PHYSICAL REVIEW A VOLUME 45, NUMBER 1 1 JANUARY 1992

Energy functionals and the Thomas-Fermi model in momentum space

Berthold-Georg Englert*
Sektion Physik, Universität München, Am Coulombwall 1, D-8046 Garching, Germany

(Received 10 May 1991)

Energy functionals of the momentum-space density are investigated. They are complementary supplements to the standard functionals of the configuration-space density and provide a self-consistent approach to computing momentum-space densities and quantities derived from these. We introduce the concept of an effective kinetic energy, analogous to the effective potential energy, and establish thereby an independent-particle picture in momentum space. In the new independent-particle energy, every electron pair is counted $\frac{5}{3}$ times, not twice. The Thomas-Fermi functionals in momentum space are given and shown to be perfectly equivalent to the configuration-space ones.

PACS number(s): 31.15.+q, 31.20.Sy, 31.20.Lr, 31.90.+s

I. INTRODUCTION

The 1964 paper by Hohenberg and Kohn [1] (HK) triggered widespread interest in energy functionals of the spatial density for many-electron systems. By now the subject has been developed to the stage at which textbooks [2,3] are written. Indeed, computation schemes based upon these functionals are regarded as the method of choice whenever refined Hartree-Fock calculations are too tedious and therefore too expensive. In addition, the functional approach enables one to arrive at analytical answers to some questions. Examples are the strikingly simple, and highly precise, formula that gives the total electronic binding energy of an atom as a function of the number of electrons [4–6], and the simple rule according to which subshells are filled as the Periodic Table is built up [7].

Whereas the theory of energy functionals of the *spatial* density has been dealt with in certainly hundreds, probably thousands of publications, the complementary energy functionals of the *momental* density—that is, the density in momentum space—have received perfunctory attention. In 1981 Henderson [8] formulated the momental analog of the spatial HK theorem [1]. A crude approximation [9] to the momental Thomas-Fermi (TF) functional was given in 1982 (and extended [10] in 1988). Also in 1982, Smith [11] reviewed the status of momentum space considerations and added a programmatic outlook. To our knowledge, nothing remarkable has happened since then in this field. For instance, functionals of the momental density are not mentioned at all in the voluminous proceedings [12] of a 1983 conference on density functional methods, and in two recent textbooks [2,3] they are discussed very briefly only.

Different physical systems—such as atoms, molecules, or solids—are mainly characterized by the external electrostatic potential to which the electrons are exposed. The structure of the standard spatial energy functionals does not depend upon this external potential. In contrast, as remarked by Henderson [8] already, the momental functionals do not possess this universality; they have to be constructed with explicit reference to the physical system under consideration. For example, momental functionals valid for atoms must not be applied to molecules. One might thus conclude—wrongly, in our opinion—that the momental functionals are less useful than the spatial ones. Could it be that this notion is responsible for the apparent lack of interest in functionals of the momental density?

The need for theoretical predictions of momental densities was, of course, always recognized. In fact, momental densities are more easily extracted [13] than spatial ones from experimental data, such as Compton profiles or angular positron-annihilation correlations [14]. Thus a fair number of rules of thumb have been produced by which one can infer momental from spatial densities [15]. The recent derivation [16] of the Scott correction to the momental density of TF atoms is in this spirit.

Rather than rely upon such rules of limited applicability one should aim at a self-consistent determination of the momental density. To this end, energy functionals of the momental density are required. It is the objective of the present paper to take a first step in this direction. In the next section, we first set the stage by reviewing the essentials of spatial functionals, and then discuss momental functionals generally. In particular, the notion of an effective kinetic energy will be introduced, which is the momental analog of the spatial effective potential energy. Section III, then, presents the momental TF approximation for atoms. Finally, in Sec. IV we shall consider briefly scaling properties of the momental functionals, and address the question of the multiple counting of electron pairs in independent-particle energies. The incorporation of the Scott correction into the momental TF functional is the subject of the following paper [17].

In the Appendix we give a negative answer to the question of whether Löwdin's "natural orbitals" [18] are identical with the single-electron states of the independent-particle description.

II. ENERGY FUNCTIONALS

We consider, quite generally, a system of many electrons, N in number, with positions $\mathbf{r}_1, \ldots, \mathbf{r}_N$ and momenta $\mathbf{p}_1, \ldots, \mathbf{p}_N$. Their dynamics is governed by the many-particle Hamilton operator

$$H_{\mathrm{MP}}=H_{\mathrm{kin}}+H_{\mathrm{ext}}+H_{e\text{-}e}\ , \tag{1}$$

which consists of the kinetic energy

$$H_{\mathrm{kin}}=\sum_{j=1}^{N}T_{\mathrm{kin}}(\mathbf{p}_j)\ , \tag{2}$$

the external (electrostatic) potential energy

$$H_{\mathrm{ext}}=\sum_{j=1}^{N}V_{\mathrm{ext}}(\mathbf{r}_j)\ , \tag{3}$$

and the electron-electron interaction energy $H_{e\text{-}e}$. For a nonrelativistic isolated atom with atomic number Z, these are actually

