PHYSICAL REVIEW A

GENERAL PHYSICS

THIRD SERIES, VOLUME 27, NUMBER 1 JANUARY 1983

Complementary variational principle for density-functional theories

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(Received 29 April 1982)

A method for determining complementary energy functionals within a density-functional framework is derived. In particular, if $H[P]$ is defined as a functional of the density equal to an energy functional $E_U[P]$ less a Coulomb energy term $(\nu/2)\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \times |x-y|^{-1}P(x)P(y)d^3y\,d^3x$ with ν a positive constant, then the functional

$$E_L[P] \equiv H[P] - \int_{\mathbb{R}^3} \frac{\delta H[P]}{\delta P(x)} P(x) d^3x - \frac{1}{8\pi\nu} \int_{\mathbb{R}^3} \left| \vec{\nabla} \frac{\delta H[P]}{\delta P(x)} \right|^2 d^3x + N[P] \lim_{|x|\to\infty} \frac{\delta H[P]}{\delta P(x)}$$

with $N[P] = \int_{\mathbb{R}^3} P(x)d^3x$ is complementary to $E_U[P]$ whenever the second variation of $H[P]$ is positive. Explicit forms of $E_L[P]$ for the Thomas-Fermi and the Thomas-Fermi—Dirac—von Weizsäcker theories are given and used to obtain both lower and upper bounds to the atomic energies of these theories. A discussion on the corresponding Hohenberg-Kohn complementary functional is also presented.

I. INTRODUCTION

Much effort has been expended in the search for an energy functional of the density which yields both good atomic energies and accurate atomic densities.[1–7] The early theory of Thomas[1] and Fermi[2] in its unmodified form, although exact for infinitely dense systems, has been found to be inappropriate for atoms. In 1935, von Weizsäcker[3] suggested a correction to the Thomas-Fermi kinetic energy which remedied three major defects of atomic TF (Thomas-Fermi) theory; in TFW (Thomas-Fermi—von Weizsäcker) theory (i) the density is finite at the nuclei, (ii) negative ions exist, and (iii) the density falls off exponentially extending out to infinity. Other corrections such as Dirac's exchange term[4] and Scott's inner-shell contribution[5] also have been of fundamental importance.[6] Recently, attempts have been made to refine the energy functional such that shell structure can be obtained.[7]

Generally, solving for atomic densities and energies becomes a more difficult problem each time the energy functional is improved. Typically, an Euler-Lagrange integro-differential equation must be solved for varying values of the chemical potential, the Lagrange multiplier, until the value is found which yields a density that integrates to the correct number of electrons. When molecules are being studied, the calculations are even more involved and often impractical since spherical symmetry is lost.

For a given N-electron system, the energy of a known functional can be determined alternatively by searching for the N-electron density that minimizes the functional. The obvious flaw with this approach is that in practice only an upper bound to the energy is obtained. In the present work, standard variational methods are combined with Poisson's equation to give a complementary energy functional. Assuming certain specified conditions hold, the new complementary functional will have a local maximum at each local minimum of the old energy functional and the value of the functionals will be identical at these extrema. Thus, one can obtain both upper and lower bounds on the energy of a system by evaluating the original energy functional and its complement at trial densities, and one can make the difference in these bounds arbitrarily small simply by improving the trial densities.

II. THEORY

The basic approach in the theory of complementary variational principles is to find two functionals which are equal at extrema but whose second variations are opposite in sign.[8] This is accomplished by first introducing a general functional which has a domain consisting of function pairs and then obtaining the desired complementary functionals by enforcing "complementary" restrictions on the domain functions.

Let L_p be a subspace of a Lebesgue space consisting of functions in $1R^n$, real n-dimensional space. Define T to be a linear operator on L_ρ onto a function space L_θ with adjoint T^*: $L_\theta \to L_\rho^*$, where L_ρ^* is the dual of L_ρ and T^* is defined such that

$$\langle \theta, T\rho \rangle = \int_{V_n} (T^*\theta)(x)\rho(x)d^nx + [\theta, \tau\rho] \tag{2.1a}$$

$$= \int_{V_n} (T^*\theta)(x)\rho(x)d^nx + \int_{\partial V_n} (\tau^*\theta)(x)\rho(x)d^{n-1}x \tag{2.1b}$$

for all $\rho \in L_\rho$, $\theta \in L_\theta$; here V_n is the domain of ρ, ∂V_n is the boundary of V_n, $\langle\ ,\ \rangle$ is an inner product on $L_\theta \times L_\theta$, and $[\ ,\ ]$ is a boundary term with τ: $L_\rho \to L_\theta$ being a linear operator and τ^*: $L_\theta \to L_\rho^*$ its adjoint.

Consider the canonical functional

$$I[\theta,\rho] \equiv \int_{V_n} (T^*\theta)(x)\rho(x)d^nx - W[\theta,\rho] \tag{2.2a}$$

$$= \langle \theta, T\rho \rangle - W[\theta,\rho] - \int_{\partial V_n} (\tau^*\theta)(x)\rho(x)d^{n-1}x \tag{2.2b}$$

defined on $L_\theta \times L_\rho$ with $W[\theta,\rho]$ assumed to be twice differentiable. Expanding $I[\theta+\epsilon\eta, \rho+\epsilon\xi]$ about (θ,ρ) gives

$$I[\theta+\epsilon\eta,\rho+\epsilon\xi] = I[\theta,\rho] + \delta I + \delta^2 I + O(\epsilon^3)\ , \tag{2.3}$$

where the first variation δI is

$$\delta I = \int_{V_n} \epsilon\xi(x) \left[(T^*\theta)(x) - \frac{\delta W}{\delta \rho(x)} \right] d^nx + \left\langle \epsilon\eta, T\rho - \frac{\delta W}{\delta\theta} \right\rangle - \int_{\partial V_n} (\tau^*\epsilon\eta)(x)\rho(x)d^{n-1}x \tag{2.4}$$

and the second variation $\delta^2 I$ is

$$\begin{aligned}\delta^2 I = {} & \frac{\epsilon^2}{2} \int_{V_n} \xi(x) \left[\left[T^* - \frac{\delta}{\delta\theta}\frac{\delta W}{\delta\rho} \right] \eta \right](x)d^nx - \frac{\epsilon^2}{2} \int_{V_n} \xi(x) \left[\frac{\delta^2 W}{\delta\rho^2}\xi \right](x)d^nx \\ & - \frac{\epsilon^2}{2}\left\langle \eta, \frac{\delta^2 W}{\delta\theta^2}\eta \right\rangle + \frac{\epsilon^2}{2}\left\langle \eta, \left[T - \frac{\delta}{\delta\rho}\frac{\delta W}{\delta\theta} \right]\xi \right\rangle - \frac{\epsilon^2}{2}\int_{\partial V_n} (\tau^*\eta)(x)\xi(x)d^{n-1}x\ .\end{aligned} \tag{2.5}$$

