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Total electron density from the s-electron density

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Based on a theorem of Theophilou [Philos. Mag. B **69**, 771 (1994)], the total electron density in a central field atom is determined from the Kohn-Sham s-electron density. Exchange-only density-functional calculations for atoms are presented. [S1050-2947(98)10105-1]

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I. INTRODUCTION

In a recent paper [1], it was shown for a bare Coulomb potential energy $-Ze^2/r$ that the total electron density for an arbitrary number of closed shells is given by

$$n(r)=\frac{2Z}{a_0}\int_r^\infty n_s(r)dr, \tag{1}$$

where n_s is the electron density of s shells. Equation (1) can also be transformed into the form

$$\frac{\partial n(r)}{\partial r}=-\frac{2Z}{a_0}n_s(r), \tag{2}$$

which is the spatial generalization of Kato's theorem [2].

Equation (1) shows that the total electron density n can be calculated if the s-electron density n_s is known. The total density can be determined from n_s, not only for a bare Coulomb field. In a spherically symmetric system one can always determine n if n_s is known. Of course, the relation between n and n_s is not so simple as in the bare Coulomb field [Eqs. (1) and (2)].

Let us consider a noninteracting electron system in a central potential $v(r)$. If the s density n_s is given, and is v representable, the number N_s of the s electrons can be computed by integrating n_s over space. Applying the minimum principle for the N_s-electron functional $\langle\Phi|\hat{H}|\Phi\rangle$, where

$$\hat{H}=\sum_{i=1}^{N_s}\left[\frac{-\nabla_i^2}{2m}+v(r_i)\right], \tag{3}$$

and the Slater determinant $|\Phi\rangle$ is constructed solely from spin orbitals belonging to the subspace characterized by the angular momentum quantum number $l=0$, one can obtain the inequalities

$$\langle\Phi_0|\hat{T}|\Phi_0\rangle+\langle\Phi_0|\hat{V}|\Phi_0\rangle<\langle\Phi_0'|\hat{T}|\Phi_0'\rangle+\langle\Phi_0'|\hat{V}|\Phi_0'\rangle, \tag{4}$$

$$\langle\Phi_0'|\hat{T}|\Phi_0'\rangle+\langle\Phi_0'|\hat{V}'|\Phi_0'\rangle<\langle\Phi_0|\hat{T}|\Phi_0\rangle+\langle\Phi_0|\hat{V}'|\Phi_0\rangle, \tag{5}$$

where $\hat{T}=\Sigma_{i=1}^{N_s}(\nabla_i^2/2m)$, $\hat{V}=\Sigma_{i=1}^{N_s}v(r_i)$, $\hat{V}'=\Sigma_{i=1}^{N_s}v'(r_i)$, v and v' are different external potentials, and $|\Phi_0\rangle$ and $|\Phi_0'\rangle$ are the ground-state Slater determinants belonging to the potentials v and v', respectively. Using the equalities

$$\langle\Phi_0|\hat{V}|\Phi_0\rangle=\int n_s v\,dr, \tag{6}$$

$$\langle\Phi_0|\hat{V}'|\Phi_0\rangle=\int n_s v'\,dr, \tag{7}$$

$$\langle\Phi_0'|\hat{V}|\Phi_0'\rangle=\int n_s' v\,dr, \tag{8}$$

$$\langle\Phi_0'|\hat{V}'|\Phi_0'\rangle=\int n_s' v'\,dr. \tag{9}$$

Eqs. (4), and (5) lead to the inequality

$$\int [n_s'(r)-n_s(r)][v(r)-v'(r)]>0; \tag{10}$$

therefore, there is a single external potential which corresponds to the given n_s, i.e., there exists a one-to-one correspondence between the potential and the s-state density. This theorem was stated and proved by Theophilou [3], not only for $l=0$ but also for arbitrary l. In a recent paper [4], Theophilou and Gidopoulos also proved the following theorem which may be regarded as the generalization of the aforementioned statement: "For a non-interacting system of N electrons, the part of the density due to the spin orbitals that transforms according to a certain irreducible representation of a group, determines uniquely the ground state." Using the Kohn-Sham method for handling the many-electron problem, it can be stated that in a spherically symmetric system the Kohn-Sham s-density uniquely determines the Kohn-Sham potential and the ground state. In this paper, a numerical iterative method is proposed to construct the Kohn-Sham potential and the total density in the knowledge of the s-electron density.