$$T_{\mathrm{kin}}(\mathbf{p})=\tfrac{1}{2}\mathbf{p}^2\ ,\quad V_{\mathrm{ext}}(\mathbf{r})=-Z/|\mathbf{r}|=-Z/r \tag{4}$$

and

$$H_{e\text{-}e}=\tfrac{1}{2}\sum_{\substack{j,k\\ j\neq k}}|\mathbf{r}_j-\mathbf{r}_k|^{-1}\ . \tag{5}$$

Here and throughout we use atomic units and employ the notational conventions of Ref. [19]. The spin degrees of freedom will be left implicit.

As expressed in

$$E_0=\min_{\psi}\langle\psi|H_{\mathrm{MP}}|\psi\rangle=\langle\psi_0|H_{\mathrm{MP}}|\psi_0\rangle\ , \tag{6}$$

which implies

$$H_{\mathrm{MP}}|\psi_0\rangle=|\psi_0\rangle E_0\ , \tag{7}$$

the ground state of H_{MP} is denoted by $|\psi_0\rangle$ and the ground-state energy by E_0.

A. Spatial energy functionals

The HK theorem [1] in its standard spatial version states that the ground-state energy E_0 of H_{MP} is the minimum of a functional of the *spatial density* $n(\mathbf{r}')$,

$$n(\mathbf{r}')=N\int(d\mathbf{r}_2')\cdots(d\mathbf{r}_N')|\langle\mathbf{r}',\mathbf{r}_2',\ldots,\mathbf{r}_N'|\psi_0\rangle|^2\ , \tag{8}$$

that is,

$$E_0=\min_n E[n]\ , \tag{9}$$

where the spatial energy functional $E[n]$ is the sum of three terms corresponding to (1),

$$E[n]=E_{\mathrm{kin}}[n]+E_{\mathrm{ext}}[n]+E_{e\text{-}e}[n]\ , \tag{10}$$

with, of course,

$$E_{\mathrm{kin}}[n]=\langle\psi_0|H_{\mathrm{kin}}|\psi_0\rangle\ , \tag{11a}$$

$$\begin{aligned}E_{\mathrm{ext}}[n]&=\langle\psi_0|H_{\mathrm{ext}}|\psi_0\rangle\\ &=\int(d\mathbf{r}')V_{\mathrm{ext}}(\mathbf{r}')n(\mathbf{r}')\ ,\end{aligned} \tag{11b}$$

$$E_{e\text{-}e}[n]=\langle\psi_0|H_{e\text{-}e}|\psi_0\rangle\ . \tag{11c}$$

All of this is based upon the central observation that both V_{ext} and $|\psi_0\rangle$ are, for given T_{kin} and $H_{e\text{-}e}$, uniquely determined by $n(\mathbf{r}')$.

It is expedient to incorporate the constraint

$$N=\int(d\mathbf{r}')n(\mathbf{r}') \tag{12}$$

into the energy functional with the aid of a Lagrangian multiplier ζ (equal to the negative of the chemical potential), so that

$$\begin{aligned}&E_0=\mathrm{extr}_{n,\zeta}E[n,\zeta]\ ,\\ &E[n,\zeta]=E[n]-\zeta\left[N-\int(d\mathbf{r}')n(\mathbf{r}')\right]\ .\end{aligned} \tag{13}$$

Upon introducing the *effective potential* (energy) $V(\mathbf{r}')$ by means of

$$-V(\mathbf{r}')\equiv\frac{\delta}{\delta n(\mathbf{r}')}E_{\mathrm{kin}}[n]+\zeta\ , \tag{14}$$

one finds that the quantity

$$E_1=E_{\mathrm{kin}}[n]+\int(d\mathbf{r}')n(\mathbf{r}')[V(\mathbf{r}')+\zeta] \tag{15}$$

is a functional of the sum $V(\mathbf{r}')+\zeta$, because

$$\delta E_1=\int(d\mathbf{r}')n(\mathbf{r}')[\delta V(\mathbf{r}')+\delta\zeta]\ . \tag{16}$$

Consequently, we now have

$$E_0=\mathrm{extr}_{V,n,\zeta}E[V,n,\zeta] \tag{17}$$

with

$$\begin{aligned}E[V,n,\zeta]=E_1[V+\zeta]-\int(d\mathbf{r}')[V(\mathbf{r}')-V_{\mathrm{ext}}(\mathbf{r}')]n(\mathbf{r}')\\ +E_{e\text{-}e}[n]-\zeta N\ .\end{aligned} \tag{18}$$

