Theor Chim Acta (1992) 83: 185–190

Theoretica
Chimica Acta

The Hiller–Sucher–Feinberg density is not integrable*

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Received April 22, 1991/Accepted October 24, 1991

Summary. The large-distance asymptotic behavior of the electron density obtained from the Hiller–Sucher–Feinberg identity is analyzed. It is shown that, unless the generating wavefunction is exact, such electron density decays like a polynomial in inverse powers of the distance. Therefore, the Hiller–Sucher–Feinberg density is not integrable in general. The sufficient conditions to be imposed upon the generating wavefunctions in order to assure integrability are spelled out.

Key words: Electron density – Hiller–Sucher–Feinberg identity – Hypervirial theorem – Multipole expansion

1. Introduction

It is well known that, in a Coulombic system described by a nonrelativistic Born–Oppenheimer Hamiltonian with the potential energy:

$$\hat{V} = -\sum_{iA} Z_A |\vec{r}_i - \vec{r}_A|^{-1} + (1/2) \sum_{ij}{}' |\vec{r}_i - \vec{r}_j|^{-1}, \tag{1}$$

and the corresponding ground-state wavefunction $\Psi(\{\vec{r}_i\})$, the long-distance behavior of the exact electron density:

$$\varrho(\vec{R}) = \langle \Psi | \sum_i \delta(\vec{r}_i - \vec{R}) | \Psi \rangle, \tag{2}$$

is governed by the asymptotic law [1, 2]:

$$\varrho(\vec{R}) \to A R^{2\alpha} \exp[-(8 I_{\min})^{1/2} R], \tag{3}$$

where

$$\alpha = -1 + (2 I_{\min})^{-1/2} \sum_A Z_A. \tag{4}$$

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* Dedicated to Prof. Klaus Ruedenberg

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In Eqs. (3) and (4), A is a constant and $I_{\min}$ is the lowest ionization potential of the system in question. The existence of the asymptotic estimate, Eq. (3), guarantees finiteness of all multipole moments of the electron density.

Another important property of the exact electron density is that given by the cusp condition of Kato [2, 3]. Unfortunately, since most of the modern *ab initio* electronic structure calculations employ cuspless Gaussian functions, usually the cusp condition is not even approximately satisfied by the computed electron densities. Moreover, the values of $\varrho(\vec{R})$ at nuclei are usually underestimated to a great extent. Hiller, Sucher, and Feinberg (HSF) [4] proposed an identity:

$$\tilde{\varrho}(\vec{R}) = (2\pi)^{-1} \langle \Psi | \sum_i \hat{D}_i(\vec{R}) | \Psi \rangle, \tag{5}$$

where

$$\hat{D}_i(\vec{R}) = |\vec{r}_i - \vec{R}|^{-3} [(\vec{r}_i - \vec{R}) \times \vec{\nabla}_i] \cdot [(\vec{r}_i - \vec{R}) \times \vec{\nabla}_i] + |\vec{r}_i - \vec{R}|^{-1} (\vec{r}_i - \vec{R}) \cdot (\vec{\nabla}_i V), \tag{6}$$

which can be used to circumvent this problem without invoking cusped basis functions. For exact wavefunctions, the densities $\varrho(\vec{R})$ and $\tilde{\varrho}(\vec{R})$ are identical. Equations (5) and (6), which follow from the hypervirial theorem, can be also generalized to scattering states [5], spin densities [6], and higher dimensions [7].

Because Eq. (5) involves a global operator, $\tilde{\varrho}(\vec{R})$ is expected to approximate the exact electron density better than $\varrho(\vec{R})$ for inexact wavefunctions. This is indeed the case for the densities at nuclei calculated with Gaussian basis functions [8]. However, one should be reminded that computation of $\tilde{\varrho}(\vec{R})$ is much more expensive than that of $\varrho(\vec{R})$ due to the fact that it involves complicated molecular integrals [8, 9, 10]. Also, as was shown by Larsson [11], $\tilde{\varrho}(\vec{R})$ computed from the Hartree–Fock limit one-determinantal wavefunction approaches only the exact Hartree–Fock electron density. This means that, in order to include correlation effects in $\tilde{\varrho}(\vec{R})$, one has to use correlated wavefunctions [12]. In such cases, at nuclei, $\tilde{\varrho}(\vec{R})$ is again found to be an improvement over $\varrho(\vec{R})$ [13]. Finally, one may note that alternative definitions of improved electron densities [14] are less suitable from the computational point of view, since they require evaluation of three-electron integrals.