II. s-STATE DENSITY WITH ONE AND TWO s SHELLS

If the s-state density is the $1s$ electron density belonging to the occupation number ω_1,

$$n_s=\omega_1|u_{1s}|^2, \tag{11}$$

from the Kohn-Sham equation

$$\left(-\frac{\nabla^2}{2}+v_{KS}(r)\right)u_{1s}(r)=\varepsilon_{1s}u_{1s}(r), \tag{12}$$

the Kohn-Sham potential can be trivially constructed:

$$v_{KS}(r)=\varepsilon_{1s}+\frac{1}{2n_s^{1/2}}\nabla^2 n_s^{1/2}. \tag{13}$$

The one-electron energy ε_{1s} can be determined from the asymptotic decay of n_s,

$$n_s\sim \exp\{-2\sqrt{2|\varepsilon_{1s}|}r\}. \tag{14}$$

If the s-state density is obtained from two s shells, i.e.,

$$n_s=\omega_1|u_{1s}|^2+\omega_2|u_{2s}|^2, \tag{15}$$

where ω_1 and ω_2 are the occupation numbers, the Kohn-Sham potential can be constructed in the following way: The method developed earlier for the ground state of the Be atom [5] is applied. Following Dawson and March [6], the phase function θ is introduced:

$$P_{1s}=\frac{1}{\sqrt{\omega_1}}\varrho_s^{1/2}\cos\theta, \tag{16}$$

$$P_{2s}=\frac{1}{\sqrt{\omega_2}}\varrho_s^{1/2}\sin\theta, \tag{17}$$

where P_{1s} and P_{2s} are the radial wave functions, and $\varrho_s=4r^2\pi n_s$ is the radial s-electron density. Equations (16) and (17) and the radial Kohn-Sham equations

$$P_{is}''+2(\varepsilon_{is}-v_{KS})P_{is}=0, \quad i=1,2 \tag{18}$$

lead to the relation between the s-state electron density ϱ_s and phase θ:

$$\theta''+\frac{\varrho_s'}{\varrho_s}\theta'=2\xi\sin(2\theta), \tag{19}$$

where

$$\xi=\frac{\varepsilon_{1s}-\varepsilon_{2s}}{2}. \tag{20}$$

ϱ_s can be explicitly written as

$$\varrho_s=\frac{1}{\theta'}\exp(2\xi h), \tag{21}$$

where

$$h(r)=\int\frac{\sin(2\theta)}{\theta'}dr. \tag{22}$$

The Kohn-Sham potential takes the form

$$v_{\mathrm{KS}}=\frac{1}{4}\frac{{\varrho_s}'}{\varrho_s}-\frac{1}{8}\left(\frac{\varrho_s'}{\varrho_s}\right)^2-\frac{1}{2}(\theta')^2+\xi\cos(2\theta)+\beta, \tag{23}$$

where

$$\beta=\frac{\varepsilon_{1s}+\varepsilon_{2s}}{2}. \tag{24}$$

From Eq. (19), θ can be determined from ϱ_s using the normalization and orthogonality conditions

$$\int\varrho_s\cos^2\theta dr=\omega_1, \tag{25}$$

$$\int\varrho_s\sin^2\theta dr=\omega_2, \tag{26}$$

$$\int\varrho_s\sin^2(2\theta)dr=0. \tag{27}$$

Then Eq. (23) gives v_{KS}. If the Kohn-Sham potential is known, the solutions of the Kohn-Sham equations yield all the occupied wave functions, and the total electron density can be given. Considering the special case of a three-level spherically system, with the obtained v_{KS} one has just to solve the third radial Kohn-Sham equation

$$P_{2p}''+2\left(\varepsilon_{2p}-v_{\mathrm{KS}}-\frac{l(l+1)}{2r^2}\right)P_{2p}=0, \quad l=1 \tag{28}$$

to obtain the total density.

III. s-STATE DENSITY WITH SEVERAL s SHELLS

Recently, there has been a considerable interest in constructing the Kohn-Sham potential with knowledge of the total density [7–12]. One of the authors [7] also proposed a numerical, iterative method that can be modified to obtain the Kohn-Sham potential, if the s-electron density is known. Starting out from a properly chosen starting potential the Kohn-Sham equations

$$[-\tfrac{1}{2}\nabla^2+v_{\mathrm{KS}}(r)]u_i(\mathbf{r})=\varepsilon_i u_i(\mathbf{r}) \tag{29}$$

are solved. Then the s-state density

$$n_s=\sum_{\substack{i\\(l=0)}}2u_i^2(\mathbf{r}) \tag{30}$$

is calculated and compared with the input s density. If the difference is larger than an appropriately chosen small constant, the potential of the following iteration is constructed. Then the Kohn-Sham equations are solved again, and so on. If convergency is achieved then the true Kohn-Sham potential is obtained, since it is uniquely determined by the s state density. In principle, in spherically symmetric systems the atomic number Z can be determined from Kato's theorem [2]

$$\left(\frac{\partial n}{\partial r}\right)_{(r=0)}=-2Zn(r=0). \tag{31}$$

The same expression can also be written for n_s. Consequently, the atomic number Z can be readily obtained from

