Variationally Determined Occupation "Numbers" in an Extended Thomas-Fermi Scheme

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Thomas-Fermi theory is generalized by the introduction of an occupation distribution function $f(s)$. The ansatz $f(s) = \theta(s_1 - s)$ of the conventional TF theory is derived from a variational principle. The implications with respect to the density functional theory are discussed. Future work is intended to include interaction, leading to deviations from the step function, which will account for correlation effects.

1. Introduction

Conventional Thomas-Fermi theory [1] is based on two assumptions: I. All particles (fermions) move in a common potential. II. The particle orbitals are replaced by plane waves, the potential being assumed as locally quasi "constant". In the corresponding quantum mechanical case the first assumption can be formulated by saving that the particles occupy one-particle states with integral occupation numbers

$$v_j = 0 \quad \text{or} \quad 1 \tag{1}$$

due to the Pauli principle. Consequently, in the Thomas-Fermi (TF) scheme each plane wave is expected to contribute with a weight factor according to (1). Since the waves form a continuum of states, the occupation numbers are then replaced by an occupation distribution function

$$f(s) = \theta(s_1 - s)\,, \tag{2}$$

where $\theta(z)$ is the unit step function. The meaning of s will be seen from (11). Equation (2) is one of the starting points for the calculation of density terms in the conventional TF scheme.

2. Extended Thomas-Fermi Scheme

In the present paper an extended Thomas-Fermi scheme (ETF) is presented where $f(s)$ is *not* assumed to have the form (2) *a priori* but has to be *derived* variationally from energy requirements. This extended framework of TF theory is characterized by keeping assumption II but replacing assumption I by a situation which corresponds to a two-body interaction in the particle movement, thus leading to fractional occupation numbers

$$0 \leqq v_j \leqq 1 \quad \text{or} \quad 0 \leqq f(s) \leqq 1\,. \tag{3}$$

In this work attention will be focused on the preliminary question whether (2) can be *deduced* if the two-body interaction is absent. For if this were not true, any variational calculation of $f(s)$ in the presence of interaction would be based on an obvious inconsistency with the TF scheme and its quantum mechanical analogy (1).

In quantum mechanics the reduced one-particle (orbital) density matrix of a system of interacting fermions is given by

$$\bar{d}_1(\boldsymbol{r};\boldsymbol{r}') = \sum_j v_j \cdot \chi_j^*(\boldsymbol{r}') \cdot \chi_j(\boldsymbol{r})\,, \tag{4}$$

where the χ_j are the natural (spin free) orbitals, and the (real) v_j are restricted by (3). The one-particle orbital density and the corresponding kinetic density are

$$\bar{n}(\boldsymbol{r}) = \bar{d}_1(\boldsymbol{r};\boldsymbol{r})\,,$$

$$\bar{t}(\boldsymbol{r}) = \frac{\hbar^2}{2m} \cdot \left[\sum_{k=1}^{3} \frac{\partial^2}{\partial x_k' \partial x_k} \bar{d}_1(\boldsymbol{r};\boldsymbol{r}') \right]_{\boldsymbol{r}'=\boldsymbol{r}}. \tag{5}$$

Let the admissible $\bar{d}_1$ be V-representable according to

$$H_V \chi_j = (T + V)\chi_j = \varepsilon_j \cdot \chi_j\,, \tag{6}$$

where $V(\boldsymbol{r})$ is an one-particle potential. Further, let the v_j be parametrized on the eigenvalues ε_j of H_V:

$$v_j = f(\varepsilon_j)\,, \tag{7}$$

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f describing the distribution of occupation numbers v_j. Then (4) can be rewritten [2–4] as

$$\bar{d}_1(\boldsymbol{r};\boldsymbol{r}') = f(H_V(\boldsymbol{r}))\,\delta(\boldsymbol{r}-\boldsymbol{r}')\,, \tag{8}$$

where the closure relation has been used. As concerning the action of the operator in (8) on

$$\delta(\boldsymbol{r}-\boldsymbol{r}') = \frac{1}{(2\pi)^3}\int e^{i\boldsymbol{k}(\boldsymbol{r}-\boldsymbol{r}')}\,\mathrm{d}^3\boldsymbol{k}\,, \tag{9}$$

