

# Density per particle as a descriptor of Coulombic systems

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**It is shown that for finite Coulombic systems the density per particle,  $\sigma \equiv \rho/N$ , determines the value of any observable quantity. The associated variational principle is derived.**

Conventional quantum mechanics tells us that the  $N$ -particle wavefunction, a function of  $4N$  coordinates that is normalized to one, can be used to compute the value of any observable quantity. Hohenberg and Kohn extended this result, proving that the ground state particle density, a function of three coordinates that is normalized to  $N$ , contains sufficient information to compute the value of any observable (1). The present paper offers a further extension: for finite Coulombic systems, knowledge of the shape function,

$$\sigma(\vec{r}) \equiv \frac{\rho(\vec{r})}{N} = \sum_{s_1, \dots, s_N} \int \int \int \Psi^*(\vec{r}_1, s_1, \dots, \vec{r}_N, s_N) \delta(\vec{r} - \vec{r}) \Psi(\vec{r}_1, s_1, \dots, \vec{r}_N, s_N) d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N, \quad [1]$$

is sufficient to compute the value of any observable quantity.  $\sigma$  is called the shape function (2) because it contains information about the relative amount of particle density at one point in space relative to other places but contains no directly accessible information about the number of particles in the system. Because multiplication of  $\sigma$  by the number of identical particles in the system gives the conventional  $N$ -particle density,  $\rho$  may be considered the “single-particle density” or “density per particle” of an  $N$ -particle system.

## Theoretical Development

The Hohenberg–Kohn theorem states that the particle density,  $\rho$ , uniquely determines the number of identical particles,  $N$ , and determines the external potential,  $v_0$ , to within an additive constant. Knowledge of  $N$  and  $v_0$  allows us to construct the Hamiltonian operator, which determines the  $N$ -particle wavefunction,  $\Psi$ , which can be used to find the value of any observable. So, in principle, one can find the value of any observable from  $\rho$ .

Hohenberg and Kohn’s observation may be viewed as the fundamental theorem of density functional theory (DFT) (so named because the Hohenberg–Kohn theorem intimates that any observable may be expressed as a functional of the particle density) (3, 4). DFT has been used by electronic-structure theorists, among others (5, 6), to design efficient computational procedures (7) and to build a conceptual framework for understanding electronic structure and molecular reactivity (3).

The present paper proceeds in much the same way, first proving that  $\sigma$  determines  $v_0$ , then showing that  $\sigma$  can be used to find  $N$ . Extension of this result to excited states is straightforward. The Hohenberg–Kohn variational principle is extended from the density to the shape function.

**THEOREM 1.** *For any Coulombic system,  $\sigma$  determines the external potential,  $v_0$ , up to an additive constant.*

*Proof:* The external potential of a Coulombic system may be expressed (in units with  $\hbar = e = m_{\text{particle}} = 1$ ) as

$$v_0(\vec{r}) = \sum_{\alpha} \left( q \frac{Z_{\alpha}}{|\vec{r} - \vec{R}_{\alpha}|} \right). \quad [2]$$

Here particles of charge  $q$  move in the field produced by stationary point charges of charge  $Z_{\alpha}$  at the points  $\vec{R}_{\alpha} = (X_{\alpha}, Y_{\alpha}, Z_{\alpha})$ . Steiner’s corollary to Kato’s theorem (8–11) provides an explicit procedure for generating the external potential from the density: the type of particle density under consideration determines  $q$  (e.g.,  $q = -1$  for electron density), the positions of cusps in the density locate the point charges, and the point charges themselves are found from the cusp condition:

$$Z_{\alpha} = \frac{1}{2q} \left( \frac{1}{\rho(\vec{r})} \cdot \frac{\partial \bar{\rho}(\vec{r})}{\partial |\vec{r} - \vec{R}_{\alpha}|} \right) \Bigg|_{\vec{r}=\vec{R}_{\alpha}}. \quad [3]$$

( $\bar{\rho}$  denotes the spherical average of the density about the point  $\vec{R}_{\alpha}$ .) Appendix A treats the exceptional case in which the density at one of the point charges is zero.