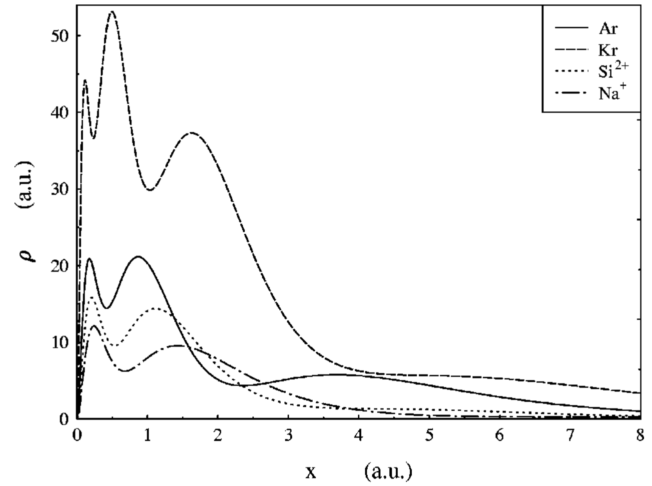

FIG. 1. The total radial electron density ρ computed numerically from the s-state density as the function of x for the atoms Ar and Kr, and the ions Na$^+$ and Si^{2+} (in a.u.). x is defined as $x = r/(\mu Z^{1/3})$, where Z is the atomic number, $\mu = (1/2)(3\pi/4)^{2/3}$, and r is the radial distance from the nucleus.

n_s. On the other hand, the asymptotic behavior of the Kohn-Sham potential is given by

$$v_{\mathrm{KS}}(r) = -\frac{Z-N-1}{r} \quad \text{as} \quad r \to \infty. \tag{32}$$

From this expression, in principle, the total number of electrons N can be extracted. With a knowledge of v_{KS} and N, the total electron density can be found by solving the Kohn-Sham equations.

IV. EXCHANGE-ONLY CALCULATIONS

In an earlier paper [7], Kohn-Sham one-electron orbitals and energies were determined from Hartree-Fock one-electron orbitals [13]. It was shown [14,15] that the Kohn-Sham potential leading to the Hartree-Fock density is very close to the exchange-only Kohn-Sham potential, so we can loosely refer to it as the exchange-only case. As a result of this kind of calculation, one obtains the exchange-only one-electron energies and orbitals, from which the exchange-only n_s can be constructed. Applying n_s as an input s-electron density following the procedure described above, the exchange-only total electron density n can be computed.

This method has been applied to several atoms and ions with closed shells. Some typical results of these calculations are displayed in the figures. Figure 1 presents the total radial electron density $\varrho = 4\pi r^2 n$ for the atoms Ar and Kr and the ions Na$^+$ and Si^{2+}. The calculations performed show that the $d = 100|\varrho - \varrho_{\mathrm{HF}}|/\varrho_{\mathrm{HF}}$ relative difference between ϱ and the Hartree-Fock density ϱ_{HF} is less than 5% for the considered systems, i.e., the Kohn-Sham density is close to the Hartree-Fock density, as expected because of the criterion for self-consistency. The Kohn-Sham potentials are plotted in Fig. 2.

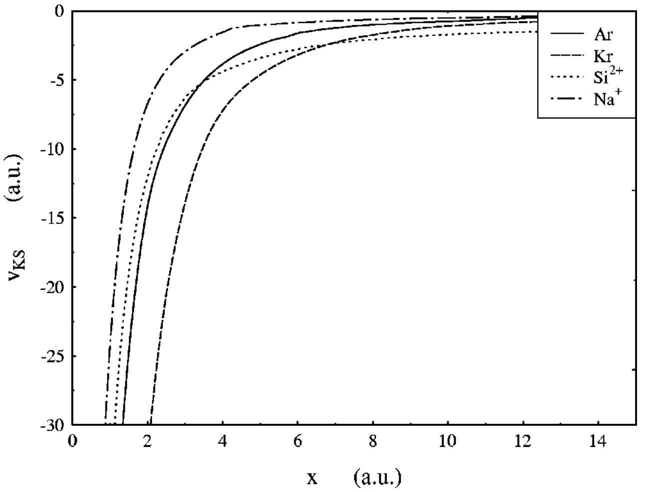

FIG. 2. The Kohn-Sham potential v_{KS} for the Ar and Kr atoms and the ions Na$^+$ and Si^{2+} (in a.u.).

V. SUMMARY AND DISCUSSION

As we pointed out, the s-state contribution to the electron density contains all information about the ground-state system. If the s-electron density is given, it is possible to compute the Kohn-Sham potential and the total electron density. In the present work this problem was solved by the aid of a numerical method described above. As an illustration, calculations were performed for spherically symmetric systems in the exchange-only density-functional case.

According to the theorem of Theophilou [3], the total electron density can be determined not only from the s-electron density, but can also be obtained from the p-electron density, a numerical demonstration of which might be the subject of another paper.

The total electron density can be calculated from the d-electron density, and so on, i.e., the l part of the density contains all the information that is needed to obtain the total electron density. These results are valid for noninteracting systems, i.e., for Kohn-Sham systems. The problem of whether a similar theorem exists for interacting system is still an open question (though there is a conjecture [3] that it is probably true).

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