For (θ,ρ) to be a stationary point of $I[\Theta,P]$, δI must be zero, implying

$$T\rho = \frac{\delta W[\theta,\rho]}{\delta\theta} \quad \text{in } V_n\ , \tag{2.6a}$$

$$T^*\theta = \frac{\delta W[\theta,\rho]}{\delta\rho} \quad \text{in } V_n\ , \tag{2.6b}$$

and

$$\tau\rho = 0 \quad \text{on } \partial V_n\ . \tag{2.6c}$$

To determine the first of the complementary functionals, it is assumed that $\Theta = \theta + \epsilon\eta$ can be obtained as an explicit functional of $P = \rho + \epsilon\xi$ by solving the equation

$$TP = \frac{\delta W[\Theta,P]}{\delta\Theta} \tag{2.7}$$

and then defining $J[P]$ to be $I[\Theta[P],P]$. Expanding $J[P]$ about $P = \rho$ gives

$$J[P] = I[\theta,\rho] + \delta^2 J + O(\epsilon^3)\ , \tag{2.8}$$

where $\delta J = 0$ at $P = \rho$ and $\delta^2 J = \delta^2 I[\Theta[P],P]$. The first variation of Eq. (2.7) leads to the additional equation

$$\left[T - \frac{\delta}{\delta\rho}\frac{\delta W}{\delta\theta} \right]\xi = \frac{\delta^2 W}{\delta\theta^2}\eta + O(\epsilon)\ . \tag{2.9}$$

Substituting this relationship into the expression for $\delta^2 I$, Eq. (2.5) gives the result

$$\delta^2 J = -\frac{\epsilon^2}{2}\int_{V_n} \xi(x) \left[\frac{\delta^2 W}{\delta\rho^2}\xi \right](x)d^nx + \frac{\epsilon^2}{2}\left\langle \eta, \frac{\delta^2 W}{\delta\theta^2}\eta \right\rangle - \epsilon^2 \int_{\partial V_n} (\tau^*\eta)(x)\xi(x)d^{n-1}x\ . \tag{2.10}$$

The complement of $J[P]$ is found by solving

$$T^*\tilde{\Theta} = \frac{\delta W[\tilde{\Theta},P]}{\delta P}\ . \tag{2.11}$$

Conventional methods dictate determining P as a functional of $\tilde{\Theta}$, but $P[\tilde{\Theta}]$ cannot be expressed in closed form when considering most energy functionals of interest; however, using Poisson's equation, Eq. (2.11) can be inverted to give $\tilde{\Theta}[P]$. Defining the complementary functional $G[P]$ as $I[\tilde{\Theta}[P],P]$ and expanding about the stationary point ρ yields

$$G[P] = I[\theta,\rho] + \delta^2 G + O(\epsilon^3)\ , \tag{2.12}$$

where $\delta G = 0$ at $P = \rho$ and $\delta^2 G = \delta^2 I[\tilde{\Theta}[P],P]$. Following similar logic to that used in determining $\delta^2 J$, the first variation of Eq. (2.11) leads to the result

$$\left[T^* - \frac{\delta}{\delta\theta}\frac{\delta W}{\delta\rho}\right]\tilde{\eta} = \frac{\delta^2 W}{\delta\rho^2} + O(\epsilon)\,, \tag{2.13}$$

which implies

$$\delta^2 G = \frac{\epsilon^2}{2}\int_{\partial V_n} \xi(x)\left[\frac{\delta^2 W}{\delta\rho^2}\xi\right](x)\,d^n x - \frac{\epsilon^2}{2}\left\langle \tilde{\eta}, \frac{\delta^2 W}{\delta\theta^2}\tilde{\eta}\right\rangle . \tag{2.14}$$

The crucial theorem has now been proved.

Let (θ,ρ) be a solution to Eqs. (2.6) and suppose that it is possible to obtain solutions to Eqs. (2.7) and (2.11) in the form $\Theta=\Theta[P]$ and $\tilde{\Theta}=\tilde{\Theta}[P]$, respectively. Then for P sufficiently close to ρ, the upper and lower bounds

$$G[P] \equiv I[\tilde{\Theta}[P],P] \le G[\rho] = I[\theta,\rho] = J[\rho] \le I[\Theta[P],P] \equiv J[P] \tag{2.15}$$

hold provided that

$$\delta^2 G = \tfrac{1}{2}\int_{V_n} (P-\rho)(x)\left[\frac{\delta^2 W}{\delta\rho^2}(P-\rho)\right](x)\,d^n x - \tfrac{1}{2}\left\langle \tilde{\Theta}-\theta, \frac{\delta^2 W}{\delta\theta^2}(\tilde{\Theta}-\theta)\right\rangle \le 0\,, \tag{2.16a}$$

$$\delta^n G:\ \mathscr{n} \text{ or } \mathscr{v};\ n=3,4,\ldots \tag{2.16b}$$

where $\mathscr{n}$ represents negligible and $\mathscr{v}$ represents vanishes and

$$\delta^2 J = -\tfrac{1}{2}\int_{V_n} (P-\rho)(x)\left[\frac{\delta^2 W}{\delta\rho^2}(P-\rho)\right](x)\,d^n x + \tfrac{1}{2}\left\langle \Theta-\theta, \frac{\delta^2 W}{\delta\theta^2}(\Theta-\theta)\right\rangle - \int_{\partial V_n}[\tau^*(\Theta-\theta)](x)(P-\rho)(x)\,d^{n-1}x \ge 0\,, \tag{2.17a}$$

$$\delta^n J:\ \mathscr{n} \text{ or } \mathscr{v};\ n=3,4,\ldots\,. \tag{2.17b}$$

If all the inequalities in Eqs. (2.15), (2.16), and (2.17) are reversed, the modified equations remain true.