the transition to assumption II can be performed formally by treating $V(\boldsymbol{r})$ as a c-number [5, 6]. In this way an ETF orbital density matrix

$$\bar{d}_1(\boldsymbol{r};\boldsymbol{r}') = \frac{1}{8\pi^3}\int f\left(\frac{\hbar^2 k^2}{2m} + V(\boldsymbol{r})\right)\cdot e^{i\boldsymbol{k}(\boldsymbol{r}-\boldsymbol{r}')}\,\mathrm{d}^3\boldsymbol{k} \tag{10}$$

is obtained which depends on *two* generating quantities V and f. The variable s in (3) is now introduced by the substitution

$$s = \frac{\hbar^2 k^2}{2m} + V(\boldsymbol{r})\,, \quad \text{hence} \quad s \geqq V(\boldsymbol{r})\,. \tag{11}$$

All information relevant to the non-interacting case is contained in (10). In particular the density and the kinetic density

$$\bar{n}[f, V](\boldsymbol{r}) = c\cdot\int_{V(\boldsymbol{r})}^{\infty} f(s)\cdot(s-V(\boldsymbol{r}))^{1/2}\,\mathrm{d}s\,, \tag{12}$$

$$\bar{t}[f, V](\boldsymbol{r}) = c\cdot\int_{V(\boldsymbol{r})}^{\infty} f(s)\cdot(s-V(\boldsymbol{r}))^{3/2}\,\mathrm{d}s\,, \tag{13}$$

with

$$c = \frac{1}{4\pi^2}\cdot\left(\frac{2m}{\hbar^2}\right)^{3/2} \tag{14}$$

are derived, these quantities being functionals of f and V in the ETF scheme.

3. A Variational Principle

If N particles move in an external potential $V_a(\boldsymbol{r})$ the total energy has the form

$$E^{(0)}[f, V] = \int\{t[f, V](\boldsymbol{r}) + V_a(\boldsymbol{r})\cdot n[f, V](\boldsymbol{r})\}\,\mathrm{d}^3\boldsymbol{r}\,, \tag{15}$$

with normalization

$$\int n[f, V](\boldsymbol{r})\,\mathrm{d}^3\boldsymbol{r} = N\,, \tag{16}$$

where

$$n = 2\bar{n}\,, \quad t = 2\bar{t} \tag{17}$$

for fully occupied spin states. But since the aim is to derive a density functional $E^{(0)}[n]$, in principle the minimization of (15) will not be performed subject to (16) but to the stronger condition

$$n[f, V](\boldsymbol{r}) = n(\boldsymbol{r})\,, \tag{18}$$

where the right hand side is a given density already obeying

$$\int n(\boldsymbol{r})\,\mathrm{d}^3\boldsymbol{r} = N\,. \tag{19}$$

According to (18) the potential energy term in (15) does no longer depend on f or V and, for the purpose of variation, may be dropped since it yields no contribution to the Euler-Lagrange equations. Hence, during the course of variation, one is only concerned with the kinetic energy term. The requirement (18) then contributes a sum of Lagrange multipliers

$$L[f, V] = \int\Phi(\boldsymbol{r})\cdot\{n[f, V](\boldsymbol{r}) - n(\boldsymbol{r})\}\,\mathrm{d}^3\boldsymbol{r}\,, \tag{20}$$

$\Phi(\boldsymbol{r}_0)$ being the multiplier corresponding to $n(\boldsymbol{r}_0)$. Since $\Phi(\boldsymbol{r})$ and $n(\boldsymbol{r})$ are constant with respect to a variation of f and V in

$$\int t[f, V](\boldsymbol{r})\,\mathrm{d}^3\boldsymbol{r} + L[f, V]\,, \tag{21}$$

the correct Euler-Lagrange equations are obtained from an "effective" energy functional

$$\tilde{E}^{(0)}[f, V] = \int\{t[f, V](\boldsymbol{r}) + \Phi(\boldsymbol{r})\cdot n[f, V](\boldsymbol{r})\}\,\mathrm{d}^3\boldsymbol{r}\,, \tag{22}$$

