"Schrödinger inequalities" and asymptotic behavior of the electron density of atoms and molecules

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Within the frame of the infinite-nuclear-mass approximation a differential inequality for the square root of the one-electron density is derived. This linear differential inequality is structured like a one-particle Schrödinger equation and leads to results on the analytic behavior of the electron density ρ in the region far from the nuclei. A domain determined by the potential and the ionization energy is given where ρ is subharmonic. For atoms it is shown that the spherically averaged electron density is a convex monotonically decreasing function outside some sphere whose radius depends on the ionization energy and the electron nuclear attraction. Furthermore, an upper bound for the electron density is given in terms of Whittaker functions which decreases exponentially and is exact for the s states of the H atom. It compares favorably with the results given in the literature.

I. INTRODUCTION

In atomic and molecular quantum mechanics the only exactly solvable problems are the one-electron problems, H, and within the Born-Oppenheimer approximation, H_2^+. To get deeper insight into the analytical properties of the one-electron density of many-electron systems, it is desirable to investigate those features of the one-electron density of one-electron systems that carry over to the many-electron case.

Mainly, two results are to be mentioned: the cusp conditions derived by Kato[1] and the results concerning the asymptotic behavior of the electron density which have been recently obtained by various authors.[2-8]

Here we give a differential inequality structured like a one-electron Schrödinger equation—therefore we call it a "Schrödinger inequality"—which the exact spinless electron density has to satisfy. This differential inequality leads to new results about the fall-off of the electron density.

II. THE "SCHRÖDINGER INEQUALITY"

We consider the electronic Schrödinger equation of a molecular system within the infinite-nuclear-mass approximation,

$$H\psi = E\psi, \tag{2.1}$$

$\psi(x_1, \ldots, x_n)$ being the normalized wave function in the configuration space R^{3n} (spin enters only by permutation symmetry of ψ), E the corresponding eigenvalue of the Hamiltonian

$$H = -\sum_{i=1}^{n} \tfrac{1}{2}\nabla_i^2 - \sum_{i=1}^{n} V(x_i) + \sum_{\substack{i,j \\ i<j}}^{n} r_{ij}^{-1}, \tag{2.2}$$

$$V(x_i) = \sum_{j=1}^{m} Z_j \, |X_j - x_i|^{-1}. \tag{2.3}$$

Thereby Z_j and X_j denote the respective charge and location of the jth nucleus and $r_{ij} = |x_i - x_j|$ the interelectronic distance. The origin of the coordinate system is conveniently chosen such that it is invariant under the symmetry operations of the molecular symmetry group G.

Since in the subsequent considerations the ionization potential ϵ plays a central role, we shall give a definition of ϵ following partly the work of Ahlrichs.[2,7] We first have to consider the permutational and spatial symmetry properties of ψ, which is associated with an irreducible representation Γ of G. Using the nomenclature of Wigner,[9] ψ can be classified according to an irreducible representation $\bar{D}^{(k)}$ of the symmetric group S_n where $0 \leq k \leq [n/2]$ due to the Pauli principle. From such a state the system can be ionized only into $(n-1)$-particle states which transform (i) according to the irreducible representations $\bar{D}'^{(i)}$ with $i = k$ or $i = k-1$ of S_{n-1} and (ii) according to an irreducible representation Γ' of G, for which an irreducible representation Γ'' of G exists such that in the decomposition of the direct product $\Gamma \otimes \Gamma''$ into irreducible representations, Γ occurs, denoted by $\Gamma \in \Gamma' \otimes \Gamma''$ in the following. Let $E_0^{(n-1)}(\bar{D}'^{(i)}, \Gamma')$ denote the ground-state energy of $H^{(n-1)}$, the Hamiltonian of the ionized system, in the subspace of functions with the symmetry properties $\bar{D}'^{(i)}$ and Γ'. Now we define $E^{(n-1)}_{\Gamma, \bar{D}^{(k)}}$ by

$$E^{(n-1)}_{\Gamma, \bar{D}^{(k)}} = \min_{\substack{i=k,\,k-1 \\ \Gamma':\, \Gamma \in \Gamma' \otimes \Gamma''}} E_0^{(n-1)}(\bar{D}'^{(i)}, \Gamma'), \tag{2.4}$$

where the right-hand side is minimized over all

Γ' for which a Γ'' exists such that $\Gamma \in \Gamma' \otimes \Gamma''$. Then the ionization potential ϵ of the state described by ψ is given by

$$\epsilon = E^{(n-1)}_{\Gamma, \bar{D}^{(k)}} - E . \tag{2.5}$$

We shall prove now a differential inequality in the distribution sense for the positive square root of the one-electron density $\rho(x_1)$, the diagonal of the one-electron density matrix

$$\rho(x_1, x_1') = n \int \psi^*(x_1', x_2, \ldots, x_n) \times \psi(x_1, \ldots, x_n) dx_2 \ldots dx_n . \tag{2.6}$$

In the following, indices will be suppressed if no confusion is possible.