III. APPLICATION

In density-functional theory, the energy E of an atomic or molecular system consisting of N electrons is defined as the infimum of an energy functional $E_U[P]$ over a set of N-electron densities,

$$L_{\partial N} \equiv \left\{ P \in L:\ \int_{\mathbb{R}^3} P(x)\,d^3x = N \right\},$$

where L is a function space chosen to ensure $E_U[P]$ will be finite. Here it will be convenient to choose L to be a Lebesgue subspace of densities P for which $\lim_{|x|\to\infty}\{\delta H[P]/\delta P(x)\}$ equals a constant independent of direction,

$$H[P] \equiv E_U[P] - \frac{\nu}{2}\int\int |x-y|^{-1} P(y) P(x)\,d^3y\,d^3x$$

and ν a positive constant (the standard value of ν is one). The extremum densities must satisfy an Euler-Lagrange equation which is found by taking the functional derivative of $E_U[P]$ over the set L with the number of electrons $N[P] \equiv \int_{\mathbb{R}^3} P(x)\,d^3x$ restricted to be constant by a Lagrange multiplier equal to the chemical potential μ:

$$0 = \frac{\delta}{\delta P(x)}(E_U[P] - \mu N[P])\,|_{P=\rho} = \left.\frac{\delta E_U[P]}{\delta P(x)}\right|_{P=\rho} - \mu\,. \tag{3.1}$$

To determine the complementary energy functionals, the stationary point equations from Sec. II, Eqs. (2.6a), (2.6b), and (2.6c) must be made equivalent to the above Euler-Lagrange equation. This is accomplished by making the following set of assignments:

$$V_n \equiv \mathbb{R}^3,\ L_\rho = L\,, \tag{3.2a}$$

$$\rho(x) = \rho(x),\ \theta(x) = (T\sigma)(x),\ \sigma \in L\,, \tag{3.2b}$$

$$(T^*T\rho)(x)=\nu\int_{\mathbb{R}^3}\frac{\rho(y)}{|x-y|}d^3y,\quad \tau=0=\tau^*\,, \tag{3.2c}$$

$$T\rho=\frac{\delta W[T\sigma,\rho]}{\delta(T\sigma)}\equiv T\sigma,\quad T^*(T\sigma)=\frac{\delta W[T\sigma,\rho]}{\delta\rho}\equiv\frac{\delta}{\delta\rho}(-H[\rho]+\mu N[\rho])=-\frac{\delta H[\rho]}{\delta\rho}+\mu\,. \tag{3.2d}$$

The densities are assumed to be defined over all space, and the variation is performed within the set L. In Eqs. (3.2b) the canonical functions are assigned; notice that θ is defined as the T image of an element in L. Since the operator $(K\rho)(x)\equiv\nu\int_{\mathbb{R}^3}|x-y|^{-1}\rho(y)d^3y$ is linear, symmetric, and positive definite, K can be decomposed as in Eq. (3.2c). Finally, $W[T\sigma,\rho]$ is defined through Eqs. (3.2d).

The form of $I[\Theta,P]$ can now be derived. Let $TS=T\sigma+\epsilon T\omega$ and $P=\rho+\epsilon\xi$, where ϵ is a small positive number and both S and P are elements of L. Integrating Eqs. (3.2d) implies

$$W[TS,P]=\tfrac{1}{2}\langle TS,TS\rangle-H[P]+\mu\int_{\mathbb{R}^3}P(x)d^3x\,. \tag{3.3}$$

From Eq. (2.2a) one obtains

$$I[TS,P]=\int_{\mathbb{R}^3}(T^*TS)(x)P(x)d^3x-\tfrac{1}{2}\langle TS,TS\rangle+H[P]-\mu\int_{\mathbb{R}^3}P(x)d^3x\,. \tag{3.4}$$

Requiring $TS=TP$ leads to the J functional:

$$J[P]=I[TP,P] \tag{3.5a}$$

$$=\int_{\mathbb{R}^3}(T^*TP)(x)P(x)d^3x-\tfrac{1}{2}\langle TP,TP\rangle+H[P]-\mu\int_{\mathbb{R}^3}P(x)d^3x \tag{3.5b}$$

$$=\frac{\nu}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{P(x)P(y)}{|x-y|}d^3y\,d^3x+H[P]-\mu\int_{\mathbb{R}^3}P(x)d^3x \tag{3.5c}$$

$$=E_U[P]-\mu N[P]\,. \tag{3.5d}$$

$G[P]$ is determined by solving

$$T^*(TS)=-\frac{\delta H[P]}{\delta P}+\mu \tag{3.6}$$

for TS. Using Poisson's equation

$$\nabla^2\int_{\mathbb{R}^3}\frac{S(y)}{|x-y|}d^3y=-4\pi S(x) \tag{3.7}$$

results in the expression

$$TS=-\frac{1}{4\pi\nu}T\nabla^2\left[-\frac{\delta H[P]}{\delta P}+\mu\right]=\frac{1}{4\pi\nu}T\nabla^2\left[\frac{\delta H[P]}{\delta P}-\mu_P\right], \tag{3.8}$$

where μ_P, defined by the limit

$$\mu_P\equiv\lim_{|x|\to\infty}\frac{\delta H[P]}{\delta P(x)}\,, \tag{3.9}$$

is included to ensure that the boundary terms below will vanish. Substituting the expression for TS into Eq. (3.4), the G functional is found

$$G[P]\equiv I\left[\frac{1}{4\pi\nu}T\nabla^2\left[\frac{\delta H[P]}{\delta P(x)}-\mu_P\right],P\right] \tag{3.10a}$$

$$=\frac{1}{4\pi\nu}\int_{\mathbb{R}^3}T^*T\left[\nabla^2\left[\frac{\delta H[P]}{\delta P(x)}-\mu_P\right]\right]P(x)d^3x+H[P]-\mu\int_{\mathbb{R}^3}P(x)d^3x-\frac{1}{32\pi^2\nu^2}\left\langle T\nabla^2\left[\frac{\delta H[P]}{\delta P(x)}-\mu_P\right],T\nabla^2\left[\frac{\delta H[P]}{\delta P(x)}-\mu_P\right]\right\rangle \tag{3.10b}$$

$$=H[P]+\frac{1}{4\pi}\int_{\mathbb{R}^3}\nabla^2\left[\frac{\delta H[P]}{\delta P(x)}-\mu_P\right]\left[\int_{\mathbb{R}^3}\frac{P(y)}{|x-y|}d^3y\right]d^3x-\mu\int_{\mathbb{R}^3}P(x)d^3x-\frac{1}{32\pi^2\nu}\int_{\mathbb{R}^3}\nabla^2\left[\frac{\delta H[P]}{\delta P(x)}-\mu_P\right]\left[\int_{\mathbb{R}^3}|x-y|^{-1}\nabla^2\left[\frac{\delta H[P]}{\delta P(y)}-\mu_P\right]d^3y\right]d^3x\,. \tag{3.10c}$$

