Bounds for the second and third derivatives of the electron density at the nucleus

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Abstract

A lower bound for $\bar{\rho}''(0)$, the second derivative of the spherically averaged atomic electronic density at the nucleus, and an upper bound for $\bar{\rho}'''(0)$, the third derivative, are obtained, respectively. It is shown that, for the ground state, $\bar{\rho}''(0) \geqslant \frac{10}{3} Z^2 \rho(0)$ and $\bar{\rho}'''(0) \leqslant -\frac{14}{3} Z^3 \rho(0)$, where Z is the charge of the nucleus, and $\rho(0)$ is the electron density at the nucleus. Tighter bounds for $\bar{\rho}''(0)$ and $\bar{\rho}'''(0)$ are also reported which are valid for both the ground state and excited states. Explicit illustration with the example of one-electron atomic ions is given.

PACS numbers: 31.15.Ew, 31.10.+z, 71.10.−w

1. Introduction

Rigorous knowledge of electron density is rather valuable in understanding the electronic structure of atoms, molecules and solids. It is also helpful in guiding the construction of the approximations for the exchange-correlation energy functional and the corresponding potential in the approach of density functional theory [1] to the problems of inhomogeneous electron systems. One of the well-known exact results is the so-called Kato theorem [2] which states that, near any nucleus,

$$\bar{\rho}'(r)|_{r=0} = -2Z\rho(0). \tag{1}$$

Here Z is the charge of the nucleus which is taken as the origin; $\bar{f}(r)$ means the spherical average of function $f(\mathbf{r})$; primes denote the derivatives with respect to r in this paper.

In recent work [3], by investigating the behavior of the wavefunctions of the interacting Schrödinger system and the corresponding noninteracting Kohn–Sham system in the vicinity of the nucleus, we established relations between the second and the third derivatives of the spherically averaged density at the nucleus. They could be understood as extensions of the cusp condition of equation (1) to higher orders of derivatives. In this paper, we derive rigorously a lower bound for the second derivative and an upper bound for the third derivative, respectively,

of the spherically averaged density at the nucleus for the ground state. The bounds are given as follows:

$$\bar{\rho}''(0) \geqslant \tfrac{10}{3} Z^2 \rho(0) \tag{2}$$

and

$$\bar{\rho}'''(0) \leqslant -\tfrac{14}{3} Z^3 \rho(0). \tag{3}$$

The results hold in general whether the system is an atom, molecule or a solid. Tighter bounds for $\bar{\rho}''(0)$ and $\bar{\rho}'''(0)$ are also reported (see equations (23) and (24) in section 3) which are valid for the excited states as well.

In section 2, we discuss the near nucleus behavior of the wavefunction of the Schrödinger equation and the density. The derivation for the bounds is presented in section 3. In section 4 explicit illustration for the case of one-electron atomic ions is given. Summarizing remarks are made in section 5.

2. Near nucleus behavior of the wavefunction and the density

The Schrödinger equation for N-electrons in an external potential $v(\mathbf{r})$ arising from their interaction with nuclei is (in au)

$$\hat{H}\Psi = (\hat{T} + \hat{V} + \hat{U})\Psi = E\Psi, \tag{4}$$

where $\hat{T} = -\frac{1}{2}\sum_i \nabla_i^2$, $\hat{V} = \sum_i v(\mathbf{r}_i)$, $\hat{U} = \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$, Ψ the wavefunction and E the energy. Following [3], we write, for limiting small r, the many-body wavefunction as

$$\Psi(\mathbf{r}, \mathbf{X}) = \Psi(0, \mathbf{X}) + a(\mathbf{X})r + b(\mathbf{X})r^2 + c(\mathbf{X})r^3 + \cdots$$
$$+ \sum_{m=-1}^{1} [a_{1m}(\mathbf{X})r + b_{1m}(\mathbf{X})r^2 + \cdots]Y_{1m}(\hat{r}) + \sum_{m=-2}^{2} [b_{2m}(\mathbf{X})r^2 + \cdots]Y_{2m}(\hat{r}) + \cdots, \tag{5}$$

where $\hat{r} = \mathbf{r}/r$, $\mathbf{X}$ denotes $s, \mathbf{r}_2 s_2, \ldots, \mathbf{r}_N s_N$, and $Y_{lm}(\hat{r})$ are the spherical harmonics. For $r \to 0$, the Schrödinger equation (4) can be rewritten as [3]

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + r\sum_{m=-1}^{1} Y_{1m}(\hat{r})g_m(\mathbf{X}) \right]\Psi(\mathbf{r}, \mathbf{X}) + H_{Z-1}^{N-1}(\mathbf{X})\Psi(\mathbf{r}, \mathbf{X}) = E\Psi(\mathbf{r}, \mathbf{X}), \tag{6}$$

where

$$g_m(\mathbf{X}) = \frac{4\pi}{3}\sum_{i=2}^{N} \frac{1}{r_i^2} Y_{1m}^*(\hat{r}_i) \tag{7}$$

and

$$H_{Z-1}^{N-1}(\mathbf{X}) = \sum_{i=2}^{N} \left[-\frac{1}{2}\nabla_i^2 + v(\mathbf{r}_i) + \frac{1}{r_i} \right] + \frac{1}{2}\sum_{i \neq j \neq 1}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{8}$$

