

## Orthonormal orbitals for the representation of an arbitrary density

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An alternative to the Gilbert construction is presented. It is shown that for any nonnegative, normalized density an arbitrary number of orthonormal orbitals can be constructed with squares which sum, with minimal restrictions on the occupation numbers, to the given density. In three dimensions substantial freedom remains in the choice of orbitals within the basic scheme. The kinetic-energy density obtained includes the Weizsäcker term and another term which, in simple cases, is proportional to the cube of the density.

### I. INTRODUCTION

An important question in density functional theory, based on the Hohenberg-Kohn theorem,<sup>1</sup> is that of the  $n$  representability<sup>2</sup> of an arbitrary density. Given a density  $\rho_n(\vec{r})$  with<sup>3</sup>

$$\rho_n(\vec{r}) \geq 0, \quad \int \rho_n(\vec{r}) d\vec{r} = n \quad (1)$$

is it always possible to find an antisymmetric,  $n$ -electron wave function leading to this density? In the Kohn-Sham<sup>4</sup> formulation the question demands even more: that  $\rho(\vec{r})$  can be obtained from a single determinant function or (equivalently) an idempotent density matrix. Gilbert<sup>5</sup> has provided an affirmative answer to this question and suggested a construction for the necessary orbitals. His construction is based on a partitioning of space, and continuous, smooth orbitals which are also orthonormal have not been explicitly formulated.

The purpose of this paper is to show by explicit construction that for any given density an arbitrary number of functions, which are continuous, smooth, orthonormal, and extend over all space, exist such that

$$\rho_n(\vec{r}) = \sum_k \lambda_k |\phi_k(\vec{r})|^2. \quad (2)$$

The occupation numbers are unrestricted (for complex  $\phi_k$ ) or restricted only to pairwise degeneracy (for real  $\phi_k$ ), apart from the fundamental  $n$  representability constraint for the 1-matrix<sup>2</sup>

$$0 \leq \lambda_k \leq 1, \quad \sum_k \lambda_k = n. \quad (3)$$

When  $n$  of the  $\lambda_k = 1$  and the remainder are zero, an idempotent density matrix is defined.

### II. ONE-DIMENSIONAL CASE

For simplicity a one-dimensional case is considered first:  $\rho(x)$  for  $x_1 \leq x \leq x_2$ . To emphasize the fact that any number of orbitals can be found,

$\rho$  is renormalized so that

$$\int_{x_1}^{x_2} \rho(x) dx = 1. \quad (4)$$

A function  $f(x)$  is now constructed as

$$f(x) = 2\pi \int_{x_1}^x \rho(y) dy \quad (5)$$

so that  $f$  is monotone increasing with  $f(x_1) = 0$ ,  $f(x_2) = 2\pi$ , and

$$\frac{df}{dx} = 2\pi\rho(x). \quad (6)$$

Another positive function is defined as

$$p(x) = [\rho(x)]^{1/2}. \quad (7)$$

The required orbitals are then<sup>6</sup>

$$\phi_k(x) = p(x) \exp[ikf(x)] \quad (8)$$

for any  $k = 0, \pm 1, \pm 2, \dots$ . It is immediately apparent that

$$|\phi_k(x)|^2 = [p(x)]^2 = \rho(x) \quad (9)$$

and if  $\rho$  itself is smooth and continuous, these functions will be as well.

The  $\{\phi_k\}$  are also orthonormal:

$$\begin{aligned} \int_{x_1}^{x_2} \phi_k^*(x) \phi_{k'}(x) dx &= \int_{x_1}^{x_2} \rho(x) \exp[i(k-k')f(x)] dx \\ &= (2\pi)^{-1} \int_{x_1}^{x_2} \exp[i(k-k')f] \frac{df}{dx} dx \\ &= (2\pi)^{-1} \int_0^{2\pi} \exp[i(k-k')f] df = \delta_{kk'}. \end{aligned} \quad (10)$$

With the present normalization, Eq. (2) becomes

$$\rho(x) = \sum_k \lambda_k |\phi_k(x)|^2, \quad (11)$$

where  $0 \leq \lambda_k \leq 1/n$ ,  $\sum_k \lambda_k = 1$  for any integer  $n \geq 1$ .