Variations of $V(\mathbf{r}')$, $n(\mathbf{r}')$, and ζ supply three coupled equations. For δV,

$$n(\mathbf{r}')=\frac{\delta}{\delta V(\mathbf{r}')}E_1[V+\zeta]\ , \tag{19a}$$

for δn,

$$V(\mathbf{r}')=V_{\mathrm{ext}}(\mathbf{r}')+\frac{\delta}{\delta n(\mathbf{r}')}E_{e\text{-}e}[n]\ , \tag{19b}$$

and for $\delta\zeta$,

$$N=\frac{\partial}{\partial\zeta}E_1[V+\zeta]\ , \tag{19c}$$

of which the first repeats (16) in part, the second expresses the stationary property of $E[n,\zeta]$ under variations of n if (14) is taken into account, and the third is equivalent to the constraint (12) because E_1 depends on the sum $V+\zeta$. As soon as one identifies the second term on the right-hand side (rhs) of (19b) with an interaction potential $V_{e\text{-}e}(\mathbf{r}')$,

$$V=V_{\mathrm{ext}}+V_{e\text{-}e}\ , \tag{19b'}$$

the effective potential is quite naturally equated to the sum of the external and the interaction potential.

One can, of course, eliminate either V or n from the description. If one solves (19a) for $V+\zeta$ in terms of n and inserts it into (18), then one returns to $E[n,\zeta]$ of (13). On the other hand, if (19b) is used to express n in terms of $V-V_{\mathrm{ext}}$, then (18) is turned into yet another spatial energy functional, $E[V,\zeta]$, in which $V(\mathbf{r}')$ and ζ are the fundamental variables [20]. In principle, all these energy functionals are equivalent. In practice, however, one must resort to approximations since $E_{\text{kin}}[n]$ and $E_{e\text{-}e}[n]$ are not known. And the quality of an approximation may very well depend on the choice of functional.

We close this brief review of spatial energy functionals by remarking that

$$E_1[V+\zeta]=\left\langle\psi_0\left|\sum_{j=1}^{N}[H(\mathbf{r}_j,\mathbf{p}_j)+\zeta]\right|\psi_0\right\rangle, \tag{20}$$

with the independent-particle Hamilton operator

$$H=T_{\text{kin}}(\mathbf{p})+V(\mathbf{r}), \tag{21}$$

from which we infer that E_1 can be written as the trace of a function of $H+\zeta$,

$$E_1=\operatorname{tr}f(H+\zeta). \tag{22}$$

(Here one might wonder, and indeed we did, whether Löwdin's "natural orbitals" [18] are identical with the eigenstates of H. The negative answer is given in the Appendix.) This invites us to approximate E_1, in the spirit of the Kohn-Sham (KS) scheme [21], by its value for noninteracting electrons, namely,

$$E_1\cong\operatorname{tr}(H+\zeta)\eta(-H-\zeta), \tag{23}$$

where $\eta(x)$ is the Heaviside unit step function

$$\eta(x)=\begin{cases}1 & \text{for } x>0,\\ 0 & \text{for } x<0,\end{cases} \tag{24}$$

which approximation corresponds to $f(x)\cong x\eta(-x)$ in (22) and, incidentally, works very well. Since (23) would be the actual answer if $|\psi_0\rangle$ were to minimize the rhs of (20), rather than H_{MP} as in (6), the approximation (23) assigns a numerical value to E_1 that is somewhat less than the actual one. When employed in (19), Eq. (23) has the consequences

$$\begin{aligned}N&\cong\operatorname{tr}\eta(-H-\zeta),\\ n(\mathbf{r}')&\cong2\langle\mathbf{r}'|\eta(-H-\zeta)|\mathbf{r}'\rangle,\end{aligned} \tag{25}$$

where the factor of 2 is the spin multiplicity left implicit in the trace function.

Note that the effective potential V is *not* identical with the KS potential. The KS formalism can be recovered by writing equal signs in (23) and (25), along with adding a so-called correlation energy $E_{\text{corr}}[n]$ to $E[V,n,\zeta]$ for compensation. Then, the KS equations emerge when eigenstates and eigenvalues of H are employed to evaluate (23) and (25).

B. Momental energy functionals

Henderson's [8] momental version of the HK theorem states that the ground-state energy E_0 of H_{MP} is the minimum of a functional of the *momental density* $\rho(\mathbf{p}')$,

$$\rho(\mathbf{p}')=N\int(d\mathbf{p}_2')\cdots(d\mathbf{p}_N')|\langle\mathbf{p}',\mathbf{p}_2',\ldots,\mathbf{p}_N'|\psi_0\rangle|^2, \tag{26}$$

that is,

$$E_0=\min\nolimits_{\rho}\tilde{E}[\rho], \tag{27}$$

where the momental energy functional $\tilde{E}[\rho]$ is the sum of three terms corresponding to (1),

