-\frac{N}{2}\int\frac{\rho(\mathbf{r}'')(\mathbf{r}'-\mathbf{r}'')}{|\mathbf{r}'-\mathbf{r}''|^3}d^3r'' \tag{25}$$

or

$$\epsilon_x(\mathbf{r}')=\frac{N}{2}\nabla_{r'}\int\frac{\rho(\mathbf{r}'')}{|\mathbf{r}'-\mathbf{r}''|}d^3r''\ , \tag{26}$$

from which we can readily remove the path integral from $w_x(\mathbf{r})$:

$$\mathbf{w}_x(\mathbf{r})=-\int_{\infty}^{\mathbf{r}}\boldsymbol{\varepsilon}_x(\mathbf{r}')\cdot\mathbf{d}'=-\frac{N}{2}\int\frac{\rho(r')}{|\mathbf{r}-\mathbf{r}'|}d^3r'\ . \tag{27}$$

$$-\frac{N}{4}\int\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3rd^3r'$$

for the system in which only one orbital is occupied.

Li and Krieger,[7] Perdew,[8] and Harbola and Sahni,[9] have independently already shown that in a closed atomic subshell system $\nabla\times\boldsymbol{\varepsilon}_x(\mathbf{r})=\mathbf{0}$, so that it is important to note that Eqs. (6) and (7) are satisfied in these systems. Here we would like to provide a simple proof that the curl of $\boldsymbol{\varepsilon}_x(\mathbf{r})$ is zero when $\rho(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r},\mathbf{r}')$. In this case Eq. (13) is simplified as follows:

$$\nabla\times\epsilon_x(\mathbf{r})=\nabla\times\hat{\mathbf{r}}\int d^3r'\frac{1}{|\mathbf{r}-\mathbf{r}'|}\frac{\partial}{\partial r}\rho_x(r,r')$$

$$=\nabla\times\hat{\mathbf{r}}\left|-4\pi\int_0^{\infty}\frac{r'^2}{r_>}\frac{\partial}{\partial r}\rho_x(r,r')dr'\right|=0\ ,$$

which ensures that the assumption and the proof in Ref. 2 is valid for this particular case.

It is a pleasure to acknowledge our colleague at Tulane University J. P. Perdew for sharing with us his unpublished results and for his valuable and patient discussions, suggestions, and encouragement. It is a pleasure to acknowledge M. K. Harbola, J. B. Krieger, Y. Li, and V. Sahni at Brooklyn College for valuable discussions and for sharing with us their unpublished results.

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[2] M. K. Harbola and V. Sahni, Phys. Rev. Lett. **62**, 489 (1989).
[3] Y. Li, M. K. Harbola, J. B. Krieger, and V. Sahni (unpublished).
[4] M. K. Harbola and V. Sahni, Phys. Rev. B **39**, 10437 (1989).
[5] Y. Wang, J. P. Perdew, J. A. Chevary, L. P. Macdonald, and S. H. Vosko, Phys. Rev. A **41**, 78 (1990).
[6] M. Levy and J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).
[7] Y. Li and J. B. Krieger (private communication).
[8] J. P. Perdew (private communication).
[9] M. K. Harbola and V. Sahni (private communication).