Electrostatic interpretation of an electron density associated with the spherical exchange-correlation potential $V_{xc}(r)$ in atoms: Application to Be

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(Received 30 June 1999; published 30 January 2002)

By means of an electrostatic analogy, an electron density is proposed that is related to the exchange-correlation potential $V_{xc}(r)$ in atoms. More precisely, such an electron density is best characterized by the amount of electronic charge $Q_{xc}(r)$, say, enclosed within a sphere of radius r centered on the atomic nucleus. Then $Q_{xc}(r)$ is related to the radial derivative of $V_{xc}(r)$ by $Q_{xc}(r)=-r^2\partial V_{xc}/\partial r$. $|Q_{xc}(r)|$ tends to unity as $r\to\infty$ and becomes zero in the limit $r\to 0$. However, it increases at first as one comes away from the point at infinity, having the form at large r $|Q_{xc}(r)|\to 1+2\alpha/r^3+O(1/r^4)$, where α is the dipole polarizability of the singly charged positive ion. This means that $|Q_{xc}(r)|$ must have at least one maximum, its height $Q_{xc}(r_m)$ and its position r_m then being important parameters characterizing the shape of $Q_{xc}(r)$. The intersection(s) with the line $|Q_{xc}|=1$ are also plainly of importance in this same context. The exact form of $Q_{xc}(r)$ involves both fully interacting one- and two-particle fermion density matrices, as well as the orbitals of the Slater-Kohn-Sham (SKS) reference system. However, the example of Be is worked out, where it is shown that, if the ground-state density $\rho(r)=\rho_{SKS}(r)$ is known from either x-ray or electron diffraction experiments or from quantal computer simulation studies, then $Q_{xc}(r)$ can be derived for this light atom.

DOI: 10.1103/PhysRevA.65.034501 PACS number(s): 31.15.Ew, 31.10.+z

The exchange-correlation potential $V_{xc}(r)$ lies at the heart of current applications of density-functional theory. While in the approach of Kohn and Sham [1], whose work represents the formal completion of the work begun by Slater [2], this potential is to be obtained by functional differentiation of the as yet unknown exchange-correlation energy $E_{xc}[\rho]$,

$$V_{xc}(\mathbf{r})=\frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})}, \tag{1}$$

the study of Holas and March [3], based on the exact differential virial theorem, expresses $V_{xc}(\mathbf{r})$ explicitly in terms of first- and second-order density matrices of the fully interacting system, plus the Slater-Kohn-Sham (SKS) one-electron orbitals found from the Schrödinger equation with one-body potential

$$V(\mathbf{r})=V_n(\mathbf{r})+V_{es}(\mathbf{r})+V_{xc}(\mathbf{r}). \tag{2}$$

Here $V_{es}(\mathbf{r})$ is generated by the ground-state density $\rho(\mathbf{r})$, these two quantities being related by Poisson's equation of electrostatics:

$$\nabla^2 V_{es}(\mathbf{r})=-4\pi\rho(\mathbf{r})e^2. \tag{3}$$

Equation (3) will now be used to motivate the central idea of this Brief Report. Let us restrict ourselves to spherically symmetric atoms, He, Be, Ne, Ar, etc., to be definite. Then Eq. (3) is readily rewritten as

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial V_{es}}{\partial r}\right)=-4\pi r^2\rho(r)e^2 \tag{4}$$

or

$$\frac{\partial V_{es}}{\partial r}=-\frac{Q(r)}{r^2}, \tag{5}$$

where the total number of electrons enclosed by a sphere of radius r centered on the atomic nucleus, $Q(r)$, is defined by

$$Q(r)=e^2\int_0^r 4\pi r^2\rho(r)dr. \tag{6}$$

Evidently, for atomic number Z,

$$Q(r)\to Z \quad \text{as} \quad r\to\infty. \tag{7}$$

Now we use the above, elementary, electrostatics to motivate the introduction of an integrated radial density $Q_{xc}(r)$, related to $V_{xc}(r)$ by

$$Q_{xc}(r)=-r^2\frac{\partial V_{xc}}{\partial r}. \tag{8}$$

This is the central idea of this Brief Report.