$$\tilde{E}[\rho]=\tilde{E}_{\text{kin}}[\rho]+\tilde{E}_{\text{ext}}[\rho]+\tilde{E}_{e\text{-}e}[\rho], \tag{28}$$

with

$$\begin{aligned}\tilde{E}_{\text{kin}}[\rho]&=\langle\psi_0|H_{\text{kin}}|\psi_0\rangle\\ &=\int(d\mathbf{p}')T_{\text{kin}}(\mathbf{p}')\rho(\mathbf{p}'),\end{aligned} \tag{29a}$$

$$\tilde{E}_{\text{ext}}[\rho]=\langle\psi_0|H_{\text{ext}}|\psi_0\rangle, \tag{29b}$$

$$\tilde{E}_{e\text{-}e}[\rho]=\langle\psi_0|H_{e\text{-}e}|\psi_0\rangle. \tag{29c}$$

The central point here is that both T_{kin} and $|\psi_0\rangle$ are, for given V_{ext} and $H_{e\text{-}e}$, uniquely determined by $\rho(\mathbf{p}')$.

Again, it is expedient to incorporate the constraint

$$N=\int(d\mathbf{p}')\rho(\mathbf{p}') \tag{30}$$

into the energy functional, whereby the Lagrangian multiplier ζ has the same significance as in the spatial functionals. The analogs of (13) are

$$\begin{aligned}E_0&=\operatorname{extr}_{\rho,\zeta}\tilde{E}[\rho,\zeta],\\ \tilde{E}[\rho,\zeta]&=\tilde{E}[\rho]-\zeta\left[N-\int(d\mathbf{p}')\rho(\mathbf{p}')\right].\end{aligned} \tag{31}$$

This time we introduce the *effective kinetic energy* $T(\mathbf{p}')$ by means of

$$-T(\mathbf{p}')\equiv\frac{\delta}{\delta\rho(\mathbf{p}')}\tilde{E}_{\text{ext}}[\rho]+\zeta, \tag{32}$$

and the quantity

$$\tilde{E}_1=\tilde{E}_{\text{ext}}[\rho]+\int(d\mathbf{p}')\rho(\mathbf{p}')[T(\mathbf{p}')+\zeta] \tag{33}$$

turns out to be a functional of the sum $T(\mathbf{p}')+\zeta$,

$$\delta\tilde{E}_1=\int(d\mathbf{p}')\rho(\mathbf{p}')[\delta T(\mathbf{p}')+\delta\zeta]. \tag{34}$$

So we have here

$$E_0=\operatorname{extr}_{T,\rho,\zeta}\tilde{E}[T,\rho,\zeta] \tag{35}$$

with

$$\begin{aligned}\tilde{E}[T,\rho,\zeta]=\tilde{E}_1[T+\zeta]&-\int(d\mathbf{p}')[T(\mathbf{p}')-T_{\text{kin}}(\mathbf{p}')]\rho(\mathbf{p}')\\ &+\tilde{E}_{e\text{-}e}[\rho]-\zeta N.\end{aligned} \tag{36}$$

The stationary property supplies now for variations δT,

$$\rho(\mathbf{p}')=\frac{\delta}{\delta T(\mathbf{p}')}\tilde{E}_1[T+\zeta], \tag{37a}$$

for $\delta\rho$,

$$\begin{aligned}T(\mathbf{p}')&=T_{\text{kin}}(\mathbf{p}')+\frac{\delta}{\delta\rho(\mathbf{p}')}\tilde{E}_{e\text{-}e}[\rho]\\ &\equiv T_{\text{kin}}(\mathbf{p}')+T_{e\text{-}e}(\mathbf{p}'),\end{aligned} \tag{37b}$$

and for $\delta\zeta$,

$$N=\frac{\partial}{\partial\zeta}\tilde{E}_1[T+\zeta]. \tag{37c}$$

Equation (37a) repeats (34) in part, (37b) expresses the stationary property of $\tilde{E}[\rho,\zeta]$ under variations of ρ if (32) is taken into account, and (37c) is equivalent to (30). There is again the option of eliminating one of the fields, either T or ρ, from the description.

In view of

$$\tilde{E}_1[T+\zeta]=\left\langle\psi_0\left|\sum_{j=1}^{N}[\tilde{H}(\mathbf{r}_j,\mathbf{p}_j)+\zeta]\right|\psi_0\right\rangle \tag{38}$$

with the independent-particle Hamilton operator

$$\tilde{H}=T(\mathbf{p})+V_{\text{ext}}(\mathbf{r}) , \tag{39}$$

one again infers that $\tilde{E}_1$ is the trace of a function of $\tilde{H}+\zeta$,

$$\tilde{E}_1=\mathrm{tr}\tilde{f}(\tilde{H}+\zeta) . \tag{40}$$

(Are the eigenstates of $\tilde{H}$ the natural orbitals? No, as shown in the Appendix). The approximation analogous to (23) is

$$\tilde{E}_1\cong\mathrm{tr}(\tilde{H}+\zeta)\eta(-\tilde{H}-\zeta) , \tag{41}$$

with the consequences

$$N\cong\mathrm{tr}\eta(-\tilde{H}-\zeta) ,$$
$$\rho(\mathbf{p}')\cong2\langle\mathbf{p}'|\eta(-\tilde{H}-\zeta)|\mathbf{p}'\rangle , \tag{42}$$

to be compared with (25).