A similar procedure can be performed for Coulombic  $\sigma$ . The charge,  $q$ , is obtained from the type of particle. Because  $\sigma = \rho/N$  and  $N$  is a constant, cusps in  $\rho$  and  $\sigma$  occur at the same places, and

$$\begin{aligned} \frac{1}{2q} \left( \frac{1}{\rho(\vec{r})} \cdot \frac{\partial \bar{\rho}(\vec{r})}{\partial |\vec{r} - \vec{R}_{\alpha}|} \right) \Bigg|_{\vec{r}=\vec{R}_{\alpha}} &= \frac{1}{2q} \left( \frac{1}{N\sigma(\vec{r})} \cdot \frac{\partial N\bar{\sigma}(\vec{r})}{\partial |\vec{r} - \vec{R}_{\alpha}|} \right) \Bigg|_{\vec{r}=\vec{R}_{\alpha}} \\ &= \frac{1}{2q} \left( \frac{N}{N\sigma(\vec{r})} \cdot \frac{\partial \bar{\sigma}(\vec{r})}{\partial |\vec{r} - \vec{R}_{\alpha}|} \right) \Bigg|_{\vec{r}=\vec{R}_{\alpha}} \\ &= \frac{1}{2q} \left( \frac{1}{\sigma(\vec{r})} \cdot \frac{\partial \bar{\sigma}(\vec{r})}{\partial |\vec{r} - \vec{R}_{\alpha}|} \right) \Bigg|_{\vec{r}=\vec{R}_{\alpha}}. \end{aligned} \quad [4]$$

Eq. 3, coupled with the analysis of Eq. 4, indicates that

$$Z_{\alpha} = \frac{1}{2q} \left( \frac{1}{\sigma(\vec{r})} \cdot \frac{\partial \bar{\sigma}(\vec{r})}{\partial |\vec{r} - \vec{R}_{\alpha}|} \right) \Bigg|_{\vec{r}=\vec{R}_{\alpha}}, \quad [5]$$

and hence the cusps in  $\sigma$  determine not only the positions of the point charges,  $\vec{R}_{\alpha}$ , but also the charges themselves,  $Z_{\alpha}$ .  $v_0$  is then obtained by substituting  $q$ , the  $\vec{R}_{\alpha}$ , and the  $Z_{\alpha}$  into Eq. 2.<sup>†</sup> □

To prove that  $\sigma$  also determines  $N$ , we need some background:

Abbreviation: DFT, density functional theory.

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<sup>†</sup>This argument is similar to E. B. Wilson’s justification of density functional theory (10).

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CONVEXITY POSTULATE. Suppose we are given a Coulombic external potential  $v_0$ . The decrease in the system's ground state energy due to the addition of a particle gets successively less as the number of particles increases until finally the energy stops decreasing at all on the addition of further particles (because these particles are no longer bound by  $v_0$ , they are no longer part of the system). Mathematically:

$$E[N + 1, v_0] = E[N, v_0] > E[N, v_0] - E[N - 1, v_0] \quad [6]$$

unless the  $N$ th particle is unbound, in which case:

$$E[N + 1, v_0] = E[N, v_0] = E[N - 1, v_0]. \quad [7]$$

Though a formal proof seems never to have been given, the convexity postulate may be assumed to be true because there are no known counterexamples for Coulombic systems (3). Lieb, for instance, in a formal discussion of density functional theory, suggests that Eq. 6 holds for all systems with a Coulombic interparticle repulsion (12). The establishment of a variational principle for the grand canonical ensemble in density functional theory requires the assumption of convexity (3, 13, 14).

The convexity postulate may be rationalized by the following argument [see also the discussion of Perdew, Parr, Levy, and Balduz (14)]. Consider that when one adds a particle to an  $N - 1$  particle system, the number of interparticle repulsion terms in the Hamiltonian increases by  $N - 1$  (for a total of  $N(N - 1)/2$  such terms). Because each successive particle contributes one more interparticle repulsion term to the Hamiltonian than did the previous particle, and because this term raises the total energy, each additional particle is expected to reduce the energy of the system less than did the previous particle, up until the extreme case where the previous particle was unbound.

An important corollary follows directly from Eq. 6:

IONIZATION POTENTIAL COROLLARY. Provided the particle removed was bound to the system, successive ground state ionization potentials (IP) of a Coulombic potential increase:

$$\text{IP}(N + 1 \rightarrow N) < \text{IP}(N \rightarrow N - 1). \quad [8]$$

This relationship between successive ionization potentials is important because the logarithmic derivative of the density asymptotically approaches the constant value (15–19)

$$\lim_{r \rightarrow \infty} \left[ \frac{\partial \ln(\rho(\vec{r}))}{\partial r} \right] = -\sqrt{8 \cdot \text{IP}}, \quad [9]$$

where  $r$  is the spherical coordinate that measures the distance to the average particle position, ( $\langle x \cdot \sigma \rangle$ ,  $\langle y \cdot \sigma \rangle$ ,  $\langle z \cdot \sigma \rangle$ ).