Theorem 1.

$$-\tfrac{1}{2}\nabla^2[\rho(x)]^{1/2} + [\epsilon - V(x)][\rho(x)]^{1/2} \leq 0. \tag{2.7}$$

Proof. Starting from

$$\psi^* H \psi = E |\psi|^2 \tag{2.8}$$

and integrating this expression over the coordinates x_2 to x_n leads to

$$-(1/2n)\nabla^2 \rho(x, x')|_{x=x'} - (1/n)[E + V(x)]\rho(x) + \int \psi^* H^{(n-1)} \psi \, dx_2 \ldots dx_n + \sum_{i=2}^{n} \int r_{1i}^{-1} |\psi|^2 dx_2 \ldots dx_n = 0 , \tag{2.9}$$

where $H^{(n-1)}$ acts on the coordinates of electrons 2 to n.

Lemma 1.

$$\int \psi^* H^{(n-1)} \psi \, dx_2 \ldots dx_n \geq E^{(n-1)}_{\Gamma, \bar{D}^{(k)}} (1/n)\rho(x) . \tag{2.10}$$

Proof. According to Carlson and Keller,[10]

$$\psi(x_1, \ldots, x_n) = \frac{1}{n^{1/2}} \sum_i \lambda_i^{1/2} F_i(x_1) G_i(x_2, \ldots, x_n), \tag{2.11}$$

where F_i and G_i are the natural orbitals corresponding to the 1- and $(n-1)$-reduced electron density matrices which both have the same eigenvalues λ_i. Obviously ψ can be represented as

$$\psi = \frac{1}{n^{1/2}} \sum_i \sum_{\substack{\Gamma', \Gamma'' \\ \Gamma \in \Gamma' \otimes \Gamma''}} \lambda_i^{1/2} c_i^{\Gamma'} d_i^{\Gamma''} f_i^{\Gamma'} g_i^{\Gamma''} , \tag{2.12}$$

where

$$G_i = \sum_{\Gamma''} d_i^{\Gamma''} g_i^{\Gamma''} , \quad F_i = \sum_{\Gamma'} c_i^{\Gamma'} f_i^{\Gamma'} \tag{2.13}$$

with $f_i^{\Gamma'}$ and $g_i^{\Gamma''}$ normalized to 1. Further it is easily seen that the functions $g_i^{\Gamma''}$ transform according to the reducible representation $\bar{D}'^{(k)} \oplus \bar{D}'^{(k-1)}$ of S_{n-1}. If we insert (2.12) into $\int \psi^* H^{(n-1)} \psi \, dx_2 \ldots dx_n$ and use the orthogonality relations between functions belonging to different irreducible representations, then the variation principle together with the definition (2.4) of $E^{(n-1)}_{\Gamma, \bar{D}^{(k)}}$ leads to inequality (2.10).

Combining (2.5) and (2.10) and neglecting the positive interelectronic repulsion term in (2.9), we obtain

$$-\tfrac{1}{2}\nabla^2 \rho(x, x')|_{x=x'} + [\epsilon - V(x)]\rho(x) \leq 0. \tag{2.14}$$

From (2.14) we shall arrive at (2.7) with the aid of Lemma 2.

Lemma 2.

$$|\nabla \rho^{1/2}|^2 \leq n \int |\nabla_1 \psi|^2 dx_2 \ldots dx_n . \tag{2.15}$$

Proof. Obviously

$$|\nabla \rho|^2 = n^2 \left| \int \nabla_1 |\psi|^2 dx_2 \ldots dx_n \right|^2 \leq 4n^2 \left| \int \psi^* \nabla_1 \psi \, dx_2 \ldots dx_n \right|^2 , \tag{2.16}$$

and by the Cauchy-Schwarz inequality we get

$$|\nabla \rho|^2 \leq 4n\rho \int |\nabla_1 \psi|^2 dx_2 \ldots dx_n . \tag{2.17}$$

Equation (2.17) together with

$$|\nabla \rho^{1/2}|^2 = |\nabla \rho|^2 / 4\rho \tag{2.18}$$

proves Lemma 2.

It is easy to see that

$$-\tfrac{1}{2}\nabla^2 \rho(x, x')|_{x=x'} = -\tfrac{1}{2}\nabla^2 \rho(x) + n \int |\nabla_1 \psi|^2 dx_2 \ldots dx_n . \tag{2.19}$$

Using Lemma 2 we have

$$-\tfrac{1}{2}\nabla^2 \rho(x, x')|_{x=x'} \geq -\tfrac{1}{2}\rho^{1/2}\nabla^2 \rho^{1/2}. \tag{2.20}$$

Combining (2.14) with this inequality completes the proof of Theorem 1.