where, after the variation with respect to f and V has been carried out, Φ is determined by the given density n. On comparing (22) with (15) shows that $\Phi(\boldsymbol{r})$ can be interpreted as a Hohenberg-Kohn external potential which is related to the required $n(\boldsymbol{r})$ of (18). Indeed, both $\Phi(\boldsymbol{r})$ and $V_a(\boldsymbol{r})$ belong to the same density n, and hence differ by a constant only, as will be verified later (cf. (56)). Thus the variational principle (22), subject to (18) turns out to be a density functional version of the original form (15). As a consequence, if one solves for all admissible Φ, one obtains the energy for all the corresponding n, and vice versa. Thus instead of starting with a given n in (18), one equivalently may drop this condition from the variational principle, and start with a given Φ. This will be done in the next section. As a result the Hohenberg-Kohn connection [7] between n and Φ, as it applies to the non-interacting ETF case, will be derived explicitly.

4. Stationarity Condition

On changing the order of the $\boldsymbol{r}$- and s-integrations, (22) may be written as

$$\tilde{E}^{(0)}[f, V] = 2c \cdot \int_{-\infty}^{\infty} f(s) \cdot G_V(s)\, \mathrm{d}s \tag{23}$$

with

$$G_V(s) = \int g(s - V(\boldsymbol{r}),\ \Phi(\boldsymbol{r}))\, \mathrm{d}^3\boldsymbol{r} \tag{24}$$

and

$$g(y, z) = \theta(y)\, y^{1/2}(y + z)\,. \tag{25}$$

Now (23) being linear in f, a stationarity condition

$$\frac{\delta \tilde{E}^{(0)}[f, V]}{\delta f} = 0 \tag{26}$$

cannot be applied since it would lead to a vanishing $G_V(s)$, and to $\tilde{E}^{(0)}[f, V] \equiv 0$. In fact, it is not the stationarity but the limitation by (3) which determines the minimizing f. To obtain $\tilde{E}^{(0)}$ for given V as low as possible one has to choose

$$f(s) = f[V](s) = \theta(-G_V(s)) \tag{27}$$

as is seen from direct inspection in (23). Thus $\tilde{E}^{(0)}$ is reduced to

$$\tilde{E}^{(0)}[V] = 2c \int_{-\infty}^{\infty} \theta(-G_V(s))\, G_V(s)\, \mathrm{d}s \leqq 0\,. \tag{28}$$

On using

$$\frac{\mathrm{d}}{\mathrm{d}x}\Big[\theta(-x)\, x\Big] = \theta(-x) \tag{29}$$

the stationarity with respect to V requires

$$0 = \frac{\delta \tilde{E}^{(0)}[V]}{\delta V} = -2c \int_{-\infty}^{\infty} \theta(-G_V(s)) \cdot \frac{\partial g(s - V(\boldsymbol{r}), \Phi(\boldsymbol{r}))}{\partial s}\, \mathrm{d}s$$

$$= 2c \int_{-\infty}^{\infty} \frac{\mathrm{d}\theta(-G_V(s))}{\mathrm{d}s}\, g(s - V(\boldsymbol{r}),\ \Phi(\boldsymbol{r}))\, \mathrm{d}s\,, \tag{30}$$

where the integrated terms in (30) vanish because of the step function in (25) and the condition

$$G_V(s) > 0 \quad \text{for} \quad s \geqq M \tag{31}$$

(M sufficiently large), which turns out to be necessary for the existence of the densities (12) and (13).

Equation (30) can be further evaluated if the relation

$$\frac{\mathrm{d}\theta(-G_V(s))}{\mathrm{d}s} = -\sum_k d_k\, \delta(s - s_k) \tag{32}$$

with

$$d_k = \left[\operatorname{sign} \frac{\mathrm{d}G_V(s)}{\mathrm{d}s}\right]_{s = s_k} \tag{33}$$

is applied where the s_k are the (single valued) roots of

$$G_V(s) = 0\,. \tag{34}$$

(Equation (34) is assumed to have no higher valued roots for general Φ.) Because of (11) and (25) roots with $s_k > V(\boldsymbol{r})$ are relevant only. Let there be m such roots

$$s_1 > s_2 > \ldots > s_m \tag{35}$$

(m is assumed to be finite for general Φ). The stationarity condition (30) then reads

$$\sum_{k=1}^{m} d_k\, g(s_k - V(\boldsymbol{r}), \Phi(\boldsymbol{r})) = 0\,. \tag{36}$$

