A density functional perspective for one-particle systems

H. L. Neal

Department of Physics
and
Center for Theoretical Studies of Physical Systems
Clark Atlanta University
Atlanta, Georgia 30314

Abstract

Density functional theory is discussed in the context of one-particle systems. We show that the ground state density \( \rho_0(x) \) and energy \( E_0 \) are simply related to a family of external potential energy functions with ground state wave functions \( \psi_n(x) \propto \rho_0(x)^n \) and energies \( E_n = 2nE_0 \) for certain integer values of \( n \).
I. INTRODUCTION

The objective of density functional theory (DFT) is to transform the many-particle problem into an equivalent one-particle problem. Therefore, it seems pedagogically reasonable to give an introductory level presentation of DFT, in the context of one-particle systems, that (briefly) ovoids references to the complications imposed by systems with two or more particles. Several papers devoted to DFT have appeared in this journal.

The basic idea of DFT is to transform from the ground state wave function \( \psi_0 \) to the one-particle density function \( \rho_0 \) as a focus of attention. This has obvious advantages for many-particle systems. For one-particle systems, it allows the exact ground state energy \( E_0 \) to be determined via the variational principle with respect to the one-particle density. For one-particle systems

\[
\rho_0(x) = |\psi_0(x)|^2,
\]

where the density function satisfies the normalization condition

\[
\int \rho_0(x) dx = 1.
\]

The wave function \( \psi_0 \) satisfies the time independent Schrödinger equation

\[
\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi_0(x) = E_0 \psi_0(x),
\]

where \( V(x) \) is the external potential energy function for the particle of mass \( m \). We consider systems where \( \psi_0 \) is real, so that the energy may be written as

\[
E_0 = \int \sqrt{\rho_0(x)} \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \sqrt{\rho_0(x)} dx.
\]

We now introduce the energy density functional

\[
E[\rho] = T[\rho] + \int \rho(x) V(x) dx,
\]

where the kinetic energy density functional \( T[\rho] \) is

\[
T[\rho] = \int \sqrt{\rho(x)} \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \sqrt{\rho(x)} dx.
\]

The arbitrary density function \( \rho \) satisfies the same normalization condition as \( \rho_0 \) in Eq. (2). According to the Hohenberg-Kohn (HK) theorem, (1) the external potential \( V(x) \) is determined uniquely by \( \rho_0(x) \), and (2) the energy density functional \( E[\rho] \) satisfies the condition

\[
E[\rho] \geq E_0.
\]
Variationally speaking, the minimum value of $E[\rho]$ with respect to $\rho$ yields the ground state energy $E_0 = E[\rho_0]$. The density functional $T[\rho]$ may be written more conveniently as

$$T[\rho] = \frac{\hbar^2}{8m} \int \left( \frac{1}{\rho(x)} \frac{d\rho(x)}{dx} \right)^2 \rho(x) dx$$  \hspace{1cm} (8)

According to the variational principle

$$\delta \left( E[\rho] - \lambda \int \rho(x) dx \right) = 0,$$  \hspace{1cm} (9)

where $\lambda$ is a Lagrange multiplier. In terms of variational (or functional) derivatives

$$\frac{\delta E[\rho]}{\delta \rho(x)} = \lambda,$$  \hspace{1cm} (10)

so that the equation for the density becomes

$$- \frac{\hbar^2}{8m} \left\{ \frac{d^2}{dx^2} \ln \rho(x)^2 + \left( \frac{d}{dx} \ln \rho(x) \right)^2 \right\} + V(x) = \lambda,$$  \hspace{1cm} (11)

This equation may be rewritten in a form similar to Eq. (3):

$$\left[ - \frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_{\text{eff}}(x; [\rho]) \right] \rho(x) = 2\lambda \rho(x),$$  \hspace{1cm} (12)

where the effective potential $V_{\text{eff}}$ is

$$V_{\text{eff}}(x; [\rho]) = 2V(x) + \frac{\hbar^2}{4m} \left( \frac{1}{\rho(x)} \frac{d}{dx} \rho(x) \right)^2.$$  \hspace{1cm} (13)