After multiple integrations by parts as well as repeated use of Poisson's equation, the following form of $G[P]$ is obtained:

$$
\begin{aligned}
G[P]=H[P]&-\int_{\mathbb{R}^3}\frac{\delta H[P]}{\delta P(x)}P(x)d^3x-\frac{1}{8\pi\nu}\int_{\mathbb{R}^3}\left|\vec{\nabla}\frac{\delta H[P]}{\delta P(x)}\right|^2 d^3x+(\mu_P-\mu)\int_{\mathbb{R}^3}P(x)d^3x\\
&+\frac{1}{8\pi\nu}\vec{\mathrm{n}}\cdot\int_{\partial\mathbb{R}^3}\vec{\nabla}\left[\frac{\delta H[P]}{\delta P(x)}-\mu_P\right]\left[\frac{\delta H[P]}{\delta P(x)}-\mu_P\right]d^2x+\frac{1}{4\pi}\vec{\mathrm{n}}\cdot\int_{\partial\mathbb{R}^3}\vec{\nabla}\left[\frac{\delta H[P]}{\partial P(x)}-\mu_P\right]\\
&\times\left[\int_{\mathbb{R}^3}\frac{P(y)}{|x-y|}d^3y\right]d^2x-\frac{1}{4\pi}\vec{\mathrm{n}}\cdot\int_{\partial\mathbb{R}^3}\left[\frac{\delta H[P]}{\delta P(x)}-\mu_P\right]\vec{\nabla}\left[\int_{\mathbb{R}^3}\frac{P(y)}{|x-y|}d^3y\right]d^2x\\
&-\frac{1}{32\pi^2\nu}\vec{\mathrm{n}}\cdot\int_{\partial\mathbb{R}^3}\vec{\nabla}\left[\frac{\partial H[P]}{\partial P(x)}-\mu_P\right]\left[\int_{\mathbb{R}^3}|x-y|^{-1}\nabla^2\left[\frac{\delta H[P]}{\partial P(y)}-\mu_P\right]d^3y\right]d^2x\\
&+\frac{1}{32\pi^2\nu}\vec{\mathrm{n}}\cdot\int_{\partial\mathbb{R}^3}\left[\frac{\delta H[P]}{\delta P(x)}-\mu_P\right]\vec{\nabla}\left[\int_{\mathbb{R}^3}|x-y|^{-1}\nabla^2\left[\frac{\delta H[P]}{\delta P(y)}-\mu_P\right]d^3y\right]d^2x\ .
\end{aligned}
\tag{3.10d}
$$

All the boundary terms vanish leaving only single integrals, and $G[P]$ simplifies to

$$
G[P]=H[P]-\int_{\mathbb{R}^3}\frac{\delta H[P]}{\delta P(x)}P(x)d^3x-\frac{1}{8\pi\nu}\int_{\mathbb{R}^3}\left|\vec{\nabla}\frac{\delta H[P]}{\delta P(x)}\right|^2 d^3x+(\mu_P-\mu)\int_{\mathbb{R}^3}P(x)d^3x\ . \tag{3.10e}
$$

It must now be verified that the extrema of $J[P]$ are necessarily extrema of $G[P]$ and that $G[\rho]=J[\rho]$ at each extremum ρ. The Euler-Lagrange equation associated with $J[P]$ implies ρ will be an extremum of $J[P]$ whenever

$$
0=\left.\frac{\delta J[P]}{\delta P(x)}\right|_{P=\rho}=\nu\int_{\mathbb{R}^3}\frac{\rho(y)}{|x-y|}d^3y+\left.\frac{\delta H[P]}{\delta P(x)}\right|_{P=\rho}-\mu\ . \tag{3.11}
$$

This guarantees that ρ is an extremum of $G[P]$ since

$$
\begin{aligned}
\left.\frac{\delta G[P]}{\delta P(x)}\right|_{P=\rho}&=\frac{\delta}{\delta P(x)}\left[H[P]-\int_{\mathbb{R}^3}\left[\frac{\delta H[P]}{\delta P(y)}-\mu_P\right]P(y)d^3y-\mu\int_{\mathbb{R}^3}P(y)d^3y\right.\\
&\qquad\left.\left.+\frac{1}{8\pi\nu}\int_{\mathbb{R}^3}\left[\frac{\delta H[P]}{\delta P(y)}-\mu_P\right]\nabla^2\left[\frac{\delta H[P]}{\delta P(y)}-\mu_P\right]d^3y\right]\right|_{P=\rho}
\end{aligned}
\tag{3.12a}
$$

$$
\begin{aligned}
&=\left.\frac{\delta H[P]}{\delta P(x)}\right|_{P=\rho}-\left.\left[\frac{\delta H[P]}{\delta P(x)}-\mu_P\right]\right|_{P=\rho}-\int_{\mathbb{R}^3}\left.\left[\frac{\delta^2 H[P]}{\delta P(x)\delta P(y)}-\frac{\delta\mu_P}{\delta P(x)}\right]\right|_{P=\rho}\rho(y)d^3y\\
&\quad-\mu+\frac{1}{4\pi\nu}\int_{\mathbb{R}^3}\left.\left[\frac{\delta^2 H[P]}{\delta P(x)\delta P(y)}-\frac{\delta\mu_P}{\delta P(x)}\right]\right|_{P=\rho}\nabla^2\left[\left.\left[\frac{\delta H[P]}{\delta P(y)}-\mu_P\right]\right|_{P=\rho}\right]d^3y
\end{aligned}
\tag{3.12b}
$$

$$
=\mu_\rho-\mu+\frac{1}{4\pi\nu}\int_{\mathbb{R}^3}\left.\left[\frac{\delta^2 H[P]}{\delta P(x)\delta P(y)}-\frac{\delta\mu_P}{\delta P(x)}\right]\right|_{P=\rho}\nabla^2\left[\left.\frac{\delta J[P]}{\delta P(x)}\right|_{P=\rho}\right]d^3y \tag{3.12c}
$$

$$
=0\ . \tag{3.12d}
$$

The fact that $G[\rho]$ equals $J[\rho]$ follows upon substituting Eq. (3.11) into Eq. (3.10e) as shown:

$$
\begin{aligned}
G[\rho]=H[\rho]&+\int_{\mathbb{R}^3}\left[\nu\int_{\mathbb{R}^3}\frac{\rho(y)}{|x-y|}d^3y-\mu\right]\rho(x)d^3x-\frac{1}{8\pi\nu}\int_{\mathbb{R}^3}\left|\vec{\nabla}\left[\nu\int_{\mathbb{R}^3}\frac{\rho(y)}{|x-y|}d^3y\right]\right|^2 d^3x\\
&+(\mu_\rho-\mu)\int_{\mathbb{R}^3}\rho(x)d^3x
\end{aligned}
\tag{3.13a}
$$