Since $G_V(s)$ is a unique and continuous function of s, it can be concluded from (31) that the signs of its derivatives at s_k are ordered according to

$$d_k = (-1)^{k+1}\,, \quad (k = 1, 2, \ldots, m)\,. \tag{37}$$

5. Theorem on the Exact Solution in the Non-Interacting Case

Next it will be proved that

$$m = 1 \tag{38}$$

is the only acceptable case. The proof is by *reductio ad absurdum*. The case $m = 0$ can be excluded because (31) would lead to $f \equiv 0$ in (27), and hence $\tilde{E}^{(0)}[V] \equiv 0$, yielding no binding. Assume now $m \geqq 2$, and let $\mathbb{P}$ be that region of $\boldsymbol{r}$-space for which

$$s_m > V(\boldsymbol{r})\,. \tag{39}$$

($V(\boldsymbol{r})$ is assumed to be continuous so that $\mathbb{P}$ comprizes a non-zero region.) Then all step functions in (36) can be dropped. With

$$s_k - V := S_k > 0\,, \quad (k = 1, 2, \ldots, m)\,, \tag{40}$$

the following estimate holds in the region $\mathbb{P}$:

$$\begin{aligned} & d_r S_r^{3/2} + d_{r+1} S_{r+1}^{3/2} = S_r S_r^{1/2} - S_{r+1} S_{r+1}^{1/2} \\ & > S_{r+1}(S_r^{1/2} - S_{r+1}^{1/2}) \geqq S_m(S_r^{1/2} - S_{r+1}^{1/2}) \\ & = S_m(d_r S_r^{1/2} + d_{r+1} S_{r+1}^{1/2}) \\ & \quad \text{for } r = 1, 3, 5, \ldots, \quad \text{and} \quad m \geqq 2 . \end{aligned} \tag{41}$$

On adding up all the pairs (41) (and eventually add a remaining unpaired term with $r = m$) and using

$$\sum_{k=1}^{m} d_k \cdot S_k^{1/2} > 0 \tag{42}$$

it shows up that

$$s_m - V(\boldsymbol{r}) + \Phi(\boldsymbol{r}) < 0 \quad \text{in } \mathbb{P} \quad \text{for} \quad m \geqq 2 . \tag{43}$$

From (39) and (43) it is now concluded that

$$\begin{aligned} G_V(s_m) = & \int\limits_{\boldsymbol{r} \in \mathbb{P}} (s_m - V(\boldsymbol{r}))^{1/2} \\ & \cdot (s_m - V(\boldsymbol{r}) + \Phi(\boldsymbol{r}))\, d^3\boldsymbol{r} < 0 \end{aligned} \tag{44}$$

which contradicts (34). Hence the existence of a non-zero region of type (39) is not nonsistent with stationarity, and, consequently,

$$V(\boldsymbol{r}) \geqq s_m . \tag{45}$$

But then the term with $k = m$ from (36) drops, and one is left with a situation where m has to be replaced by $m - 1$. On starting in (39) with this replacement again, one may repeat the proof in a sequence of cycles until $m = 2$ is disproved. For $m = 1$, the only remaining case, (41) is no longer valid, and (43) changes into

$$s_1 - V(\boldsymbol{r}) + \Phi(\boldsymbol{r}) = 0 \tag{46}$$

as is seen from (36). Since (46) leads to $G_V(s_1) = 0$, there is no inconsistency with (34) in that case. This completes the proof.