Inequality (2.7) holds in the domain

$$D = \{x \in R^3 \mid \epsilon - V(x) \geq 0, \ [\rho(x)]^{1/2} \neq 0\}$$

in the classical sense. Hence $\rho^{1/2}$ is subharmonic in D. Since $\rho^{1/2}$ is nonconstant, the maximum principle[11] implies that $\rho^{1/2}$ cannot attain a local maximum at any interior point of D.

Especially for atoms, inequality (2.7) reads

$$-\tfrac{1}{2}\nabla^2[\rho(x)]^{1/2} + (\epsilon - Zr^{-1})[\rho(x)]^{1/2} \leq 0. \tag{2.21}$$

Equation (2.21) also holds for the square root of the spherically averaged electron density

$$\rho_{av}(r)=\frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi}\rho(r,\theta,\phi)\sin\theta\,d\theta\,d\phi. \quad (2.22)$$

The proof is straightforward by observing $-\nabla^2 \geq p_r^2$ (p_r being the radial momentum) and

$$|\nabla[\rho_{av}(r)]^{1/2}|^2 \leq \frac{n}{4\pi}\int\left|\frac{\partial\psi}{\partial r}\right|^2 dx_2\ldots dx_n\sin\theta\,d\theta\,d\phi, \quad (2.23)$$

where (2.23) is implied by Lemma 2.

Denoting $r[\rho_{av}(r)]^{1/2}$ by $u(r)$, we see that

$$-\tfrac{1}{2}u''+(\epsilon-Zr^{-1})u\leq 0. \quad (2.24)$$

From (2.24), elementary considerations show that $r\rho_{av}^{1/2}$, $\rho_{av}^{1/2}$, $r^2\rho_{av}$ and ρ_{av} are convex and monotonically decreasing for $r\geq Z/\epsilon$.

The analogous result to Theorem 1 for the k-electron density

$$\rho_k(x_1,\ldots,x_k)=\binom{n}{k}\int|\psi|^2 dx_{k+1}\cdots dx_n, \quad k\leq n \quad (2.25)$$

is

$$\sum_{i=1}^{k}\left[-\tfrac{1}{2}\nabla_i^2\rho_k^{1/2}+\left(\epsilon_i-V(x_i)+\sum_{i<j}^{k}r_{ij}^{-1}\right)\rho_k^{1/2}\right]\leq 0, \quad (2.26)$$

ϵ_i denoting the ionization potential of the $(i-1)$-fold ionized state obtained from ψ. For $k=n$ this inequality becomes

$$H|\psi|\leq E|\psi|, \quad (2.27)$$

which can be also deduced by Kato's inequality.[12]

The proof of (2.26) runs just the same way as before. In the following we shall deal only with the one-electron density, and therefore we shall not discuss (2.26) any further.

III. ASYMPTOTIC BEHAVIOR OF THE ELECTRON DENSITY

In this section the existence of upper bounds to the electron density ρ of an atom decaying like $r^{2[Z/(2\epsilon)^{1/2}-1]}e^{-2(2\epsilon)^{1/2}r}$ will be shown and an analogous result for molecular systems will be given. This improves the results so far known[2-8] that $\rho(x)\leq Ce^{-2\alpha r}$ with $\alpha<(2\epsilon)^{1/2}$ and C a constant.

We consider the quantum-mechanical system given by (2.2). The following theorem holds:

Theorem 2. Let

$$Z=\sum_{j=1}^{m}Z_j,\quad p=\max_{1\leq j\leq m}|X_j|,$$

and let $r_0\geq Z/\epsilon+p$; then

$$[\rho(x)]^{1/2}\leq cr^{-1}W_{Z/(2\epsilon)^{1/2},1/2}(2(r-p)/(2\epsilon)^{1/2}) \quad \text{for } |x|=r\geq r_0, \quad (3.1)$$

where

$$c=v_0r_0[W_{Z/(2\epsilon)^{1/2}}(4Z/(2\epsilon)^{1/2})]^{-1},$$

$$v_0\geq\max_{|x|=r_0}[\rho(x)]^{1/2} \quad (3.2)$$

and $W_{Z/(2\epsilon)^{1/2},1/2}$ denotes the Whittaker function.[13]

Theorem 2 generalizes the results of Bazley and Fox[14] (BF) on the electron density of one-electron molecular systems to many-electron systems. The only difference is the occurrence of the ionization energy ϵ rather than the corresponding energy of the one-electron system.

The proof of Theorem 2 is—with minor modifications—parallel to the method of demonstration used by BF and will therefore be only sketched.