$$=H[\rho]+\frac{\nu}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}d^3y\,d^3x-\mu\int_{\mathbb{R}^3}\rho(x)d^3x \tag{3.13b}$$

$$=J[\rho]\,. \tag{3.13c}$$

The final condition that must be satisfied if $J[P]$ and $G[P]$ are to be complementary functionals is that their second variations be opposite in sign. Assuming $J[P]$ is truly a minimum, then

$$\delta^2 J[P-\rho]=\tfrac{1}{2}\int_{\mathbb{R}^3}(P-\rho)(x)h[P-\rho](x)d^3x+\frac{\nu}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{(P-\rho)(x)(P-\rho)(y)}{|x-y|}d^3x\,d^3y \tag{3.14}$$

will be positive for P sufficiently close to ρ, where

$$h[P-\rho](x)\equiv\int_{\mathbb{R}^3}\left.\frac{\delta^2 H[\tilde{P}]}{\delta\tilde{P}(x)\delta\tilde{P}(y)}\right|_{\tilde{P}=\rho}(P-\rho)(y)d^3y\,. \tag{3.15}$$

Thus, $G[P]$ will be the complement of $J[P]$ at $P=\rho$ only if

$$\delta^2 G[P-\rho]=-\tfrac{1}{2}\int_{\mathbb{R}^3}(P-\rho)(x)h[P-\rho](x)d^3x-\frac{1}{2\nu}\int_{\mathbb{R}^3}|\vec{\nabla}h[P-\rho](x)|^2d^3x$$
$$+\int_{\mathbb{R}^3}(P-\rho)(y)d^3y\int_{\mathbb{R}^3}\left.\frac{\delta\mu_{\tilde{P}}}{\delta\tilde{P}(x)}\right|_{\tilde{P}=\rho}(P-\rho)(x)d^3x \tag{3.16}$$

is negative.

Under what condition is $\delta^2 G$ indeed negative? Restricting the search over trial densities to $L_{\partial N}$ so that $\int_{\mathbb{R}^3}(P-\rho)(y)d^3y=0$, it would be more than sufficient if

$$\delta^2 H[P-\rho]=\tfrac{1}{2}\int_{\mathbb{R}^3}(P-\rho)(x)h[P-\rho](x)d^3x \tag{3.17}$$

were greater than zero for all trial functions near ρ. This result also follows from the general theorem[8] which states that if $W[TS,P]$ is convex in TS and concave in P, then the inequalities

$$G[P]\le I[T\rho,\rho]\le J[P] \tag{3.18}$$

are satisifed. (In addition, it should be noted that if the concave-convex behavior of $W[TS,P]$ is strictly obeyed, then the extremum density ρ is unique.) Since the kernel $|x-y|^{-1}$ in Eq. (3.2c) is positive definite, $W[TS,P]$ is strictly convex in TS. It therefore suffices to show that $W[TS,P]$ is concave in P. The term $\mu\int_{\mathbb{R}^3}P(x)dx$ is linear, thus convexity of $H[P]$ will guarantee the complementary nature of $G[P]$ and $J[P]$. Unfortunately, $H[P]$ is not always of a convex form in energy density functionals. For specific theories which yield an $H[P]$ that is not convex, it will simply be assumed in this paper that Eq. (3.18) is valid.

When $J[P]$ and $G[P]$ are indeed complementary functionals, then $G[P]$ obtains a maximum at the extremum ρ. This implies that the chemical potential in Eq. (3.10e) plays the role of a Lagrange multiplier on the number of electrons. Therefore, the energy E of an atomic or molecular system consisting of N electrons is simply the supremum of $E_L[P]$ over the set $L_{\partial N}$ where

$$E_L[P]\equiv H[P]-\int_{\mathbb{R}^3}\frac{\delta H[P]}{\delta P(x)}P(x)d^3x-\frac{1}{8\pi\nu}\int_{\mathbb{R}^3}\left|\vec{\nabla}\frac{\delta H[P]}{\delta P(x)}\right|^2d^3x+\mu_P\int_{\mathbb{R}^3}P(x)d^3x\,. \tag{3.19}$$

Henceforth $E_L[P]$ will be referred to as the Poisson complementary functional.

IV. EXAMPLES

In this section the form of the Poisson complementary functional is derived for the TF, the TFDW (Thomas-Fermi—Dirac—von Weizsäcker), and the HK (Hohenberg-Kohn) functionals. The function space over which the supremum of the Poisson complement equals the energy is discussed for each theory. Trial functions are then used to obtain lower and upper bounds on the TF and TFDW atomic energies as well as estimates to the true TF and TFDW densities.

A. Thomas-Fermi theory (Ref. 9)

In atomic TF theory, the energy functional of the density is the sum of a Coulomb term, a kinetic energy term, and a nuclear electronic term

$$E_U^{\rm TF}[P] \equiv \tfrac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{P(x)P(y)}{|x-y|}d^3y\,d^3x + \tfrac{3}{5}\gamma\int_{\mathbb{R}^3}P^{5/3}(x)d^3x - Z\int_{\mathbb{R}^3}\frac{P(x)}{|x|}d^3x\ , \tag{4.1}$$

where $\gamma=(3\pi^2)^{2/3}/2$ in atomic units is the kinetic energy coefficient and $Z>0$ is the nuclear charge. Remembering that the H functional is the energy functional less the Coulomb term, Eq. (4.1) implies

$$H^{\rm TF}[P] = \tfrac{3}{5}\gamma\int_{\mathbb{R}^3}P^{5/3}(x)d^3x - Z\int_{\mathbb{R}^3}\frac{P(x)}{|x|}d^3x\ . \tag{4.2}$$

Therefore, Poisson's functional, Eq. (3.19), in TF theory has the form

$$E_L^{\rm TF}|P| = -\tfrac{2}{5}\gamma\int_{\mathbb{R}^3}P^{5/3}(x)d^3x - \frac{1}{8\pi}\int_{\mathbb{R}^3}\left|\vec{\nabla}\left[\gamma P^{2/3}(x)-\frac{Z}{|x|}\right]\right|^2 d^3x + \mu_P^{\rm TF}\int_{\mathbb{R}^3}P(x)d^3x\ , \tag{4.3}$$

where

$$\mu_P^{\rm TF} \equiv \lim_{|x|\to\infty}\left[\gamma P^{2/3}(x) - \frac{Z}{|x|}\right]\ . \tag{4.4}$$