Although all previous studies investigated the HSF density at nuclei, one might argue that $\tilde{\varrho}(\vec{R})$ could be also used in calculations of expectation values involving local operators, such as multipole moments. This is so because often the regions having large values of the electron density (such as those in the proximity to nuclei) contribute the most to the respective integrals. However, as this paper is intended to demonstrate, an unmodified HSF density cannot be used for such purposes. This is due to a fundamental flaw of $\tilde{\varrho}(\vec{R})$, namely the fact that it is generally not integrable (i.e., the integral $\int \tilde{\varrho}(\vec{R})\, d\vec{R}$ is infinite).

2. Large-distance asymptotic behavior of the Hiller–Sucher–Feinberg density

Using the convenient definitions:

$$\vec{R} = R\vec{\eta}, \qquad R = |\vec{R}|, \tag{7}$$

and

$$r_i = |\vec{r}_i|, \qquad \xi_i = r_i^{-1} (\vec{r}_i \cdot \vec{\eta}), \tag{8}$$

Eq. (6) can be rewritten as:

$$\hat{D}_i(\vec{R}) = |\vec{r}_i - \vec{R}|^{-3}[\hat{A}_i + R\hat{B}_i(\vec{\eta}) + R^2\hat{C}_i(\vec{\eta})] + |\vec{r}_i - \vec{R}|^{-1}[\hat{U}_i + R\hat{W}_i(\vec{\eta})], \quad (9)$$

with the auxiliary operators given by:

$$\hat{A}_i = (\vec{r}_i \times \vec{\nabla}_i) \cdot (\vec{r}_i \times \vec{\nabla}_i), \quad (10)$$

$$\hat{B}_i(\vec{\eta}) = -[(\vec{r}_i \times \vec{\nabla}_i) \cdot (\vec{\eta} \times \vec{\nabla}_i) + (\vec{\eta} \times \vec{\nabla}_i) \cdot (\vec{r}_i \times \vec{\nabla}_i)], \quad (11)$$

$$\hat{C}_i(\vec{\eta}) = (\vec{\eta} \times \vec{\nabla}_i) \cdot (\vec{\eta} \times \vec{\nabla}_i), \quad (12)$$

$$\hat{U}_i = \vec{r}_i \cdot (\vec{\nabla}_i \hat{V}), \quad (13)$$

and

$$\hat{W}_i(\vec{\eta}) = -\vec{\eta} \cdot (\vec{\nabla}_i \hat{V}). \quad (14)$$

Derivation of the large R expansion of the HSF density is aided by the fact that, for large R, the integration over electronic coordinates in Eq. (5) can be confined to the inside of a hypersphere with a radius R. The error introduced by this truncation dies off with increasing R as quickly as $|\Psi|^2$ does, i.e. exponentially. On the other hand, as demonstrated in the following, the leading asymptotic terms for $\tilde{\varrho}(R)$ have the form of negative powers of R.

The derivation commences with the familiar multipole expansion (valid for $r_i < R$) [15]:

$$|\vec{r}_i - \vec{R}|^{-1} = R^{-1} \sum_{l=0}^{\infty} (r_i/R)^l P_l(\xi_i), \quad (15)$$

where P_l is the l-th Legendre polynomial. Differentiating both sides of Eq. (15) with respect to ξ_i, followed by dividing by $r_i R$, yields:

$$|\vec{r}_i - \vec{R}|^{-3} = R^{-3} \sum_{l=0}^{\infty} (r_i/R)^l P'_{l+1}(\xi_i), \quad (r_i < R). \quad (16)$$

Combining Eqs. (9), (15), and (16), one arrives at:

$$\hat{D}_i(\vec{R}) = \sum_{l=0}^{\infty} (r_i/R)^l \{P'_{l+1}(\xi_i)[R^{-3}\hat{A}_i + R^{-2}\hat{B}_i(\vec{\eta}) + R^{-1}\hat{C}_i(\vec{\eta})]$$
$$+ P_l(\xi_i)[R^{-1}\hat{U}_i + \hat{W}_i(\vec{\eta})]\}, \quad (17)$$

which is again valid for $r_i < R$.

Equation (17) is the basis for the long-distance asymptotic expansion for $\tilde{\varrho}(\vec{R})$. From Eq. (5) one obtains:

$$\tilde{\varrho}(\vec{R}) \rightarrow \sum_{l=0}^{\infty} \tilde{\varrho}_l(\vec{\eta}) R^{-1}, \quad (18)$$

where

$$\tilde{\varrho}_l(\vec{\eta}) = (2\pi)^{-1} \langle \Psi | \sum_i \hat{D}_i^{(l)}(\vec{\eta}) | \Psi \rangle. \quad (19)$$