Equation (12) is an example of the nonlinear Schrödinger equation that is encountered in DFT calculations. The standard method of solution is to solve it iteratively, starting with an initial guess for $V_{\text{eff}}$. At the solution point $\rho = \rho_0$ and $\lambda = E_0$. Equation (11) may be transformed into a first order differential equation for $y(x) = d \ln \rho(x)/dx$:

$$- \frac{\hbar^2}{8m} \left\{ 2 \frac{d}{dx} y(x) + y(x)^2 \right\} + V(x) = \lambda.$$  \hspace{1cm} (14)

This is a version of the Riccati equation. A solution method for this equation has been discussed in some detail by Haley.\textsuperscript{6}

In Sec. II, we derive equations that give the external potentials and ground state energies for the family of ground state wave functions $\psi_n(x) \propto \rho_0(x)^n$, where $n = 2^j$ and $j (j \geq 0)$ is an integer. In Sec. III, we apply the results of Sec. II to several well known systems. In Sec. IV, we give a summary and some closing remarks.
II. GENERATING EXTERNAL POTENTIALS WITH THE GROUND STATE DENSITY

In this section we demonstrate one consequence of the HK theorem: The ground state density $\rho_0(x)$ determines a family of external potentials and their respective ground state energies. We give some examples in the next section.

Consider the wave functions given by

$$\psi_n(x) = c_n \rho_0(x)^n,$$  \hspace{1cm} (15)

where the integer $n = 2^j$ for the integer $j$, and the constants $c_n$ are chosen to normalize $\psi_n(x)$. Each ground state wave function given by Eq. (15) satisfies the Schrödinger equation

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_n(x) \right] \psi_n(x) = E_n \psi_n(x),$$  \hspace{1cm} (16)

where $E_n$ is the ground state energy for the external potential $V_n(x)$. For example, applying Eqs. (12) and (13) iteratively for $n = 1, 2, \text{ and } 4$ yields

$$V_1(x) = V_{\text{eff}}(x; \rho_0)$$
$$= 2V(x) + \frac{\hbar^2}{4m} \left( \frac{1}{\rho_0(x)} \frac{d}{dx} \rho_0(x) \right)^2; \hspace{1cm} (17)$$

$$V_2(x) = 2V_1(x) + (2)^2 \frac{\hbar^2}{4m} \left( \frac{1}{\rho_0(x)} \frac{d}{dx} \rho_0(x) \right)^2; \hspace{1cm} (18)$$

$$V_4(x) = 2V_2(x) + (4)^2 \frac{\hbar^2}{4m} \left( \frac{1}{\rho_0(x)} \frac{d}{dx} \rho_0(x) \right)^2. \hspace{1cm} (19)$$

In the Appendix, we show that the family of external potential energy functions and ground state energies are given, respectively, by

$$V_n(x) = 2nV(x) + (2n - 1) n \frac{\hbar^2}{4m} \left( \frac{1}{\rho_0(x)} \frac{d}{dx} \rho_0(x) \right)^2;$$  \hspace{1cm} (20)

$$E_n = 2nE_0. \hspace{1cm} (21)$$

III. EXAMPLES

We have applied Eq. (20) to (i) the particle in a box, (ii) the harmonic oscillator, and (iii) the attractive delta potential. The results for these systems are summarized in Table I.
IV. SUMMARY AND REMARKS

We have presented DFT for one-particle systems. As a consequence of the HK theorem, the ground state density $\rho_0(x)$ determines the external potential $V(x)$ and a family of related external potentials $V_n(x)$ given by Eq. (20). Moreover, the ground state energies for these external potentials are given by Eq. (21). These results are directly applicable to higher dimensional systems by replacing $x$ by the position vector $\mathbf{r}$ and the derivative operator $d/dx$ by the vector operator $\nabla$.

We hope that our presentation will be useful and insightful to teachers and students of quantum mechanics.

Acknowledgments

The author thanks Professor R. E. Mickens for helpful discussions.