Substituting the expression of equation (5) into equation (6) and equating the coefficients of the terms of $r^{-1}, r^0 Y_{1m}(\hat{r}), r^0$, and r^1, respectively, one has

$$a(\mathbf{X}) + Z\Psi(0, \mathbf{X}) = 0, \tag{9}$$

$$2b_{1m}(\mathbf{X}) + Za_{1m}(\mathbf{X}) = 0, \tag{10}$$

$$3b(\mathbf{X}) - Z^2\Psi(0, \mathbf{X}) = \left[H_{Z-1}^{N-1}(\mathbf{X}) - E \right]\Psi(0, \mathbf{X}), \tag{11}$$

$$6c(\mathbf{X}) + Zb(\mathbf{X}) = Z\big[E - H_{Z-1}^{N-1}(\mathbf{X})\big]\Psi(0, \mathbf{X}). \tag{12}$$

We note that the behavior of the wavefunction in the vicinity of the nucleus has been extensively investigated [2–4]. In fact, equations (9) and (10) have been obtained previously. On the other side, equations (11) and (12), which shall play a key role in the derivation in section 3, have not been previously reported *in this separate form*.

The density is defined as

$$\rho(\mathbf{r}) = N \int d\mathbf{X}|\Psi(\mathbf{r}, \mathbf{X})|^2, \tag{13}$$

where $\int d\mathbf{X}$ denotes $\sum_s \int d\mathbf{x}_2 \cdots d\mathbf{x}_N$. With the relations in equations (9) and (10), it can be shown that

$$\bar{\rho}''(0) = 2Z^2\rho(0) + 4N \int d\mathbf{X} \operatorname{Re}[\Psi^*(0, \mathbf{X})b(\mathbf{X})] + 2N \int d\mathbf{X} \sum_{m=-1}^{1} \frac{1}{4\pi}|a_{1m}(\mathbf{X})|^2 \tag{14}$$

and

$$\bar{\rho}'''(0) = 12N \int d\mathbf{X} \operatorname{Re}[\Psi^*(0, \mathbf{X})(c(\mathbf{X}) - Zb(\mathbf{X}))] - 6ZN \int d\mathbf{X} \sum_{m=-1}^{1} \frac{1}{4\pi}|a_{1m}(\mathbf{X})|^2 \tag{15}$$

(see also [3].) This completes the discussion of the behavior of the wavefunction and the density near the nucleus.

3. Derivation of equations (2) and (3)

We observe that equations (11), (12) and equation (13) lead to

$$N \int d\mathbf{X} \operatorname{Re}[\Psi^*(0, \mathbf{X})b(\mathbf{X})] \geqslant \frac{1}{3}\big(Z^2 - E + E_{Z-1,0}^{N-1}\big)\rho(0), \tag{16}$$

$$N \int d\mathbf{X} \operatorname{Re}[\Psi^*(0, \mathbf{X})c(\mathbf{X})] \leqslant \frac{1}{18}Z\big(-Z^2 + 4E - 4E_{Z-1,0}^{N-1}\big)\rho(0), \tag{17}$$

where $E_{Z-1,0}^{N-1}$ is the ground state energy of the Hamiltonian $H_{Z-1}^{N-1}(\mathbf{X})$. Inequalities (16) and (17) are critical equations in the following derivation. Comparing them with equation (14) and equation (15), respectively, one has

$$\bar{\rho}''(0) \geqslant \frac{10}{3}Z^2\rho(0) + \frac{4}{3}\big(E_{Z-1,0}^{N-1} - E\big)\rho(0) + 2N \int d\mathbf{X} \sum_{m=-1}^{1} \frac{1}{4\pi}|a_{1m}(\mathbf{X})|^2 \tag{18}$$

and

$$\bar{\rho}'''(0) \leqslant -\frac{14}{3}Z^3\rho(0) - \frac{20}{3}Z\big(E_{Z-1,0}^{N-1} - E\big)\rho(0) - 6ZN \int d\mathbf{X} \sum_{m=-1}^{1} \frac{1}{4\pi}|a_{1m}(\mathbf{X})|^2. \tag{19}$$

In passing, we mention that, at the nucleus, the kinetic energy density, which is defined as

$$t(\mathbf{r}) = \frac{1}{2}N \int d\mathbf{X} \, \nabla \Psi^*(\mathbf{r}, \mathbf{X}) \cdot \nabla \Psi(\mathbf{r}, \mathbf{X}), \tag{20}$$

has been shown in [3] as

$$\bar{t}(0) - \frac{1}{2}Z^2\rho(0) = N \int d\mathbf{X} \sum_{m=-1}^{1} \frac{3}{8\pi}|a_{1m}(\mathbf{X})|^2. \tag{21}$$

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Equation (21) indicates that

$$\bar{t}(0) \geqslant \tfrac{1}{2} Z^2 \rho(0). \tag{22}$$

The existence of the term on the right-hand side of equation (21) had not been recognized before [5].