THEOREM 2. For the ground state of any Coulombic system,  $\sigma$  determines the number of particles bound to the system,  $N$ . Equivalently, in Coulombic systems  $N$  is a functional of  $\sigma$ .

Proof: The logarithmic derivative of the density equals the logarithmic derivative of the shape function, because

$$\begin{aligned} \frac{\partial \ln(\rho(\vec{r}))}{\partial r} &= \frac{\partial \ln(N\sigma(\vec{r}))}{\partial r} = \frac{\partial(\ln(N) + \ln(\sigma(\vec{r})))}{\partial r} \\ &= \frac{\partial \ln(N)}{\partial r} + \frac{\partial \ln(\sigma(\vec{r}))}{\partial r} = \frac{\partial \ln(\sigma(\vec{r}))}{\partial r}. \end{aligned} \quad [10]$$

Substituting this result into Eq. 9, we find that

$$\lim_{r \rightarrow \infty} \left[ \frac{\partial \ln(\sigma(\vec{r}))}{\partial r} \right] = -\sqrt{8 \cdot \text{IP}}. \quad [11]$$

Now we show that it is impossible for one Coulombic shape function,  $\sigma$ , to correspond to two different particle numbers,  $N_1$  and  $N_2$ . First, obtain  $v_0$  from the procedure of Theorem 1. Eq. 11

implies that if the system  $(v_0, N_1)$  and the system  $(v_0, N_2)$  have the same shape function, their ionization potentials are also the same. Because the ionization potential corollary indicates that the ionization potential is a strictly decreasing function of  $N$ , if the ionization potentials for the  $N_1$ -particle and  $N_2$ -particle systems are the same, then  $N_1 = N_2$ . Just as  $f$  is a function of  $x$  when every  $x$  corresponds to one and only one value of  $f$ ,  $N$  is a functional of  $\sigma$  because every Coulombic  $\sigma$  corresponds to one and only one value of  $N$ .

The argument is clarified by an explicit procedure for computing  $N$  from  $\sigma$ . Use the methods of Theorem 1 to find  $v_0[\sigma]$ . Now, construct the Hamiltonian for  $v_0[\sigma]$  and every possible number of particles,  $N = 1, 2, 3, \dots$ . Solve the Schrödinger equation for each of these systems and get the ionization potentials of their ground states. It follows from the ionization potential corollary that no two of these systems have the same IP; hence only one of these IPs is consistent with the asymptotic decay of  $\sigma$  (Eq. 11).  $N[\sigma]$  is the number of particles corresponding to that IP.  $\square$

Theorem 2's proof is similar to the original Hohenberg–Kohn proof (1), where it is shown that it is impossible for one density,  $\rho(\vec{r})$ , to correspond to two external potentials,  $v_1$  and  $v_2$ , which differ by more than a constant. Hence the external potential may be considered a functional of the ground state density. [(Analogous to the second part of the proof, there is a search procedure for finding the external potential that goes with a given density (12, 20)).

THEOREM 3. For the ground state of any Coulombic system, knowledge of  $\sigma$  is sufficient for finding the value of any observable.

Proof:  $\sigma$  determines both  $v_0$  (Theorem 1) and  $N$  (Theorem 2). Knowledge of  $N$  and  $v_0$  allows construction of the Hamiltonian operator, which determines the ground state  $N$ -particle wavefunction,  $\Psi$ , which can be used to find the value of any observable.  $\square$

Theorem 3 implies that, for Coulombic systems, any observable property is a functional of the shape function. The following alternative proofs of Theorems 2 and 3 are instructive.

Alternative Proof of Theorem 2: Consider the following asymptotic series for the logarithmic derivative of  $\sigma$  (16–19):

$$\begin{aligned} \left[ \frac{\partial \ln(\sigma(\vec{r}))}{\partial r} \right] \xrightarrow{\text{large } r} & -\sqrt{8 \cdot \text{IP}} + 2 \left( \frac{(Z_{\text{total}} + q(N - 1))}{\sqrt{2 \cdot \text{IP}}} - 1 \right) \left( \frac{1}{r} \right) \\ & + \left( \text{terms with higher powers of } \frac{1}{r} \right), \end{aligned} \quad [12]$$

where  $Z_{\text{total}}$  is the total nuclear charge (the sum of all the  $Z_\alpha$ ),  $N$  is the number of particles, and all other terms have the same meaning as in Eq. 11. Just as in the derivation of Eq. 11, we use the equivalence of the logarithmic derivatives of  $\rho$  and  $\sigma$  (Eq. 10 to derive Eq. 12 from the analogous expression for the density (16–19).