Here, too, one has the option of adopting the KS scheme by regarding (41) and (42) as true equalities, along with $\tilde{E}_{\text{corr}}[\rho]$ added to $\tilde{E}[T,\rho,\zeta]$ for compensation. As discussed in the Appendix, the two independent-particle Hamilton operators H and $\tilde{H}$ do not commute, and therefore the momental KS wave functions obtained here are different from what one gets by Fourier transformation of the standard spatial KS wave functions [22].

In summary, the momental energy functionals are quite analogous to the spatial ones. The roles played by position and momentum, V_{ext} and T_{kin}, n and ρ, V and T, $V_{e\text{-}e}$ and $T_{e\text{-}e}$, E_{ext} and $\tilde{E}_{\text{kin}}$, E_{kin} and $\tilde{E}_{\text{ext}}$, are analogs of each other. Since the interaction $H_{e\text{-}e}$ of (5) depends on position only, and T_{kin} and V_{ext} are very different functions of their respective arguments, the functional dependence of, say, $E_1[V+\zeta]$ and $\tilde{E}_1[T+\zeta]$ will obviously be totally different. Nevertheless, there is this clear structural analogy and, therefore, momental functionals must be considered just as useful as their spatial counterparts.

III. THOMAS-FERMI FUNCTIONALS

The TF functionals represent a threefold approximation to the actual ones. First, one accepts (23) and (41); second, the quantum-mechanical traces are replaced by their semiclassical counterparts; third, only the classical electrostatic contribution to the interaction energy functionals $E_{e\text{-}e}$ and $\tilde{E}_{e\text{-}e}$ is taken into account (so that, in particular, the exchange energy is neglected).

For nonrelativistic atoms we get, with T_{kin} and V_{ext} from (4),

$$E_1^{\text{TF}}[V+\zeta]=2\int\frac{(d\mathbf{r}')(d\mathbf{p}')}{(2\pi)^3}[\tfrac{1}{2}p'^2+V(\mathbf{r}')+\zeta]\times\eta[-\tfrac{1}{2}p'^2-V(\mathbf{r}')-\zeta] \tag{43}$$

and

$$\tilde{E}_1^{\text{TF}}[T+\zeta]=2\int\frac{(d\mathbf{r}')(d\mathbf{p}')}{(2\pi)^3}\left[T(\mathbf{p}')-\frac{Z}{r'}+\zeta\right]\times\eta\left[-T(\mathbf{p}')+\frac{Z}{r'}-\zeta\right] , \tag{44}$$

where the factors of 2 account for the spin multiplicity. The step functions confine the range of p' in (43) and r' in (44) to

$$p'\le\{-2[V(\mathbf{r}')+\zeta]\}^{1/2}\equiv P(\mathbf{r}') \tag{45}$$

and

$$r'\le Z[T(\mathbf{p}')+\zeta]^{-1}\equiv R(\mathbf{p}') , \tag{46}$$

respectively (square roots of negative numbers are understood to equal zero). In analogy to calling $P'=P(\mathbf{r}')$ the Fermi momentum, we shall speak of the Fermi radius $R'=R(\mathbf{p}')$. Thus one finds the familiar expression for E_1^{TF},

$$E_1^{\text{TF}}[V+\zeta]=\int(d\mathbf{r}')\left[-\frac{1}{15\pi^2}\right]P'^5=\int(d\mathbf{r}')\left[-\frac{1}{15\pi^2}\right]\{-2[V(\mathbf{r}')+\zeta]\}^{5/2} \tag{47}$$

and $\tilde{E}_1^{\text{TF}}$ turns out to be given by

$$\tilde{E}_1^{\text{TF}}[T+\zeta]=\int(d\mathbf{p}')\left[-\frac{Z}{6\pi^2}\right]R'^2=\int(d\mathbf{p}')\left[-\frac{Z^3}{6\pi^2}\right][T(\mathbf{p}')+\zeta]^{-2} . \tag{48}$$

Equations (19a) and (37a) appear here as

$$n(\mathbf{r}')=\frac{1}{3\pi^2}\{-2[V(\mathbf{r}')+\zeta]\}^{3/2}=\frac{1}{3\pi^2}P'^3 , \tag{49}$$

$$\rho(\mathbf{p}')=\frac{Z^3}{3\pi^2}[T(\mathbf{p}')+\zeta]^{-3}=\frac{1}{3\pi^2}R'^3 . \tag{50}$$