Sketch of the proof. According to Theorem 1, $\rho^{1/2}$ satisfies inequality (2.7) which can be written as an inhomogenous differential equation:

$$-\tfrac{1}{2}\nabla^2[\rho(x)]^{1/2}+[\epsilon-V(x)][\rho(x)]^{1/2}=q(x) \quad \text{with } q(x)\leq 0. \quad (3.3)$$

Let f be the radially symmetric function defined by

$$f(r)=\epsilon-Z(r-p)^{-1}. \quad (3.4)$$

Then obviously

$$0<f(r)\leq\epsilon-V(x) \quad \text{for } |x|>r_0. \quad (3.5)$$

It can be shown[14] that the differential boundary-value problem,

$$-\tfrac{1}{2}\nabla^2 v+fv=0,\quad |x|\geq r_0, \quad (3.6)$$

v square-integrable for $|x|\geq r_0$, $v(x)=v_0$ for $|x|=r_0$, $v_0\geq\max_{|x|=r_0}[\rho(x)]^{1/2}$, has the unique radially symmetric solution

$$v=cr^{-1}W_{Z/(2\epsilon)^{1/2}}(2(r-p)/(2\epsilon)^{1/2}), \quad (3.7)$$

c given by (3.2).

Now $\rho^{1/2}\leq v$ for $|x|\geq r_0$ has to be shown. For this purpose we define w by $w(x)=v(x)-[\rho(x)]^{1/2}$, which satisfies

$$-\tfrac{1}{2}\nabla^2 w+(\epsilon-V)w=-q+(\epsilon-V-f)v, \quad (3.8)$$

$$w(x)\geq 0 \text{ for } |x|=r_0$$

according to (3.3) and (3.6). Then we consider the functional

$$Q(g)=\int_{|x|\geq r_0}\{\tfrac{1}{2}|\nabla g|^2+(\epsilon-V)g^2-2[(\epsilon-V-f)v-q]g\}\,dx, \quad g\in\Gamma \quad (3.9)$$

where Γ denotes the class of real functions g being

bounded and continuous, with bounded piecewise-continuous partial derivatives of first order, with $g(x)=w(x)$ for $|x|=r_0$, and for which the occurring integrals in Q exist. It is easy to see that (3.8) is the Euler equation corresponding to Q.

In order to prove $w \geq 0$ for $|x| \geq r_0$, $w, |w| \in \Gamma$ has to be shown. But this follows easily from the properties of v and $\rho^{1/2}$ together with (3.3) and

$$\int_{R^3} |\nabla \rho^{1/2}|^2 \, dx \leq 2T, \tag{3.10}$$

T being the kinetic energy. Thereby, the last inequality is an immediate consequence of Lemma 2.

In exactly the same way as BF, it can be shown now that Q is minimized uniquely by w and that $Q(|w|) \leq Q(w)$, which implies the positivity of w.

For large argument t, $W_{Z/(2\epsilon)^{1/2},1/2}(t)$ has the asymptotic expansion

$$W_{Z/(2\epsilon)^{1/2},1/2}(t) = t^{Z/(2\epsilon)^{1/2}} e^{-t/2}[1+O(t^{-1})]. \tag{3.11}$$

Hence for sufficiently large r_0 there is a constant $k(\epsilon, Z, p, r_0)$ such that

$$[\rho(x)]^{1/2} \leq k r^{-1}(r-p)^{Z/(2\epsilon)^{1/2}} e^{-(2\epsilon)^{1/2}(r-p)}, \quad |x| \geq r_0 \tag{3.12}$$

a result which has been already conjectured by Ahlrichs.[7]

For atoms $p=0$ and the last inequality reads

$$[\rho(x)]^{1/2} \leq k r^{Z/(2\epsilon)^{1/2}-1} e^{-(2\epsilon)^{1/2}r}, \quad |x| \geq r_0. \tag{3.13}$$

We note that for s states of one-electron atoms, (3.1) becomes optimal.

However, one should expect on physical grounds that $[\rho(x)]^{1/2}$ behaves asymptotically like

$$k r^{-1}(r-p)^{Z^*/(2\epsilon)^{1/2}-1} e^{-(2\epsilon)^{1/2}(r-p)}, \quad Z^* = Z-n+1.$$

This conjecture[15] follows from a simple physical picture. One places one electron far away from the nuclei and the other electrons near the nuclei. Then the electron certainly "sees" an effective charge Z^*. To prove this conjecture an adequate handling of the electron repulsion is necessary, which we have not achieved so far. Therefore our rigorous upper bounds—though assumingly showing the correct exponential decrease—are not quite satisfactory concerning the Z dependence of the pre-exponential factor.

Since $(\rho_{av})^{1/2}$ satisfies inequality (2.21), the estimates (3.1) and (3.13) are valid also for $(\rho_{av})^{1/2}$. In order to compute (3.1) an upper bound to $[\rho_{av}(r_0)]^{1/2}$ is needed. For this purpose the bounds given by Hoffmann-Ostenhof[8] or by Redei[16] may be used.

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