The partial operators $\hat{D}_i^{(l)}(\vec{\eta})$ contain only the angular dependence on $\vec{R}$ and are given by (compare Eq. (17)):

$$\hat{D}_i^{(0)}(\vec{\eta}) = P_0(\xi_i)\hat{W}_i(\vec{\eta}) = \hat{W}_i(\vec{\eta}), \quad (20)$$

$$\hat{D}_i^{(1)}(\vec{\eta}) = P'_1(\xi_i)\hat{C}_i(\vec{\eta}) + P_0(\xi_i)\hat{U}_i + P_1(\xi_i) r_i \hat{W}_i(\vec{\eta})$$
$$= \hat{C}_i(\vec{\eta}) + \hat{U}_i + (\vec{r}_i \cdot \vec{\eta})\hat{W}_i(\vec{\eta}), \quad (21)$$

$$\hat{D}_i^{(2)}(\vec{\eta}) = P_1'(\xi_i)\hat{B}_i(\vec{\eta}) + P_2'(\xi_i) r_i \hat{C}_i(\vec{\eta}) + P_1(\xi_i) r_i \hat{U}_i + P_2(\xi_i) r_i^2 \hat{W}_i(\vec{\eta})$$
$$= \hat{B}_i(\vec{\eta}) + 3(\vec{r}_i \cdot \vec{\eta})\hat{C}_i(\vec{\eta}) + (\vec{r}_i \cdot \vec{\eta})\hat{U}_i + (1/2)[3(\vec{r}_i \cdot \vec{\eta})^2 - r_i^2]\hat{W}_i(\vec{\eta}). \quad (22)$$

For $l \geqslant 3$, one arrives at a general expression:

$$\hat{D}_i^{(l)}(\vec{\eta}) = P_{l-2}'(\xi_i) r_i^{l-3}\hat{A}_i + P_{l-1}'(\xi_i) r_i^{l-2}\hat{B}_i(\vec{\eta}) + P_l'(\xi_i) r_i^{l-1}\hat{C}_i(\vec{\eta})$$
$$+ P_{l-1}(\xi_i) r_i^{l-1}\hat{U}_i + P_l(\xi_i) r_i^l \hat{W}_i(\vec{\eta}). \quad (23)$$

3. Sufficient conditions for integrability of the Hiller–Sucher–Feinberg density

The sufficient conditions for integrability of the HSF density are obtained by setting the first four partial densities, $\{\tilde{\varrho}_l(\vec{\eta}), 0 \leqslant l \leqslant 3\}$, to zero. In this section we consider explicitly two of the resulting conditions namely:

$$\tilde{\varrho}_0(\vec{\eta}) = (2\pi)^{-1}\langle \Psi | \sum_i \hat{D}_i^{(0)}(\vec{\eta}) | \Psi \rangle = -(2\pi)^{-1}\vec{\eta} \cdot \langle \Psi | \sum_i (\vec{\nabla}_i \hat{V}) | \Psi \rangle = 0, \quad (24)$$

and

$$\tilde{\varrho}_1(\vec{\eta}) = (2\pi)^{-1}\langle \Psi | \sum_i \hat{D}_i^{(1)}(\vec{\eta}) | \Psi \rangle$$
$$= (2\pi)^{-1}\langle \Psi | \sum_i \{(\vec{\eta} \times \vec{\nabla}_i) \cdot (\vec{\eta} \times \vec{\nabla}_i) + \vec{r}_i \cdot (\vec{\nabla}_i \hat{V})$$
$$- (\vec{r}_i \cdot \vec{\eta})[\vec{\eta} \cdot (\vec{\nabla}_i \hat{V})]\} | \Psi \rangle = 0. \quad (25)$$

Equations (24) and (25) can be greatly simplified by noting that:

$$\sum_i (\vec{\nabla}_i \hat{V}) + \sum_A (\vec{\nabla}_A \hat{V}) = 0, \quad (26)$$

$$\sum_i \vec{r}_i \cdot (\vec{\nabla}_i \hat{V}) + \sum_A \vec{r}_A \cdot (\vec{\nabla}_A \hat{V}) = -\hat{V}, \quad (27)$$

$$(\vec{\eta} \times \vec{\nabla}_i) \cdot (\vec{\eta} \times \vec{\nabla}_i) = \hat{\nabla}_i^2 - (\vec{\eta} \cdot \vec{\nabla}_i)(\vec{\eta} \cdot \vec{\nabla}_i), \quad (28)$$

and

$$[(\vec{\eta} \cdot \vec{r}_i)(\vec{\eta} \cdot \vec{\nabla}_i), \hat{H}] = (\vec{\eta} \cdot \vec{r}_i)[\vec{\eta} \cdot (\vec{\nabla}_i \hat{V})] + (\vec{\eta} \cdot \vec{\nabla}_i)(\vec{\eta} \cdot \vec{\nabla}_i), \quad (29)$$

where $\hat{H}$ is the Hamiltonian of the system under consideration.