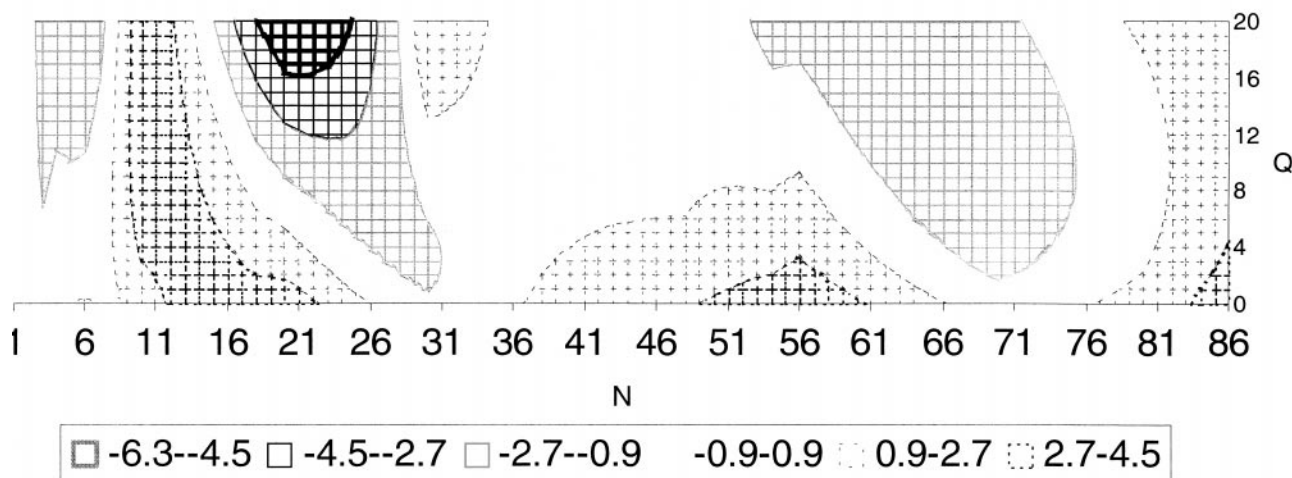
By going to very long range (where  $1/r$  is infinitesimal), we can find the value of the IP from  $\sigma$ . We can find  $Z_{\text{total}}$  by summing the result of Eq. 5 over all the nuclear cusps. Using

$$\lim_{r \rightarrow \infty} \left[ \frac{\partial \left\{ \frac{\partial \ln(\sigma(\vec{r}))}{\partial r} \right\}}{\partial \left( \frac{1}{r} \right)} \right] = 2 \left( \frac{(Z_{\text{total}} + q(N - 1))}{\sqrt{2 \cdot \text{IP}}} - 1 \right), \quad [13]$$

we obtain

$$N = 1 - \frac{1}{q} \left[ Z_{\text{total}} + \frac{1}{4} \cdot \lim_{r \rightarrow \infty} \left[ \frac{\partial \ln(\sigma(\vec{r}))}{\partial r} \left( \frac{\partial^2 \ln(\sigma(\vec{r}))}{\partial \left( \frac{1}{r} \right) \partial r} + 2 \right) \right] \right]. \quad [14]$$

## Absolute Error in N-1 (computed using Eq. [16])



**Fig. 1.** The absolute error in the particle number as computed by Eq. 16 for atoms with atomic numbers 1 through 86 and their first 20 positive ions.  $N$  is the number of electrons in the atom, and  $Q$  is the total charge on the atom. The atomic number is  $Q + N$ . The legend relates patterns of crosshatching to ranges of absolute error.

Because Eq. 14 is an explicit formula for  $N$  in terms of  $\sigma$  and  $Z_{\text{total}}$  (which we calculate from  $\sigma$  using Eq. 5), *Theorem 2* is proved.  $\square$

This proof suggests an alternative proof of *Theorem 3* that does not require knowledge of the external potential (but only the knowledge of  $Z_{\text{total}}$  needed to prove *Theorem 2*).

*Alternative Proof of Theorem 3:* *Theorem 2* establishes that  $\sigma$  can be used to find  $N$ . Invoking the definition of the shape function ( $N\sigma = \rho$ ), we see that  $\sigma$  determines  $\rho$ . Invoking the Hohenberg–Kohn theorem (1), we have *Theorem 3*.  $\square$

It seems prudent to explore whether there are practical methods for determining  $N$  from  $\sigma$ . Eqs. 5 and 14 imply that  $(N - 1)$  is homogeneous of degree one with respect to the coordinate scaling (21–23) of  $\sigma$ :

$$(N - 1)[\sigma(\alpha x, \alpha y, \alpha z)] = \alpha(N - 1)[\sigma(x, y, z)]. \quad [15]$$