APPENDIX A: A DERIVATION OF EQUATIONS (20) AND (21)

1. Equation (20)

The equations for the external potentials discussed in Sec. II may be transformed into the linear difference equation

$$z_{j+1} = 2z_j + \left(2^{j+1}\right)^2 f(x),$$

where $z_j = V_{2j}(x)$ and the function $f(x)$ is

$$f(x) = \frac{\hbar^2}{4m} \left( \frac{1}{\rho_0(x)} \frac{d}{dx} \rho_0(x) \right)^2.$$  (A2)

The solution to Eq. (A1) is

$$z_j = 2^j z_0 + 2^j f(x) \sum_{i=0}^{j-1} 2^{i+1}$$

$$= 2^j z_0 + 2^{j+1} f(x) \left(2^j - 1\right).$$  (A3)

In terms of $n = 2^j$

$$V_n(x) = nV_1(x) + 2n (n-1) f(x).$$  (A4)

Inserting the expression for $V_1(x)$ given by Eq. (17) into this equation yields Eq. (20).
2. Equation (21)

Consider the two equations resulting from the insertion of the ground state densities \( \rho_0(x) \) and \( \rho_n(x) \propto \rho_0(x)^{2n} \), respectively, into Eq. (11):

\[
-\frac{\hbar^2}{8m} \left\{ \frac{d^2}{dx^2} \ln \rho_0(x)^2 + \left( \frac{d}{dx} \ln \rho_0(x) \right)^2 \right\} + V(x) = E_0; \quad \text{(A5)}
\]

\[
-\frac{\hbar^2}{8m} \left\{ 2n \frac{d^2}{dx^2} \ln \rho_0(x)^2 + 4n^2 \left( \frac{d}{dx} \ln \rho_0(x) \right)^2 \right\} + V_n(x) = E_n. \quad \text{(A6)}
\]

Multiplying the first equation by \( 2n \) and then subtracting the resulting equation from the second equation yields Eq. (21).

\[ \text{a) Electronic mail: hneal@cau.edu.} \]

1. P. Hohenberg and W. Kohn, “Inhomogeneous electron gas,” Phys. Rev. 136, B864–B871 (1964);
   W. Kohn and L. Sham, “Self-consistent equations including exchange and correlation effects,”
   ibid. 140, A1133–A1138 (1965).

2. H. L. Neal, “Density functional theory of one-dimensional two-particle systems,” Am. J. Phys. 66, 512–516 (1998); Arno Schindlmayr. “Universality of the Hohenberg–Kohn functional,” ibid. 67, 933–934 (1999); Nathan Argaman and Guy Makov, “Density functional theory: an introduction,”
   ibid. 68, 69–79 (2000).

3. If the potential \( V(x) \) is determined by \( \rho_0(x) \), then the potential \( V'(x) = V(x) + C \) is also
determined by \( \rho_0(x) \), where \( C \) is a constant.

4. G. Arfken, Mathematical Methods for Physicists (Academic Press, New York, 1985), Chap. 17.

5. Daniel Zwillinger, Handbook of Differential Equations (Academic Press, New York, 1989),
   pp. 288–291.

6. Stephen B. Haley, “An underrated entanglement: Riccati and Schrödinger equations,” Am. J. Phys. 65, 237–243 (1997).

7. V. Lakshmikantham and D. Trigiante, Theory of Difference Equations: Numerical Methods and
   Applications (Academic Press, New York, 1988), p. 38.
TABLE I: The external potential $V(x)$, the ground state density $\rho_0(x)$, the ground state energy $E_0$, and the external potential $V_n(x)$ given by Eq. [20] for (i) the particle in a box, (ii) the harmonic oscillator, and (iii) the attractive delta potential.

| System | $V(x)$ | $\rho_0(x)$ | $E_0$ | $V_n(x)$ |
|--------|--------|-------------|-------|----------|
| (i)    | $\begin{cases} 0 \text{ for } |x| < L/2 \\ \infty \text{ otherwise} \end{cases}$ | $(2/L)\cos^2(\pi x/L)$ | $(\hbar\pi/L)^2/2m$ | $2n (2n - 1) E_0 \tan^2(\pi x/L)$ |
| (ii)   | $m\omega^2 x^2/2$ | $\sqrt{m\omega/\hbar} \exp(-m\omega x^2/\hbar)$ | $\hbar\omega/2$ | $4n^2 V(x)$ |
| (iii)  | $-g\delta(x)$ | $(mg/\hbar^2) \exp(-2mg |x|/\hbar^2)$ | $-mg^2/2\hbar^2$ | $2n V(x) - 2n (2n - 1) E_0$ |