6. Hohenberg-Kohn Connection and Density Functional

Thus according to (46) the stationary V differs from Φ by a constant only, and hence itself is a Hohenberg-Kohn potential. On combining (46) with (24) yields the stationary $G_V(s)$:

$$G_V(s) = (s - s_1) \cdot Q_V(s) \tag{47}$$

with

$$Q_V(s) = \int \theta(s - V(\boldsymbol{r})) \cdot (s - V(\boldsymbol{r}))^{1/2}\, \mathrm{d}^3\boldsymbol{r} . \tag{48}$$

Since

$$Q_V(s) > 0 \quad \text{for} \quad s > V(\boldsymbol{r}) \tag{49}$$

one obtains in (27)

$$f(s) = \theta(s_1 - s) \quad \text{for} \quad s \geqq V(\boldsymbol{r}) \tag{50}$$

(the value of f at $s = V$ being irrelevant in (12), (13), and (23)). Hence (2) turns out to be a *stationary property* of (28). On evaluating (12) and (13) and using (46) one derives the well known relations

$$n(\boldsymbol{r}) = \frac{4c}{3} \cdot (-\Phi(r))^{3/2} , \tag{51}$$

$$t(\boldsymbol{r}) = \frac{4c}{5} \cdot (-\Phi(\boldsymbol{r}))^{5/2} , \tag{52}$$

hence

$$t[n](\boldsymbol{r}) = \varkappa_k \cdot n^{5/3}(\boldsymbol{r}) , \quad \varkappa_k = \frac{3}{5} \cdot \left(\frac{3}{4c}\right)^{2/3} , \tag{53}$$

where $\varkappa_k$ is in agreement with conventional TF theory. From (15), (18), and (53) the TF energy functional

$$E^{(0)}[n] = \int \{\varkappa_k \cdot n^{5/3} + V_a \cdot n\}\, \mathrm{d}^3\boldsymbol{r} \tag{54}$$

is obtained. Eq. (51) represents the Hohenberg-Kohn connection. On varying (54), subject to condition (19), yields

$$\tfrac{5}{3} \cdot \varkappa_k \cdot n^{2/3} + V_a - \lambda = 0 \tag{55}$$

where $\lambda = \lambda[V_a]$ is the TF Lagrange multiplier. From (55) and (46), (51) one finds

$$V - s_1 = \Phi = V_a - \lambda[V_a] , \tag{56}$$

showing that V_a too plays the the role of a Hohenberg-Kohn potential. It is seen in (47), (48) that s_1 does not depend on V. Hence V and V_a differ by an arbitrary constant as one would expect from the quantum mechanical analogy. On choosing $s_1 = \lambda[V_a]$ yields

$$V(\boldsymbol{r}) = V_a(\boldsymbol{r}) , \quad f(s) = \theta(\lambda[V_a] - s) . \tag{57}$$

7. Discussion and Further Suggestions

The consistency of conventional TF theory rests on the coincidence of the relations (51), (46) with (55). The ETF scheme throws some light on that coincidence: the common source of both these rela-

tions is the Hohenberg-Kohn connection for general Φ, stemming from the variational principle (22). In fact, once assumption II of Sect. 1 has been introduced, the stationary $\tilde{E}^{(0)}[n]$ of (22), (18) is strictly analogous to the energy density functional of quantum mechanics [8]. Thus Kohn-Hohenberg theory is not destroyed by assumption II. This also can be seen from the work of Stoddard and March [9]. Strictly speaking, the validity of the approach of these authors depends on the convergence of their series used in handling the Kohn-Hohenberg connection. While this series could be summed up in the TF case its convergence in a more general situation seems far from being established. In fact, Stoddard and March did not consider a framework where assumption I of Sect. 1 has been dropped. On following the approach of the present paper, a rigorous deduction of TF theory within a wider framework of flexible $f(s)$ is given, which strictly avoids any representation by infinite series. Further, $f(s)$ being determined variationally, this treatment applies to the case of interaction in a quite natural way.

It should be emphasized that a minimum property of the variational principle (28) has not been proved so far, the weeker condition (30) being sufficient to derive the main results.

In a subsequent paper the author hopes to show how an approximate explicit relation between $d_1(\boldsymbol{r};\boldsymbol{r}')$ and the two-particle density $n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ can be set up. It would be then straightforward to write down an EFT energy functional $E = E[f, V]$ in the presence of an interaction, and to employ it as a stationarity principle to determine V *and* f. Since deviations from (1) will indicate that correlation effects are taken into account one has to expect that the ETF scheme will provide for a density functional yielding exchange *and* correlation terms [10]. Ultimately, such an approach might be valid in constructing suitable potentials for Kohn-Sham calculations [11–13].

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