We choose to express the functional  $(N - 1)$  as a linear combination of moments of the shape function that have the correct coordinate scaling (24, 25). Choosing seven evenly spaced moments, we then optimize the coefficients in the moment expansion by minimizing the least squares error on the data set of the Hartree–Fock shape functions for all neutral atoms with atomic numbers between 1 and 86 and their first 20 positive ions. Doing so, one obtains the fit:

$$\begin{aligned} [N - 1]_{\text{moments}} = & 38,450 \cdot \langle r^{-2} \cdot \sigma(r) \rangle^{\frac{1}{2}} \\ & - 192,300 \cdot \langle r^{-1.8} \cdot \sigma(r) \rangle^{\frac{5}{9}} + 398,900 \cdot \langle r^{-1.6} \cdot \sigma(r) \rangle^{\frac{5}{8}} \\ & - 442,300 \cdot \langle r^{-1.4} \cdot \sigma(r) \rangle^{\frac{5}{7}} + 278,300 \langle r^{-1.2} \cdot \sigma(r) \rangle^{\frac{5}{6}} \\ & - 94,760 \langle r^{-1.0} \cdot \sigma(r) \rangle^1 + 13,710 \langle r^{-.8} \cdot \sigma(r) \rangle^{\frac{5}{4}}, \quad [16] \end{aligned}$$

which has an rms absolute error of 1.78. Fig. 1 provides a plot of the absolute error of Eq. 16. Considering the simplistic functional form of Eq. 16 and that 1,806 systems are fit with

just 7 constants, the accuracy obtained is remarkable.<sup>†</sup> Although this numerical test does not constitute a proof of *Theorem 2*, it does support the assertion that the shape function determines the number of particles. Moreover, this numerical test indicates that practical ways to determine properties from the shape function are within the purview of current theoretical methods.

### Excited States

**THEOREM 4.** *If  $\sigma$  is the shape function for either a ground or excited state of a Coulombic system, then  $\sigma$  determines everything.*

*Proof:* Suppose we are given a Coulombic shape function,  $\sigma_0(\vec{r})$ . To prove the theorem, we need to show that  $\sigma_0$  determines  $\nu_0$ ,  $N$ , and also the state (ground state, first excited state, etc.) of the system. Once we know that we want the  $k$ th eigenstate of the Hamiltonian,  $\hat{H}(N, \nu_0)$ , then we can find the appropriate wavefunction  $\Psi_k$  and hence all properties of the system.

**Part 1.** Getting  $\nu_0$ . *Theorem 1* applies to both ground and excited state Coulombic shape functions because Kato’s theorem applies to both ground and excited states (8, 9, and 26). In the rare case where  $\sigma_0$  is zero at a nuclear cusp (as in the 2p state of the hydrogen atom), the more elaborate treatment of *Appendix A* is necessary.

**Part 2.** Getting  $N$ . Eq. 12 can be generalized to excited states, hence both ground and excited state shape functions determine  $N$  through Eq. 14.<sup>‡</sup>

<sup>†</sup>One could argue that it is dangerous to evaluate a functional’s reliability on the set of data to which it was fitted. Because (no. of fitted parameters/no. of systems fit) = 0.0039, this is not expected to be a problem. This was confirmed by performing a calculation in which the fitted set consisted only of atomic systems (atomic numbers 1 to 86) whose net charges were even (0, +2, +4, . . . , +20). This fit differed negligibly from that presented in the text.

<sup>‡</sup>To treat excited states (as the hydrogen 2p state) whose shape functions are not asymptotically spherically symmetric, it is necessary to use the spherical average of  $\sigma$  in Eqs. 14 and 17.

**Part 3.** Getting  $k$ . Parts 1 and 2 of this proof show that  $\sigma_0$  determines  $N$  and  $v_0$  and hence the Hamiltonian operator,  $\hat{H}(N, v_0)$ . Now we need to find which eigenstate of this Hamiltonian corresponds to  $\sigma_0$ . To do so, we first find the energy of  $\sigma_0$ . Then, we find which eigenstate with this energy has  $\sigma_0$  as its shape function.

To find the energy of the excited state, we consider the asymptotic behavior of the spherically averaged shape function<sup>‡</sup>:

$$\lim_{r \rightarrow \infty} \left[ \frac{\partial \ln(\bar{\sigma}(\tilde{r}))}{\partial r} \right] = -\sqrt{8 \cdot \text{IP}_k}, \quad [17]$$

where  $\text{IP}_k$  is defined as (16):

$$\text{IP}_k \equiv E[N, v_0, k\text{th excited state}] - E[N - 1, v_0, \text{ground state}]. \quad [18]$$

Given the ground state energy of the  $N - 1$  particle system, Eqs. 17 and 18 determine the energy of  $\sigma_0$ .