Application of the above relations yields:

$$\tilde{\varrho}_0(\vec{\eta}) = (2\pi)^{-1}\vec{\eta} \cdot \langle \Psi | \sum_A (\vec{\nabla}_A \hat{V}) | \Psi \rangle = -(2\pi)^{-1}\left(\vec{\eta} \cdot \sum_A \vec{f}_A\right), \quad (30)$$

with $\vec{f}_A$ denoting the Hellmann–Feynman force acting upon nucleus A, and:

$$\tilde{\varrho}_1(\vec{\eta}) = (2\pi)^{-1}\langle \Psi | \sum_i \{\hat{\nabla}_i^2 - (\vec{\eta} \cdot \vec{\nabla}_i)(\vec{\eta} \cdot \vec{\nabla}_i) + \vec{r}_i \cdot \vec{\nabla}_i \hat{V} - (\vec{r}_i \cdot \vec{\eta})[\vec{\eta} \cdot (\vec{\nabla}_i \hat{V})]\} | \Psi \rangle$$
$$= -(2\pi)^{-1}\left\{\langle \Psi | 2\hat{T} + \hat{V} + \sum_A \vec{r}_A \cdot (\vec{\nabla}_A \hat{V}) | \Psi \rangle\right.$$
$$\left. + \langle \Psi | \sum_i [(\vec{\eta} \cdot \vec{r}_i)(\vec{\eta} \cdot \vec{\nabla}_i), \hat{H}] | \Psi \rangle\right\}, \quad (31)$$

where $\hat{T}$ is the kinetic energy operator. The higher-order partial densities can be obtained in an analogous way by applying hypervirial commutators similar to that of Eq. (29).

Inspection of Eq. (30) reveals that the magnitude of the zeroth-order partial density is closely related to the sum of the Hellmann–Feynman forces on nuclei. This sum vanishes for many types of trial wavefunctions. Since $\tilde{\varrho}_0(\vec{\eta})$ yields zero upon spherical averaging, in principle it could be integrated, but only if the integration over the angular variables was carried out first. The same is true about all partial densities $\tilde{\varrho}_k(\vec{\eta})$ with even values of k. The magnitude of the first-order partial density reflects the accuracy to which the virial theorem is satisfied by the trial wavefunction. This becomes obvious when one considers a spherically averaged $\tilde{\varrho}_1(\vec{\eta})$:

$$\begin{aligned}\tilde{\varrho}_1^{\text{aver}} &= (3\pi)^{-1}\langle \Psi | \sum_i [\hat{\vec{V}}_i^2 + \vec{r}_i \cdot (\vec{\nabla}_i \hat{V})] | \Psi \rangle \\ &= -(3\pi)^{-1}\langle \Psi | 2\hat{T} + \hat{V} + \sum_A \vec{r}_A \cdot (\vec{\nabla}_A \hat{V}) | \Psi \rangle. \end{aligned} \tag{32}$$

To illustrate the above points, let us consider the case of the 1s state of the hydrogen-like atom with:

$$\hat{V} = -Zr^{-1}, \tag{33}$$

and a general trial wavefunction $\Psi(r)$ that decays at least exponentially for large r. Direct application of Eqs. (5) and (6) yields:

$$\begin{aligned}\tilde{\varrho}(R) = (4/3R) &\int_0^R r\Psi^*(Z\Psi + 2\Psi' + r\Psi'')\,dr \\ &+ (2/3)\int_R^\infty r^{-2}\Psi^*[-Z(R^2 - 3r^2)\Psi - 2R^2(\Psi' - r\Psi'')]\,dr. \end{aligned} \tag{34}$$

One immediately notes that, for large R, the second integral dies off at least exponentially and the asymptotic behavior of $\tilde{\varrho}(R)$ is given by the first term of Eq. (34), which can be easily shown to be equal (in the limit of large R) to

$$\tilde{\varrho}(R) \to -(1/3\pi R)\langle \Psi | 2\hat{T} + \hat{V} | \Psi \rangle, \tag{35}$$

in agreement with Eqs. (30)–(32).

4. Conclusions

The Hiller–Sucher–Feinberg identity does not afford electron density that is integrable in general. This conclusion is drawn from the long-distance asymptotic expansion for $\tilde{\varrho}(R)$. Although this means that an unmodified HSF density cannot be utilized in evaluation of expectation values of one-electron operators, knowledge of its long-distance behavior makes suitable renormalization of $\tilde{\varrho}(R)$ possible, which might result in elimination of the infinities encountered in the integrations over electronic coordinates.

Acknowledgements. Research described in this publication was supported by the National Science Foundation under contract CHE-9015566, the Camille and Henry Dreyfus Foundation New Faculty Award Program, the US Department of Energy under contract DE-FC05-85ER250000.

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