We immediately note from the work of Almbladh and von Barth [4] that the asymptotic form of $V_{xc}(r)$ in neutral atoms is given by (now in atomic units)

$$V_{xc}(r)=-\frac{1}{r}-\frac{\alpha}{2r^4}, \tag{9}$$

where α is the dipole polarizability of the singly charged positive ion. Hence, from the definition (8) of $Q_{xc}(r)$ we find

$$|Q_{xc}(r)|=1+\frac{2\alpha}{r^3}+O\left(\frac{1}{r^4}\right) \tag{10}$$

at sufficiently large r.

Since $Q_{xc}(r)\to 0$ as $r\to 0$, the asymptotic result (10) shows that, since $|Q_{xc}(r)|$ exceeds unity at large r, it must have at least one maximum. In addition, $|Q_{xc}(r)|$ as r is reduced from the position r_m of the above maximum must intersect the value unity at least once. The point to be emphasized here is that therefore there are very characteristic features associated with the (presently necessary) modeling of $Q_{xc}(r)$, namely, (i) the dipole polarizability α, (ii) the position r_m and height $|Q_{xc}(r_m)|$ of the above maximum, (iii) the position, r_1 say, where $|Q_{xc}(r_1)|=1$, and (iv) the limit $Q_{xc}(r)$, which tends to zero as r tends to zero.

We conclude with the (admittedly somewhat complicated) example of the Be atom. We bypass the need for fully interacting low-order density matrices by assuming that the ground-state density $\rho(r)$ is known: e.g., from x-ray or electron diffraction experiments or from quantal computer studies. The idempotent first-order density matrix $\gamma(\mathbf{r},\mathbf{r}')$ generated by the one-body potential $V(r)$ in Eq. (2) then takes the form [5]

$$\gamma(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r})^{1/2}\rho(\mathbf{r}')^{1/2}\cos[\theta(r)-\theta(r')], \tag{11}$$

where the phase $\theta(r)$ is characterized solely by $\nabla\rho/\rho$ and physical boundary conditions through the eigenvalue equation [5]

$$\nabla^2\theta+\frac{\nabla\rho}{\rho}\cdot\nabla\theta+\lambda\sin 2\theta=0. \tag{12}$$

Hence the eigenvalue λ and the eigenfunction θ are uniquely determined by knowledge of the (assumed exact) ground-state electron density $\rho(r)$ of the Be atom.

Going back to the equation of motion of the density matrix $\gamma(\mathbf{r},\mathbf{r}')$, namely [5,6],

$$\nabla^2_{\mathbf{r}}\gamma-\nabla^2_{\mathbf{r}'}\gamma=2[V(r)-V(r')]\gamma, \tag{13}$$

it is a straightforward if tedious matter to extract the radial derivative $\partial V/\partial r$ of the one-body potential (2) in terms of the electron density $\rho(r)$ and the phase $\theta(r)$ to be obtained from $\nabla\rho/\rho$ by solving Eq. (12).

The result is given by

$$\begin{aligned}2\frac{\partial V}{\partial r}=&\frac{\partial}{\partial r}\left\{\frac{\rho''}{\rho}-\frac{1}{2}\left(\frac{\rho'}{\rho}\right)^2\right\}-4\theta'\theta''-\frac{1}{r^2}\frac{\rho'}{\rho}+\frac{1}{r}\left[\frac{\rho\rho''-\rho'^2}{\rho^2}\right]\\&+\left[\theta'\left\{\frac{\rho\rho''-\rho'^2}{\rho^2}\right\}+\theta''\frac{\rho'}{\rho}+\theta'''-\frac{2}{r^2}\theta'+\frac{2}{r}\theta''\right]\\&\times(\cot\theta-\tan\theta)+2\left[\rho'\frac{\theta'}{\rho}+\theta''+\frac{2}{r}\theta'\right]\frac{\partial}{\partial r}(\cot 2\theta).\end{aligned} \tag{14}$$