These relations hold in the TF regime. We can now make use of Eqs. (15) and (33) to obtain the TF versions of E_{kin} and $\tilde{E}_{\text{ext}}$. The first one is again a familiar result,

$$E_{\text{kin}}^{\text{TF}}[n]=\int(d\mathbf{r}')\frac{1}{10\pi^2}P'^5=\int(d\mathbf{r}')\frac{1}{10\pi^2}[3\pi^2n(\mathbf{r}')]^{5/3} , \tag{51}$$

and the second one is found to be

$$\widetilde{E}^{\mathrm{TF}}_{\mathrm{ext}}[\rho]=\int(d\mathbf{p}')\left[-\frac{Z}{2\pi^2}\right]R'^2 =\int(d\mathbf{p}')\left[-\frac{Z}{2\pi^2}\right][3\pi^2\rho(\mathbf{p}')]^{2/3} . \tag{52}$$

We note that this states that the coefficient C_0 of Ref. [9] equals $\frac{3}{2}(3\pi^2)^{-1/3}=0.4849$, about ten percent more than the value 0.434 found there by numerical data fitting.

To find the momental analog $\widetilde{E}^{\mathrm{TF}}_{e\text{-}e}[\rho]$ of the spatial

$$E^{\mathrm{TF}}_{e\text{-}e}[n]=\frac{1}{2}\int(d\mathbf{r}')(d\mathbf{r}'')\frac{n(\mathbf{r}')n(\mathbf{r}'')}{|\mathbf{r}'-\mathbf{r}''|} \tag{53}$$

we need to express $n(\mathbf{r}')$ in the momental language. In the TF regime, this is achieved by

$$n(\mathbf{r}')\cong\mathrm{tr}[\delta(\mathbf{r}-\mathbf{r}')\eta(-\widetilde{H}-\zeta)] \cong 2\int\frac{(d\mathbf{p}')}{(2\pi)^3}\eta[-T(\mathbf{p}')+Z/r'-\zeta] , \tag{54}$$

where, once more, a trace is evaluated semiclassically. In terms of the Fermi radius, it reads

$$n(\mathbf{r}')=2\int\frac{(d\mathbf{p}')}{(2\pi)^3}\eta[R(\mathbf{p}')-r'] . \tag{55}$$

As evidence in favor of this relation we note that it reproduces (52) when used in

$$E_{\mathrm{ext}}=\int(d\mathbf{r}')\left[-\frac{Z}{r'}\right]n(\mathbf{r}') . \tag{56}$$

Now we insert (55) into (53) twice, perform the spatial integrations and get

$$\widetilde{E}^{\mathrm{TF}}_{e\text{-}e}=\frac{1}{12\pi^4}\int(d\mathbf{p}')(d\mathbf{p}'')(R^2_{>}R^3_{<}-\tfrac{1}{5}R^5_{<}) \tag{57}$$

with $R_{>}$ $(R_{<})$ being the larger (smaller) one of the two Fermi radii $R(\mathbf{p}')$ and $R(\mathbf{p}'')$. Then we employ Eq. (50) to replace these Fermi radii by the corresponding momental densities and arrive at the final answer,

$$\widetilde{E}^{\mathrm{TF}}_{e\text{-}e}[\rho]=\tfrac{3}{4}(3\pi^2)^{-1/3}\int(d\mathbf{p}')(d\mathbf{p}'')(\rho^{2/3}_{>}\rho_{<}-\tfrac{1}{5}\rho^{5/3}_{<}) , \tag{58}$$

wherein the significance of $\rho_{>}$ and $\rho_{<}$ is immediately obvious.

Here then are the TF functionals. The familiar spatial one combines (18), (47), and (53) into

$$\begin{aligned}E^{\mathrm{TF}}[V,n,\zeta]=&\int(d\mathbf{r}')\left[-\frac{1}{15\pi^2}\right]\{-2[V(\mathbf{r}')+\zeta]\}^{5/2}\\&-\int(d\mathbf{r}')\left[V(\mathbf{r}')+\frac{Z}{r'}\right]n(\mathbf{r}')\\&+\tfrac{1}{2}\int(d\mathbf{r}')(d\mathbf{r}'')\frac{n(\mathbf{r}')n(\mathbf{r}'')}{|\mathbf{r}'-\mathbf{r}''|}-\zeta N ,\end{aligned} \tag{59}$$

and in the new momental one,

$$\begin{aligned}\widetilde{E}^{\mathrm{TF}}[T,\rho,\zeta]=&\int(d\mathbf{p}')\left[-\frac{Z^3}{6\pi^2}\right][T(\mathbf{p}')+\zeta]^{-2}-\int(d\mathbf{p}')[T(\mathbf{p}')-\tfrac{1}{2}p'^2]\rho(\mathbf{p}')\\&+\tfrac{3}{4}(3\pi^2)^{-1/3}\int(d\mathbf{p}')(d\mathbf{p}'')(\rho^{2/3}_{>}\rho_{<}-\tfrac{1}{5}\rho^{5/3}_{<})-\zeta N ,\end{aligned} \tag{60}$$

Eqs. (36), (48), and (58) are put together. On this TF level, the spatial and momental descriptions are perfectly equivalent, as we shall now demonstrate.