Sometimes several eigenstates of  $\hat{H}(N, v_0)$  have the same energy. By computing the shape function for each of these eigenstates, we can find which eigenstate (or linear combination of eigenstates) is consistent with  $\sigma_0$ . This mapping from  $\sigma_0$  to a Coulombic wavefunction allows us to determine the value of any observable. Similar to the degenerate state problem in ground state density functional theory, sometimes several degenerate eigenfunctions of  $\hat{H}(N, v_0)$  have  $\sigma_0$  as their shape function; in this case, we may allow  $\sigma_0$  to correspond to a family of degenerate eigenstates.  $\square$

This proof is easily extended into density functional theory; for a Coulombic system, both ground and excited state densities determine everything (26). The proof is similar: Eqs. 4 and 10 indicate that changing from the shape function to the density does not change the ideas in parts 1 and 3 of the proof. Because we can find  $N$  by integrating the density, part 2 of the proof is eliminated.

### Variational Principle

The Hohenberg–Kohn proof that  $\rho$  determines the value of every observable would be of less practical importance without the computationally useful variational principle:

**DFT VARIATIONAL PRINCIPLE.** *If  $\rho_0$  is the ground state density of the  $N$ -particle system with external potential  $v_0$ , then the total energy,  $E_{v_0}[\rho_0]$ , is less than  $E_{v_0}[\rho]$ , where  $\rho$  is a different  $N$ -particle density (1).*

Recognizing that the practical importance of *Theorem 3* is enhanced if there is a variational principle for the energy as a functional of  $\sigma$ , we now develop a variational principle.

The DFT variational principle applies to a situation in which we are given a specific  $N$  and  $v_0$ . Using the fact that  $N$  and  $v_0$  are given, we define the energy as a functional of  $\sigma$  according to:

$$E_{v_0, N}[\sigma] \equiv E_{v_0}[N\sigma] = E_{v_0}[\rho]. \quad [19]$$

If  $E_{v_0}[\rho_0] \leq E_{v_0}[\rho]$  at constant  $N$ , then  $E_{v_0}[N\rho_0] \leq E_{v_0}[N\rho]$ . Eq. 19 then indicates that  $E_{v_0, N}[\rho_0] \leq E_{v_0, N}[\rho]$ . Hence, the variational principle for the density is easily extended the shape function.

As an example, consider the Levy constrained search energy functional (27):

$$E_{v_0}[\rho] = \min_{\left\{ \Psi \mid \int \rho(\tilde{r}) = N \iint \Psi^*(\tilde{r}_1, \dots, \tilde{r}_N) \delta(\tilde{r}_1 - \tilde{r}) \Psi(\tilde{r}_1, \dots, \tilde{r}_N) d\tilde{r}_1, \dots, d\tilde{r}_N \right\}} \cdot \left( \frac{\langle \Psi | \hat{H}(N, v_0) | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right), \quad [20]$$

where the notation indicates that we search for the  $\Psi$  consistent with  $\rho$ , which minimizes  $\langle \Psi | \hat{H}(N, v_0) | \Psi \rangle / \langle \Psi | \Psi \rangle$ . We can write an equivalent functional for  $\sigma$ , namely:

$$E_{v_0, N}[\sigma] = \min_{\left\{ \Psi \mid \int \sigma(\tilde{r}) = \iiint \Psi^*(\tilde{r}_1, \dots, \tilde{r}_N) \delta(\tilde{r}_1 - \tilde{r}) \Psi(\tilde{r}_1, \dots, \tilde{r}_N) d\tilde{r}_1, \dots, d\tilde{r}_N \right\}} \cdot \left( \frac{\langle \Psi | \hat{H}(N, v_0) | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right). \quad [21]$$

Comparison of Eqs. 20 and 21 reveals that  $E_{v_0, N}[\sigma] = E_{v_0}[\rho]$ , in accord with Eq. 19 (the Euler–Lagrange equations associated with the variational principles for  $\sigma$  and  $\rho$  are discussed in depth in ref. 2). A different constrained search approach to  $E_{v_0, N}[\sigma]$  has been developed by Lieb (12).

One can concoct other variational principles for  $\sigma$ ; for instance, by not constraining the number of particles, one arrives at a different variational principle. Because the energy vs. the number of bound particles is a strictly decreasing function, this variational principle minimizes at the shape function corresponding to the maximum number of particles bound by the external potential,  $v_0$ .