To ensure that $E_U^{\rm TF}[P]$ and $E_L^{\rm TF}[P]$ are truly complementary functionals, it suffices to show that $\delta^2 H^{\rm TF}[P-\rho]$ is positive; this is easily demonstrated:

$$\delta^2 H^{\rm TF}[P-\rho] = \tfrac{1}{3}\gamma\int_{\mathbb{R}^3}\rho^{5/3}(x)\left[\frac{P(x)}{\rho(x)}-1\right]^2 d^3x > 0\ . \tag{4.5}$$

Bounds on atomic TF energies can be determined by substituting a trial function into Eqs. (4.1) and (4.3). Noting that the gradient term in Eq. (4.3) is integrable only if $\gamma\rho^{2/3}(x)=Z/|x|$ near $|x|=0$, the following function was selected:

$$P^{2/3}(x) = \left[\frac{Z}{\gamma}\right]\frac{1}{|x|(1+\alpha|x|)^3}\ ; \tag{4.6}$$

here α equals $(32/105)(35/3\pi^2)^{1/3}ZN^{-2/3}$ to ensure normalization

$$\int_{\mathbb{R}^3}P(x)d^3x = N\ . \tag{4.7}$$

This trial function not only satisfies the "TF cusp condition" but also falls off as $|x|^{-6}$ as in the exact case. Furthermore, the chosen form of $P(x)$ can easily be integrated analytically and yields the result

$$\frac{E_L^{\rm TF}(N,Z)}{Z^2N^{1/3}} = -\frac{16}{35}\left[\frac{35}{3\pi^2}\right]^{1/3}\left[\frac{512}{429}+\frac{3Z}{7N}\right] \le \frac{E^{\rm TF}(N,Z)}{Z^2N^{1/3}} \le -\frac{1}{35}\left[\frac{35}{3\pi^2}\right]^{1/3}\left[\frac{5056}{143}-\frac{567N}{56Z}\right] = \frac{E_U^{\rm TF}(N,Z)}{Z^2N^{1/3}}\ . \tag{4.8}$$

In the neutral case these inequalities imply

$$-0.7840Z^{7/3} < E^{\rm TF}(Z,Z) < -0.7622Z^{7/3}\ ; \tag{4.9}$$

the exact expression is $E^{\rm TF}(Z,Z) = -0.7687Z^{7/3}$. Using the TF functional along with its Poisson complement the zero-parameter trial function chosen here bounds the neutral TF energy to within better than 1.4%.

B. Thomas-Fermi—Dirac—von Weizsäcker theory

For atomic calculations, the TFDW theory is more appropriate than the TF theory because the TFDW functional includes a gradient correction to the kinetic energy as well as an exchange term:

$$E_U^{\mathrm{TFDW}}[P]=E_U^{\mathrm{TF}}[P]+\frac{w}{2}\int_{\mathrm{1R}^3}|\vec{\nabla}P^{1/2}(x)|^2d^3x-\tfrac{3}{4}C_e\int_{\mathrm{1R}^3}P^{4/3}(x)d^3x\ . \tag{4.10}$$

Often w and C_e are left as parameters in the theory, but it will be convenient in this subsection to assign these coefficients their standard values of 1^3 and $(3/\pi)^{1/3}$,[4] respectively. Continuing as above,

$$\begin{aligned}H^{\mathrm{TFDW}}[P]=\tfrac{1}{2}\int_{\mathrm{1R}^3}|\vec{\nabla}P^{1/2}(x)|^2d^3x+\tfrac{3}{10}(3\pi^2)^{2/3}\int_{\mathrm{1R}^3}P^{5/3}(x)d^3x\\-\frac{3}{4}\left[\frac{3}{\pi}\right]^{1/3}\int_{\mathrm{1R}^3}P^{4/3}(x)d^3x-Z\int_{\mathrm{1R}^3}\frac{P(x)}{|x|}d^3x\end{aligned} \tag{4.11}$$

which implies

$$\begin{aligned}E_L^{\mathrm{TFDW}}[P]=-\tfrac{1}{5}(3\pi^2)^{2/3}\int_{\mathrm{1R}^3}P^{5/3}(x)d^3x+\frac{1}{4}\left[\frac{3}{\pi}\right]^{1/3}\int_{\mathrm{1R}^3}P^{4/3}(x)d^3x+\mu_P^{\mathrm{TFDW}}\int_{\mathrm{1R}^3}P(x)d^3x\\-\frac{1}{8\pi}\int_{\mathrm{1R}^3}\left|\vec{\nabla}\left[-\frac{\nabla^2P^{1/2}(x)}{2P^{1/2}(x)}-\frac{Z}{|x|}+\frac{(3\pi^2)^{2/3}}{2}P^{2/3}(x)-\left[\frac{3}{\pi}\right]^{1/3}P^{1/3}(x)\right]\right|^2d^3x\ ,\end{aligned} \tag{4.12}$$

where

$$\mu_P^{\mathrm{TFDW}}\equiv\lim_{|x|\to\infty}\left[-\frac{\nabla^2P^{1/2}(x)}{2P^{1/2}(x)}-\frac{Z}{|x|}+\frac{(3\pi^2)^{2/3}}{2}P^{2/3}(x)-\left[\frac{3}{\pi}\right]^{1/3}P^{1/3}(x)\right]\ . \tag{4.13}$$

One hopes to be able to prove that for each extremum ρ, the second variation of $J^{\mathrm{TFDW}}[P]\equiv E_U^{\mathrm{TFDW}}[P]-\mu N[P]$ is positive and the second variation of $G^{\mathrm{TFDW}}[P]\equiv E_L^{\mathrm{TFDW}}[P]-\mu N[P]$ is negative whenever P is "near" ρ. Unfortunately, the addition of Dirac's exchange term makes it difficult to determine the sign of the second variations in general (see Lieb's discussion of TFDW theory[10]). Direct computation gives

$$\begin{aligned}\delta^2J[P-\rho]=\tfrac{1}{8}\int_{\mathrm{1R}^3}\rho(x)\left|\vec{\nabla}\left[\frac{P(x)}{\rho(x)}-1\right]\right|^2d^3x-\frac{1}{6}\left[\frac{3}{\pi}\right]^{1/3}\int_{\mathrm{1R}^3}\rho^{4/3}(x)\left[\frac{P(x)}{\rho(x)}-1\right]^2d^3x\\+\frac{(3\pi^2)^{2/3}}{6}\int_{\mathrm{1R}^3}\rho^{5/3}(x)\left[\frac{P(x)}{\rho(x)}-1\right]^2d^3x\\+\tfrac{1}{2}\int_{\mathrm{1R}^3}\int_{\mathrm{1R}^3}\frac{\rho(x)\rho(y)}{|x-y|}\left[\frac{P(x)}{\rho(x)}-1\right]\left[\frac{P(y)}{\rho(y)}-1\right]d^3y\,d^3x\end{aligned} \tag{4.14}$$