For (59), Eq. (19a) is identical to (49). We use it to rewrite the TF version of (19b),

$$V(\mathbf{r}')=-\frac{Z}{r'}+\int(d\mathbf{r}'')\frac{n(\mathbf{r}'')}{|\mathbf{r}'-\mathbf{r}''|} \tag{61}$$

in the form

$$V(r')+\frac{Z}{r'}=\frac{1}{3\pi^2}\int(d\mathbf{r}'')\frac{\{-2[V(r'')+\zeta]\}^{3/2}}{\max(r',r'')} , \tag{62}$$

where, in addition, the spherical symmetry of V, n, and P has been utilized. Then, Eq. (19c) supplements this integral equation for $V(r')$ with the constraint

$$r'V(r')\rightarrow-(Z-N) \quad \text{as } r'\rightarrow\infty . \tag{63}$$

Likewise for (60), Eq. (37a) repeats (50), which we employ to rewrite the TF version of (37b),

$$T(\mathbf{p}')=\tfrac{1}{2}p'^2+(3\pi^2)^{-1/3}\int(d\mathbf{p}'')[\eta(\rho'-\rho'')\rho'^{-1/3}\rho''+\eta(\rho''-\rho')(\tfrac{3}{2}\rho''^{2/3}-\tfrac{1}{2}\rho'^{2/3})] \tag{64}$$

with $\rho'=\rho(\mathbf{p}')$ and $\rho''=\rho(\mathbf{p}'')$, in the form

$$\frac{Z}{R'}-\tfrac{1}{2}p'^2-\zeta=\frac{1}{3\pi^2}\int(d\mathbf{p}'')\left[\eta(R'-R'')\frac{R''^3}{R'}+\eta(R''-R')(\tfrac{3}{2}R''^2-\tfrac{1}{2}R'^2)\right] , \tag{65}$$

where preference is given to the Fermi radius as the fundamental function of $\mathbf{p}'$. In the limit $p' \to \infty$, when $\rho' \to 0$, Eq. (64) [in conjunction with (50) and (60)] tells us that, in view of the stationary property of $\tilde{E}^{\mathrm{TF}}[T,\rho,\zeta]$,

$$T(\mathbf{p}') - \tfrac{1}{2}p'^2 \to -\frac{\partial}{\partial Z}\tilde{E}^{\mathrm{TF}}[T,\rho,\zeta] \ . \tag{66}$$

Upon denoting the actual energy of the TF atom by $E^{\mathrm{TF}}(Z,N)$, so that $\zeta = -(\partial/\partial N)E^{\mathrm{TF}}(Z,N)$, we thus find that $T(\mathbf{p}')$ and $R(\mathbf{p}')$ are well approximated by

$$\begin{aligned} T(\mathbf{p}') &\cong \tfrac{1}{2}p'^2 - \frac{\partial}{\partial Z}E^{\mathrm{TF}}(Z,N) \ , \\ R(\mathbf{p}') &\cong Z\left[\tfrac{1}{2}p'^2 - \left[\frac{\partial}{\partial Z} + \frac{\partial}{\partial N}\right]E^{\mathrm{TF}}(Z,N)\right]^{-1} , \end{aligned} \tag{67}$$

if p' is large enough. On the other hand, for $p' \to 0$ we have $R(\mathbf{p}') \to R_0 > 0$, where the possibility $R_0 = \infty$ is actually realized in neutral atoms. Here we learn from (64) that

$$T_0 = T(p'=0) = \frac{N}{R_0} \ , \tag{68}$$

and therefore

$$\zeta = \frac{Z-N}{R_0} \ . \tag{69}$$

This identifies R_0 as the spatial radius of the TF atom; the TF potential of (62) obeys $V(R_0) = -\zeta$. And since

$$V(r') + \frac{Z}{r'} \to -\frac{\partial}{\partial Z}E^{\mathrm{TF}}(Z,N) \ \text{ for } r' \to 0 \ , \tag{70}$$

we recognize that the range of values occurring on the left-hand side (lhs) of (65) is identical with the range covered by the lhs of (62), provided that r' does not exceed R_0. In this r' range, we can express Eq. (62) in terms of the Fermi momentum,

$$\frac{Z}{r'} - \tfrac{1}{2}P'^2 - \zeta = \frac{1}{3\pi^2}\int (d\mathbf{r}'')\frac{P''^3}{\max(r',r'')} \ . \tag{71}$$