### Discussion

Density functional theory is motivated by the observation that, compared to the wavefunction, the density represents a simpler, more compact package that still contains all of the essential information about the system. The shape function represents a package that is marginally simpler than the density, yet still contains all of the essential information about finite Coulombic systems.

The restriction to finite systems is induced by the use of asymptotic decay in the proofs of *Theorem 2*. In essence, this restriction reflects the fact that systems with an infinite number of particles (but finite particle density) have a  $\sigma$  that is zero everywhere. (Actually, such a  $\sigma$  may be thought of as a generalized function (as the  $\alpha \rightarrow 0^+$  limit of  $(\alpha^3/8\pi)e^{-\alpha r}$ ) that is zero everywhere but normalized to one.) We may be able to extend the applicability of shape functional theory to infinite systems by treating an infinite system as the limit of an appropriate sequence of finite systems.

More severe than the restriction to finite systems is the restriction to Coulombic systems. Because there is no easy test for determining whether a shape function is Coulombic,<sup>§</sup> it is desirable to extend *Theorem 3*'s domain of applicability to a topologically well-defined set of shape functions. The present author believes that it will be possible to extend the domain of *Theorem 3* to the set of normalized and continuous shape functions.<sup>¶</sup> Once such an extension is established, approximate functionals whose domain is the set of normalized and continuous shape functions can be defined. If these functionals are sufficiently smooth, their functional derivatives exist and can be used to predict how the energy, chemical potential, etc., change as our system evolves from one Coulombic system (reactants) to another (products). However, even after an appropriate extension is established, developing approximate functionals may be

<sup>§</sup>A method does exist: find  $v_0$  from Eq. 29 and  $N$  from Eq. 14. Solve the Schrödinger equation for  $\hat{H}(N, v_0)$ ;  $\sigma$  is Coulombic if and only if one of the eigenvectors of  $\hat{H}(N, v_0)$  has this shape function.

<sup>¶</sup>The set of Coulombic shape functions is a tiny subset of the set of  $v$ -representable shape functions. This indicates that shape functional theory suffers from problems that are similar in form to, but more severe in magnitude than, those associated with the Hohenberg–Kohn formulation of density functional theory.

difficult since the shape function is not size consistent—the shape function for  $H_2$  at infinite internuclear distance is not the sum of the shape functions for the isolated hydrogen atoms (as that shape function would not be normalized).

The result that  $\sigma$  determines everything for finite Coulombic systems provides a fundamental insight into the character of Coulombic systems. But studies of the shape function are more than theoretical bric-a-brac: the shape function is an experimentally observable quantity. Most experimental methods for measuring the density of Coulombic systems in fact measure the shape function. For instance, an experiment might find that the signal caused by the electron density at the point  $\vec{r}_0$  is  $0.2\mathcal{Q}$ , whereas the signal caused by the density at  $\vec{r}_1$  is  $0.6\mathcal{Q}$ . Such directly accessible experimental data are enough to determine the shape function, which is just the amount of density at  $\vec{r}_1$  relative to that at  $\vec{r}_0$ . (By contrast, one does not know that the density at  $\vec{r}_1$  is  $15[\text{electrons}/(\text{Angstrom})^3]$  until one has calibrated the apparatus with a system of known density.) Because molecular reaction, rearrangement, and spectroscopy are changes from one finite Coulombic system to another, we may study chemistry by observing changes in the shape function. This motivates the author's pursuit of a shape function based description of chemical reactivity.

## Appendix A

This appendix extends the cusp condition (8, 9, 11) (Eq. 3) to the case where the density at the point charge is zero. The development is patterned after that of Pack and Brown (11).

Assume that

$$\frac{1}{|\vec{r} - \vec{R}_\alpha|} \gg \frac{1}{|\vec{r}_i - \vec{R}_\beta|}, \frac{1}{|\vec{r}_i - \vec{r}_j|}, \frac{1}{|\vec{R}_\beta - \vec{R}_\gamma|}. \quad [22]$$