and

$$\begin{aligned}\delta^2G[P-\rho]=-\tfrac{1}{8}\int_{\mathrm{1R}^3}\rho(x)\left|\vec{\nabla}\left[\frac{P(x)}{\rho(x)}-1\right]\right|^2d^3x+\frac{1}{6}\left[\frac{3}{\pi}\right]^{1/3}\int_{\mathrm{1R}^3}\rho^{4/3}(x)\left[\frac{P(x)}{\rho(x)}-1\right]^2d^3x\\-\frac{(3\pi^2)^{2/3}}{6}\int_{\mathrm{1R}^3}\rho^{5/3}(x)\left[\frac{P(x)}{\rho(x)}-1\right]^2d^3x-\tfrac{1}{2}\int_{\mathrm{1R}^3}|\vec{\nabla}h[P-\rho](x)|^2d^3x\\+\int_{\mathrm{1R}^3}(P-\rho)(y)d^3y\int_{\mathrm{1R}^3}\left.\frac{\delta\mu_{\tilde{P}}}{\delta\tilde{P}(x)}\right|_{\tilde{P}=\rho}(P-\rho)(x)d^3x\ ,\end{aligned} \tag{4.15}$$

where $h[P-\rho](x)$ is defined in Eq. (3.15). Although the exchange term in each of these expressions does not have the desired sign, the integrand of these exchange terms is dominated by the integrand of the TF kinetic energy for all x such that $\rho(x)\geq(3\pi^5)^{-1}$. It is assumed in this work that the N-electron trial functions $P(x)$ do indeed satisfy the condition that $\delta^2J^{\mathrm{TFDW}}[P-\rho]>0>\delta^2G^{\mathrm{TFDW}}[P-\rho]$; however, it is important to note that this necessary conjecture has not been proved.

The following form was chosen for the TFDW trial functions:

$$P(x)=\frac{Z^3C^2}{\pi}\left\{e^{-Z|x|}\left[\frac{\sinh\beta|x|}{\beta|x|}-(-1)^n\sum_{k=1}^{n-1}D_k\left[-\frac{\sinh\beta|x|}{\beta|x|}\right]^{1-k}\right]\right\}^2,\quad 0<\beta<Z \tag{4.16}$$

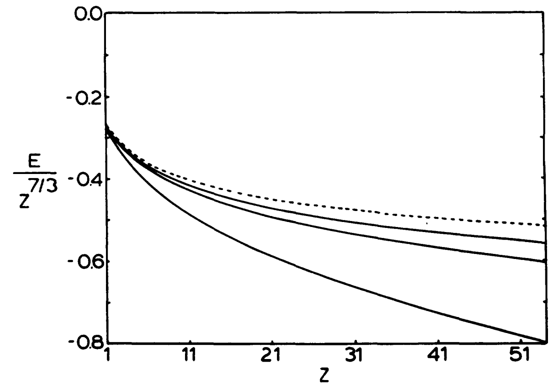

FIG. 1. Curves bounding the exact TFDW atomic energies (in hartrees). The dashed curve of energies divided by nuclear charge raised to the $\frac{7}{3}$ power results from two-parameter functions being substituted into the TFDW functional. The three lower curves were derived using Poisson's complementary functional with two-, four-, and six-parameter functions.

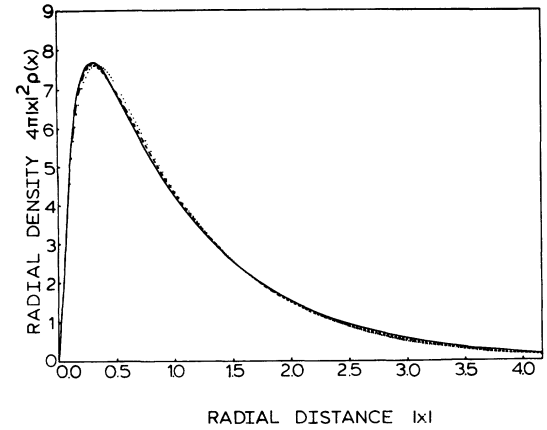

FIG. 2. Exact TFDW radial density (a.u.) for the neutral neon atom—solid curve. The dashed curve arises from the six-parameter lower bound radial density and the dotted curve arises from the two-parameter upper bound radial density.

with C^2 chosen to ensure normalization

$$\int_{\mathbb{R}^3} P(x) d^3x = N \,. \tag{4.17}$$

The exponential part of this function guarantees the cusp condition will be satisfied and the first term in the square brackets gives the correct long-range behavior for a TFDW density with the additional terms tending to refine the density's behavior near the atomic center.

Convergence to a good upper bound on the neutral TFDW atomic energies requires use of only the first two terms in the expression for $P(x)$:

$$P(x) = \frac{Z^3 C^2}{\pi} \left[e^{-Z|x|} \left[\frac{\sinh\beta|x|}{\beta|x|} - D_1 \right] \right]^2 . \tag{4.18}$$

TABLE I. For five neutral atomic systems, the TFDW energy (hartrees) is given along with the upper and lower bounds obtained from two- and six-parameter functions when applied to the TFDW functional and its Poisson complement, respectively.

Z	$E_U^{\mathrm{TFDW}}/Z^{7/3}$ $(n=2)$	$E^{\mathrm{TFDW}}/Z^{7/3}$	$E_L^{\mathrm{TFDW}}/Z^{7/3}$ $(n=6)$
1	−0.261 72	−0.261 83	−0.263 37
4	−0.334 03	−0.334 36	−0.339 21
7	−0.371 97	−0.372 42	−0.380 04
10	−0.397 43	−0.397 94	−0.408 33
18	−0.440 07	−0.440 63	−0.457 66

Upon optimizing β and D_1, the results of Table I and Fig. 1 are obtained. The table indicates that the absolute percent error in E_U^{TFDW} increases with Z, but even for argon, $Z=18$, the error resulting from the two-term function is less than 0.13%.