But from Eq. (2)

$$r^2\frac{\partial V_{xc}(r)}{\partial r}=r^2\frac{\partial V}{\partial r}-4-r^2\frac{\partial V_{es}(r)}{\partial r}, \tag{15}$$

since for Be $V_n=-4/r$. The last term on the right-hand side (RHS) of Eq. (15) is given in terms of $\rho(r)$ by Eqs. (5) and (6) and hence, using the definition (8),

$$-Q_{xc}(r)=r^2\frac{\partial V}{\partial r}-4+Q(r). \tag{16}$$

Everything on the RHS of Eq. (16) can be determined from the (assumed exact) ground-state density $\rho(r)$ and hence the exchange-correlation integrated electron density $Q_{xc}(r)$ can be found.

Before summarizing, it is of some importance to compare and contrast this electrostatic interpretation of the exchange-correlation potential via the integrated density $Q_{xc}(r)$ with the customary treatment of the exchange-correlation energy E_{xc} via the exchange-correlation hole n_h [7,8]. In this latter case one has

$$E_{xc}=\frac{1}{2}e^2\int d\mathbf{r}\,\rho(\mathbf{r})\int d\mathbf{r}'\,n_h(\mathbf{r},\mathbf{r}'). \tag{17}$$

This fundamentally nonlocal "kernel" $n_h(\mathbf{r},\mathbf{r}')$ determining E_{xc} is then to be obtained as an integral over a coupling parameter λ $(0\leqslant\lambda\leqslant 1)$ introduced to scale the electron-electron interaction $e^2/|\mathbf{r}-\mathbf{r}'|$ to $\lambda e^2/|\mathbf{r}-\mathbf{r}'|$ [7,8]. Although the practical implementation of this coupling strength integration remains an obstacle, as does the dependence stressed already of the exchange-correlation hole n_h on the two vectors $\mathbf{r}$ and $\mathbf{r}'$, there is the important physical constraint expressed through the sum rule

$$\int n_h(\mathbf{r},\mathbf{r}')d\mathbf{r}'=-1 \tag{18}$$

for all $\mathbf{r}$. The corresponding constraint on the integrated charge density $Q_{xc}(r)$ is expressed in the atomic example presented in this Brief Report through Eq. (10). But $Q_{xc}(r)$ is then related not to the exchange-correlation energy E_{xc} but to the exchange-correlation potential V_{xc}, thus bypassing the need for the functional derivative in Eq. (1). Of course, both treatments based, respectively, on $n_h(\mathbf{r},\mathbf{r}')$ and $Q_{xc}(r)$, have fundamentally electrostatic interpretations, the former being through Eqs. (17) and (18) while the latter, with its focus directly on the functional derivative of the exchange-correlation energy, $V_{xc}(r)$, is more akin to the Gauss theorem of classical electrostatics.

In summary, the definition of the exchange-correlation integrated density $Q_{xc}(r)$ is proposed as in Eq. (8), by analogy with the classical electrostatic result in Eq. (5). For large r, Eq. (10) gives the asymptotic form of $Q_{xc}(r)$, which also tends to zero as $r\to 0$. The form (10) shows that $|Q_{xc}(r)|$ must have at least one maximum, and must intersect the value unity at least once for finite r. For Be, Eqs. (16) and (14) give $|Q_{xc}(r)|$ in a form characterized solely by the ground-state electron density $\rho(r)$, the phase $\theta(r)$ being determined by solution of Eq. (12), into which $\nabla\rho/\rho$ is the only input information.

It is a pleasure to thank Professor A. Holas and Professor A. Nagy, together with Professor V. E. Van Doren and his colleagues in Antwerp, for many most stimulating discussions on the area embraced by this study.

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