It is also possible to define real orthonormal functions whose squares sum to  $\rho$ . Let

$$\begin{aligned}\psi_0(x) &= p(x), \\ \psi_{2j-1}(x) &= 2^{1/2} p(x) \sin[jf(x)], \\ \psi_{2j}(x) &= 2^{1/2} p(x) \cos[jf(x)], \quad j > 0.\end{aligned}\quad (12)$$

These are readily shown to be orthonormal and

$$\begin{aligned}(\psi_0)^2 &= \rho, \\ (\psi_{2j-1})^2 + (\psi_{2j})^2 &= 2\rho.\end{aligned}\quad (13)$$

If these real orbitals are to be used to construct  $\rho$ , it is necessary that  $\lambda_{2j-1} = \lambda_{2j}$ .

### III. THREE-DIMENSIONAL CASE

In three dimensions the coordinates are taken to be  $a, b, c$  with  $a_1 \leq a \leq a_2$ , etc., and volume element<sup>7</sup>  $d\vec{r} = \alpha(a)\beta(b)\gamma(c) da db dc$ . A density integrated over two of the variables is introduced:

$$\bar{\rho}(a) = \int_{b_1}^{b_2} \int_{c_1}^{c_2} \rho(a, b, c) \beta(b) \gamma(c) db dc \quad (14)$$

$$\begin{aligned}\int \phi_k^*(\vec{r}) \phi_k(\vec{r}) d\vec{r} &= \int_{a_1}^{a_2} da \alpha(a) \left( \int_{b_1}^{b_2} db \beta(b) \int_{c_1}^{c_2} dc \gamma(c) \rho(a, b, c) \right) \exp[i(k - k')f(a)] \\ &= \int_{a_1}^{a_2} \alpha(a) \bar{\rho}(a) \exp[i(k - k')f(a)] da = \int_0^{2\pi} \exp[i(k - k')f] df.\end{aligned}\quad (17)$$

The change is most readily made for a function of a single variable, so such a function must (somewhat arbitrarily) be introduced in the three-dimensional case. In three dimensions not only is the choice of coordinate system arbitrary, but any of the three coordinates can be chosen as  $a$ .<sup>8</sup>

In the case of a spherically symmetric density it is natural to use spherical polar coordinates with  $a = r$ . Then  $\rho(\vec{r})$  and  $\bar{\rho}(r)$  differ only by a factor of  $4\pi$ . A further still more arbitrary decomposition can be made, based on the fact that

$$\sum_{m=-l}^l [Y_l^m(\theta, \phi)]^* Y_l^m(\theta, \phi) = \frac{2l+1}{4\pi}. \quad (18)$$

The density can be divided into pieces

$$\rho = \sum_l \rho_l \quad (19)$$

with

$$\rho_l = g_l \rho, \quad (20)$$

where the  $g_l$  are polynomials in  $r$  summing to 1. Orbitals are then defined as

$$\phi_{klm} = c_l \rho_l^{1/2} \exp(ikf_l) Y_l^m \quad (21)$$

with  $f_l$  an indefinite integral of  $\rho_l$ , etc. The effect of the normalization constant  $c_l$  can be offset by an occupation number.

and the phase function  $f$  is taken to be

$$f(a) = 2\pi \int_{a_1}^a \alpha(a') \bar{\rho}(a') da'. \quad (15)$$

The complex, orthonormal orbitals are then

$$\phi_k(\vec{r}) = [\rho(\vec{r})]^{1/2} \exp[ikf(a)] \quad (16)$$

and real orbitals  $\psi$  can be expressed in terms of sines or cosines of  $kf(a)$ . The proof of orthonormality proceeds as in the one-dimensional case.