From equations (18) and (19), one obtains

$$\bar{\rho}''(0) \geqslant \tfrac{10}{3} Z^2 \rho(0) + \tfrac{4}{3} \big(E_{Z-1,0}^{N-1} - E \big) \rho(0), \tag{23}$$

and

$$\bar{\rho}'''(0) \leqslant -\tfrac{14}{3} Z^3 \rho(0) - \tfrac{20}{3} Z \big(E_{Z-1,0}^{N-1} - E \big) \rho(0). \tag{24}$$

Up to this point, all the calculations are in fact not restricted to the ground state. The bounds shown in equations (23) and (24) are valid for *both the ground state and excited states*. For the ground state we further obtain equations (2) and (3) from equations (23) and (24).

4. Illustration for one-electron atomic ions

For one-electron atomic ions (including hydrogen atom), equations (23) and (24) become

$$\bar{\rho}''(0) \geqslant \tfrac{2}{3}(5Z^2 - 2E)\rho(0) \tag{25}$$

and

$$\bar{\rho}'''(0) \leqslant -\tfrac{2}{3} Z(7Z^2 - 10E)\rho(0). \tag{26}$$

The wavefunctions are exactly known for both the ground state and excited states: $\Psi(\mathbf{r}) = R_{nl}(r) Y_{lm}(\hat{r})$, with [6]

$$R_{nl}(r) = -\left\{ \alpha_n^{3+2l} \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{1/2} \mathrm{e}^{-\alpha_n r/2} r^l L_{n+l}^{2l+1}(\alpha_n r), \tag{27}$$

where $\alpha_n = 2Z/n$, and $L_{n+l}^{2l+1}(\alpha_n r)$ are the Laguerre polynomials. It is easy to see that for $l \neq 1, a_{1m} = 0$ in equations (18) and (19), and equations (23) and (24) in fact become equalities:

$$\bar{\rho}''(0) = \tfrac{2}{3}(5Z^2 - 2E)\rho(0), \tag{28}$$

and

$$\bar{\rho}'''(0) = -\tfrac{2}{3} Z(7Z^2 - 10E)\rho(0). \tag{29}$$

We next give an explicit illustration of the results with the exactly known wavefunctions. Obviously for $l \geqslant 2$ equations (28) and (29) are trivially true since all $\rho(0)$, $\bar{\rho}''(0)$, and $\bar{\rho}'''(0)$ are zero. For $l = 0$, one can obtain from equation (27)

$$\bar{\rho}(r) = \frac{Z^3}{\pi n^3} \left[1 - 2Zr + \frac{1}{3} Z^2 \left(5 + \frac{1}{n^2} \right) r^2 - \frac{1}{9} Z^3 \left(7 + \frac{5}{n^2} \right) r^3 + \cdots \right]. \tag{30}$$

Equations (28) and (29) are hence confirmed with the help of the fact that $E = -Z^2/2n^2$. For $l = 1$, one has

$$\bar{\rho}(r) = \frac{1}{9\pi} \left(\frac{Z}{n} \right)^5 (n^2 - 1) r^2 (1 - Zr + \cdots). \tag{31}$$

The inequalities of equations (25) and (26) are satisfied. Note that in this case $a_{1m} \neq 0$ in equations (18) and (19).

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5. Summary

In summary, in this paper, we have established for the ground state the lower bound for $\bar{\rho}''(0)$, the second derivative of the spherically averaged electron density at the nucleus, in equation (2), and the upper bound for $\bar{\rho}'''(0)$, the third derivative, in equation (3). Tighter bounds for $\bar{\rho}''(0)$ and $\bar{\rho}'''(0)$, valid for both the ground state and excited states, are also reported in equations (23) and (24). These results add some to our rigorous information of the electron density, which might be valuable in the calculation of the electronic structure of atomic systems.

Whether the opposite bounds exist for $\bar{\rho}''(0)$ and $\bar{\rho}'''(0)$ remains an interesting question. Not unrelated to this question is the fact that both upper and lower bounds have been extensively explored for $\rho(0)$ (and, according to equation (1), equally for $\bar{\rho}'(0)$) [7].

Note added. During the preparation of this manuscript, the author became aware of related work [8]. The bounds shown in equations (2) and (3) in this paper are indeed the same as those in equations (1.25) and (1.32) in [8] (up to a different form of Hamiltonians). There are, however, minor differences between inequalities (23) and (24) of the present paper and the first inequalities of equations (1.25) and (1.32) in [8]. In fact, $E_{Z-1,0}^{N-1} - E$ can be rewritten as $E_{Z-1,0}^{N-1} - E_{Z,0}^{N-1} - \mu$, where $\mu = E - E_{Z,0}^{N-1}$ is the minus the ionization energy and denoted as $-\epsilon$ in equation (1.20) in [8]. Since $E_{Z-1,0}^{N-1} - E_{Z,0}^{N-1} \geqslant 0$, it is easy to see that the bounds in equations (23) and (24) are tighter than those given by the first inequalities of equations (1.25) and (1.32). The differences were also recognized and analyzed in Remark 1.4 in [8], though equations like inequalities (23) and (24) were not explicitly given there.

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