That is, the only nearly singular point in the Hamiltonian is associated with the coalescence of a particle at  $\vec{r}$  with a point charge at  $\vec{R}_\alpha$ . In this case, we may write the Schrödinger equation as

$$\left[ -\frac{1}{2}\nabla_{\vec{r}}^2 + \frac{Zq}{r} + (\text{terms of order } r^0 \text{ and higher}) \right] \Psi(\vec{r}|\tau) = 0, \quad [23]$$

where we have chosen to center the coordinate system at  $\vec{R}_\alpha$ , and we have denoted the parametric dependence of the wavefunction on the other spatial and spin coordinates by  $\tau \equiv (s_1, \vec{r}_2, s_2, \dots, \vec{r}_N, s_N)$ . Following Pack and Brown, we then expand  $\Psi(\vec{r}|\tau)$  according to:

$$\Psi(\vec{r}|\tau) = \sum_{l=0}^{\infty} \sum_{m=-l}^l f_{l,m}(r|\tau) r^l Y_{l,m}(\theta, \phi) \quad [24]$$

$$f_{l,m}(r|\tau) = \sum_{k=0}^{\infty} f_{l,m}^{(k)}(\tau) r^k,$$

where  $Y_{l,m}(\theta, \phi)$  are the spherical harmonics. Substitution of Eq. 24 into Eq. 23 and the resulting recursion relation for the  $f_{l,m}^{(k)}(\tau)$  gives Eq. 15 of ref. 11, which in our notation is:

$$\Psi(\vec{r}|\tau) = r^\lambda \left\{ \sum_{m=-\lambda}^{\lambda} f_{\lambda,m}^{(0)}(\tau) Y_{\lambda,m}(\theta, \phi) \left( 1 + \frac{Zq}{\lambda+1} r \right) + r \sum_{m=-(\lambda+1)}^{\lambda+1} f_{\lambda+1,m}^{(0)}(\tau) Y_{\lambda+1,m}(\theta, \phi) + O(r^2) \right\}. \quad [25]$$

Here  $\lambda$  is chosen such that  $f_{\lambda,m}^{(0)}(\tau) \neq 0$ , and  $f_{l,m}^{(0)}(\tau) = 0$  for  $0 \leq l < \lambda$ .

These results are extended by considering the form of the spherically averaged  $N$ th order density matrix,  $\bar{\Gamma}_N(\vec{r}|\tau)$ . Near  $\vec{R}_\alpha$ ,

$$\bar{\Gamma}_N(\vec{r}|\tau) = r^{2\lambda} \left\{ \sum_{m=-\lambda}^{\lambda} (f_{\lambda,m}^{(0)}(\tau))^2 \left( 1 + \frac{Zq}{\lambda+1} r \right) + O(r^2) \right\}. \quad [26]$$

Eq. 26 is simpler than Eq. 25, because the orthonormality of the spherical harmonics causes many terms to vanish upon spherical averaging. Dividing  $\bar{\Gamma}_N(\vec{r}|\tau)$  by  $r^{2\lambda}$  and differentiating reveals that

$$\left[ \frac{\partial \left( \frac{\bar{\Gamma}_N(r|\tau)}{r^{2\lambda}} \right)}{\partial r} \right]_{r=0} = 2 \frac{Zq}{\lambda+1} \bar{\Gamma}_N(0|\tau). \quad [27]$$

To get results for the spherical average of the density, we integrate both sides of Eq. 26 with respect to the spatial variables  $\vec{r}_2, \vec{r}_3, \dots, \vec{r}_N$  and sum both sides with respect to the spin variables  $s_1, s_2, \dots, s_N$ . Defining  $(f_{\lambda,m}^{(0)})^2 \equiv \iiint (f_{\lambda,m}^{(0)}(\tau))^2 d\tau$ , we find that

$$\bar{\rho}(\vec{r}) = r^{2\lambda} \left\{ \sum_{m=-\lambda}^{\lambda} (f_{\lambda,m}^{(0)})^2 \left( 1 + \frac{Zq}{\lambda+1} r \right) + O(r^2) \right\}, \quad [28]$$

and hence

$$\left[ \frac{\partial \left( \frac{\bar{\rho}(r)}{r^{2\lambda}} \right)}{\partial r} \right]_{r=0} = 2 \frac{Zq}{\lambda+1} \bar{\rho}(0). \quad [29]$$

Because of Eq. 4, Eq. 29 also applies to the spherically averaged shape function.

The revised procedure for finding the external potential from the density is then:

- (i) Find the cusps in the density; at these points,  $\lambda = 0$ , and Eq. 29 reduces to Eq. 3.
- (ii) Find the points,  $\vec{r}_0$ , where  $\rho(\vec{r}) = 0$ . These points correspond either to the location of point charges, nodal surfaces, or both. When a point charge is coincident with a nodal surface, the point charge will generally be located at the point of highest symmetry along the surface (as in the 2p state of hydrogen).
- (iii) At the position of each point charge, find the smallest integer,  $k$ , such that:

$$\lim_{r \rightarrow r_0} \left\{ \frac{\rho(\vec{r})}{|\vec{r} - \vec{r}_0|^{2k}} \right\} \neq 0. \quad [30]$$

- (iv) Apply Eq. 29 with  $\lambda = k$ .

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