It may seem somewhat strange that the phase factor in three dimensions involves only one coordinate. A phase factor of some sort is necessary if different orbitals are to be orthogonal. In the method used here the phase function must be an indefinite integral of the density so that a relationship analogous to Eq. (6) will hold and the critical change of variables corresponding to that between the second and the third lines of Eq. (10) can be made. In the three-dimensional case this is

### IV. KINETIC ENERGY

One reason for expressing  $\rho$  as a sum of squares of orbitals is to obtain an expression for the kinetic energy. If  $\rho$  is given by either Eq. (2) or Eq. (11) then it corresponds to a density matrix

$$\gamma(\vec{r}; \vec{r}') = \sum_k \lambda_k \phi_k(\vec{r}) \phi_k^*(\vec{r}'). \quad (22)$$

If the density, and thus the  $\phi_k$ , approach 0 at infinity (for finite systems) or satisfy appropriate periodicity conditions (for infinite, periodic systems) then the kinetic energy can be expressed as

$$T = \frac{1}{2} \sum_k \lambda_k \int |\nabla \phi_k|^2 d\vec{r}. \quad (23)$$

For orbitals of the type considered here

$$\nabla \phi_k = [\nabla p(\vec{r}) + ikp(\vec{r}) \nabla f(a)] \exp[ikf(a)], \quad (24)$$

so that the contribution of  $\phi_k$  to the kinetic energy density is

$$\begin{aligned}\frac{\lambda_k}{2} |\nabla \phi_k|^2 &= \frac{\lambda_k}{2} \{ (\nabla p)^2 + k^2 p^2 [\nabla f(a)]^2 \} \\ &= \lambda_k \left( \frac{(\nabla \rho)^2}{8\rho} + \frac{k^2}{2} \rho [\nabla f(a)]^2 \right).\end{aligned}\quad (25)$$

The first term is of the familiar Weizsäcker form.<sup>9</sup> The second term depends on the specific choice of  $f$ . For a one-dimensional density or a

spherical density with  $a=r$  it will be proportional to  $\rho^3$ .

#### V. DISCUSSION

It has been shown that any density corresponds to an  $n$ -representable density matrix for any  $n$ . The natural orbitals are continuous, smooth, and extend over all space, as well as being orthonormal. In three dimensions substantial freedom remains in the choice of orbitals, even within the general scheme considered here.

The kinetic-energy density includes the familiar Weizsäcker term and another term which, in

simple cases, is proportional to  $\rho^3$ . It is not suggested that the orbitals constructed here have any physical significance, but because of the flexibility which remains in their choice, some relationship to physically significant orbitals may be possible.

An investigation of noninteracting fermions in one dimension<sup>10</sup> suggests that orbitals of the form developed here are not likely to be eigenfunctions of a single Hamiltonian with a local potential unless the density satisfies special conditions. Non-local effective potentials appropriate to these orbitals will be considered in the future.

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<sup>1</sup>P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).

<sup>2</sup>A. J. Coleman, *Rev. Mod. Phys.* **35**, 668 (1963).

<sup>3</sup>The density considered here could be the total change density or the density for spin-up or spin-down electrons only. The association of spin functions with the orbitals defined here is straightforward and will not be explicitly considered.

<sup>4</sup>W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1964).

<sup>5</sup>T. L. Gilbert, *Phys. Rev. B* **12**, 2111 (1975).

<sup>6</sup>The construction of orbitals as the square root of the density times a phase factor has a long history. Cf., e.g., W. Macke, *Ann. Phys. (Leipzig)* **17**, 1 (1955), as well as Ref. 5. The novel feature in the present work is the form of the phase factor.

<sup>7</sup>Cartesian, spherical polar, and cylindrical coordinates are all of this form; elliptic coordinates are not.

<sup>8</sup>It would still be possible to use elliptic coordinates but with the rather peculiar choice of  $a = \phi$ .

<sup>9</sup>C. F. von Weizsäcker, *Z. Phys.* **96**, 431 (1935).

<sup>10</sup>J. E. Harriman (unpublished).