To obtain reasonable lower bounds to the TFDW energies, a six-parameter function was used. As seen in Table I, the lower bound energies are not as close to the exact values as are the upper bound energies (the error in E_L^{TFDW} for argon is 3.86%). However, the convergence to the exact energy is surprisingly rapid as can be seen in Fig. 1 where the lower bound curves are plotted for $N=2$, 4, and 6.

One might expect that the Poisson complementary functional would more easily yield better densities than the TFDW functional, because obtaining a given degree of accuracy in the energy requires the lower bound to use a function with more parameters than the corresponding upper bound function; this turns out to be the case. In Fig. 2, the neon densities that give the energies of Table I are plotted. The radial density that results from the Poisson functional predicts the position of the true maximum quite accurately and follows the exact curve more closely than the corresponding upper bound curve. Furthermore, the value of the density at the nucleus predicted by the lower bound curve is 168.19 in error less than 0.75% from the true value of 169.46; the upper bound curve gives $\rho(0)=186.39$. These results strongly attest to the validity of using complementary variational methods in studying TFDW theory.

C. Hohenberg and Kohn theory

In 1964, Hohenberg and Kohn[11] proved the electronic energy of a molecular system with potential $V(x)$ is a universal functional of the density

$$E_U^{\mathrm{HK}}[P]=T[P]+\tfrac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{P(x)P(y)}{|x-y|}d^3y\,d^3x+K[P]-\int_{\mathbb{R}^3}V(x)P(x)d^3x\ , \tag{4.19}$$

where $T[P]$ and $K[P]$ are the kinetic energy and exchange energy functionals, respectively. Furthermore, Hohenberg and Kohn showed that their functional satisfies a variational principle obtaining a minimum at the true ground-state density. Using the theory from Sec. III, the Poisson complement of $E_U^{\mathrm{HK}}[P]$ can be derived

$$\begin{aligned}E_L^{\mathrm{HK}}[P]=\ &T[P]-\int_{\mathbb{R}^3}\frac{\delta T[P]}{\delta P(x)}P(x)d^3x+K[P]-\int_{\mathbb{R}^3}\frac{\delta K[P]}{\delta P(x)}P(x)d^3x+\mu_P^{\mathrm{HK}}\int_{\mathbb{R}^3}P(x)d^3x\\&-\frac{1}{8\pi}\int_{\mathbb{R}^3}\left|\vec{\nabla}\left[\frac{\delta T[P]}{\delta P(x)}+\frac{\delta K[P]}{\delta P(x)}-V(x)\right]\right|^2d^3x\ ,\end{aligned} \tag{4.20}$$

where

$$\mu_P^{\mathrm{HK}}\equiv\lim_{|x|\to\infty}\left[\frac{\delta T[P]}{\delta P(x)}+\frac{\delta K[P]}{\delta P(x)}-V(x)\right]. \tag{4.21}$$

In practice, the functional $E_L^{\mathrm{HK}}[P]$ will only be of interest in a function space over which the supremum of $E_L^{\mathrm{HK}}[P]$ equals the electronic energy. This space consists of those densities $P(x)$ for which the second variation of $G^{\mathrm{HK}}[P]\equiv E_L^{\mathrm{HK}}[P]-\mu N[P]$ about the extremum density ρ is negative. Writing

$$\begin{aligned}\delta^2G^{\mathrm{HK}}[P-\rho]=&-\tfrac{1}{2}\int_{\mathbb{R}^3}(P-\rho)(x)h^{\mathrm{HK}}[P-\rho](x)d^3x-\tfrac{1}{2}\int_{\mathbb{R}^3}|\vec{\nabla}h^{\mathrm{HK}}[P-\rho](x)|^2d^3x\\&+\int_{\mathbb{R}^3}(P-\rho)(y)d^3y\int_{\mathbb{R}^3}\left.\frac{\delta\mu_{\tilde{P}}(x)}{\delta\tilde{P}(x)}\right|_{\tilde{P}=\rho}(P-\rho)(x)d^3x\end{aligned} \tag{4.22}$$

with

$$h^{\mathrm{HK}}[P-\rho](x)=\int_{\mathbb{R}^3}\frac{\delta^2}{\delta\tilde{P}(x)\delta\tilde{P}(y)}(T[\tilde{P}]+K[\tilde{P}])\,|_{\tilde{P}=\rho}(P-\rho)(y)d^3y\ , \tag{4.23}$$

it is observed that the space of density differences $(P-\rho)(x)$ is independent of $V(x)$ and thus universal. The third term in Eq. (4.22) vanishes when only N-electron densities are considered, and, as above, it suffices to prove that

$$\delta^2H[P-\rho]=\tfrac{1}{2}\int_{\mathbb{R}^3}(P-\rho)(x)h^{\mathrm{HK}}[P-\rho](x)d^3x$$

is positive. This term is simply the sum of the second variation of the kinetic energy functional and the second variation of the exchange energy functional. With the explicit form of these functionals unknown, it is difficult (and maybe impossible) to determine a function space over which $\delta^2H[P-\rho]$ is positive. Here, it must be assumed that such a function space can be found.

One final observation can be made concerning the HK Poisson functional. Whenever $V(x)$ is Coulombic, the gradient integral in Eq. (4.20) is unbounded unless

$$\frac{\delta T[P]}{\delta P(x)}+\frac{\delta K[P]}{\delta P(x)}=V(x) \tag{4.24}$$

at each nucleus. This implies that only trial densities that satisfy the cusp condition yield finite lower bounds to the true energy of a system and that the search for a nontrivial lower bound should be restricted accordingly.

V. CONCLUSIONS

This work has produced a new method for determining the energy of an atomic or molecular system within a density-functional framework. Using complementary variational principles, complementary energy functionals of the density have been derived which sandwiched the true energy of a system between upper and lower bounds. Calculations were performed on atomic TF and TFDW systems. Values for the energies and analytic densities were obtained for these systems and then shown to be accurate when compared to the exact values. This verified the validity of using complementary variational methods in the study of atomic systems.

As a more severe test, attempts should be made to use the complementary functional methods to determine energies and densities of systems for which solving the Euler-Lagrange equation has failed to be profitable. Presently, the author is pursuing work on diatomic systems using the TFDW functional along with its Poisson complement.

ACKNOWLEDGMENTS

Thanks are due to Dr. Robert G. Parr, Dr. Libero J. Bartolotti, Dr. Prabhat Kumar Acharya, and Mr. Joseph Fulvio Capitani for many helpful discussions, and also to Dr. Libero J. Bartolotti for providing the program used to determine the exact TFDW energies and densities. This work was aided by a research grant to the University of North Carolina from the National Science Foundation.

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