Consequently, the lhs's of (65) and (71) are the same if the functions $P(r')$ and $R(p')$ invert each other for $r' \le R_0$,

$$P(R(p')) = p', \quad R(P(r')) = r' \ . \tag{72}$$

To show that the rhs's are also identical, we treat p'' as a function of R'' in (65) and transform the $(d\mathbf{p}'')$ integral into one over $(d\mathbf{R}'')$. After a partial integration, and with the understanding that $p''=0$ for $R'' > R_0$, this gives

$$\frac{Z}{R'} - \tfrac{1}{2}p'^2 - \zeta = \frac{1}{3\pi^2}\int (d\mathbf{R}'')\frac{p''^3}{\max(R',R'')} \ . \tag{73}$$

Indeed, Eqs. (72) establish perfect equivalence between (71) and (73) and, therefore, between the spatial and the momental TF functionals. As additional evidence we mention that, when the same change of variables is performed in Eq. (55), the result is (49).

In summary, the momental density $\rho(p')$ and the effective kinetic energy $T(p')$ that obey (30), (50), and (64), are given by

$$\rho(p') = \frac{1}{3\pi^2}r'^3 \ , \quad T(p') = \frac{Z}{r'} - \zeta \tag{74}$$

with r' determined by

$$V(r') + \zeta = -\tfrac{1}{2}p'^2 \ , \tag{75}$$

where $V(r')$ is the corresponding effective TF potential. As an illustration we remark that for neutral TF atoms one has $\zeta = 0$, $R_0 = \infty$ as well as $T_0 = 0$ and the large-r' form of the effective potential is the well known

$$V(r') \cong -\tfrac{1}{2}\left[\frac{9\pi}{2r'^2}\right]^2 , \tag{76}$$

implying

$$\begin{aligned} \rho(p') &\cong 9/(8\pi p'^3)^{1/2} \ , \\ T(p') &\cong Z\left[\frac{2}{9\pi}p'\right]^{1/2} , \end{aligned} \tag{77}$$

for $p' \to 0$. These small-p' dependences are confirmed by Fig. 1. In weakly ionized TF atoms ($N \lesssim Z$) one gets

$$R_0 = \frac{Z-N}{\zeta} \cong \frac{1}{2}\left[\frac{3\pi}{4}\Lambda\right]^{2/3}(Z-N)^{-1/3} \tag{78}$$

with [23] $\Lambda = 32.73$, so that there

$$\begin{aligned} \rho(p'=0) &\cong \frac{3}{128}\frac{\Lambda^2}{Z-N} \ , \\ T(p'=0) &\cong 2\left[\frac{3\pi}{4}\Lambda\right]^{-2/3} N(Z-N)^{1/3} \ . \end{aligned} \tag{79}$$

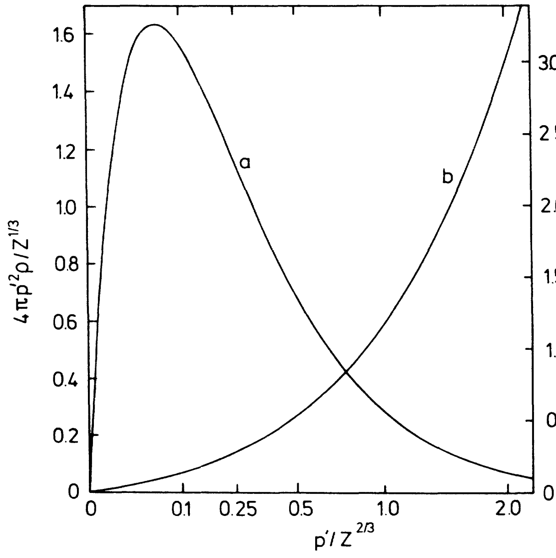

FIG. 1. Radial momental density $4\pi p'^2\rho(p')$ (curve a) and effective kinetic energy $T(p')$ (curve b) in the neutral TF atom, as functions of p'. The abscissa is linear in the square root of p'.

Of course, the TF approximation is not reliable for $r' \to 0$ and $r' \cong R_0$, that is, for $p' \to \infty$ and $p' \gtrsim 0$. Matters are improved for $p' \to \infty$ as soon as the Scott correction is included into the description [16,17]. For a realistic treatment of the small-p' range, one has to take the exchange energy into account as well as quantum corrections to $\widetilde{E}_1$ [24], which represent a step beyond the semiclassical phase-space integral of (44) and are thus essentially in the spirit of the von Weizsäcker correction to E_{kin}. Work on the latter subject is in progress and will be reported in due course.

IV. MISCELLANEA

A. Scaling

As has been shown recently by Levy and Perdew [25], the intuitive scaling laws

$$\begin{aligned} E_{\text{kin}}[n_\mu] &= \mu^2 E_{\text{kin}}[n] , \\ E_{e\text{-}e}[n_\mu] &= \mu E_{e\text{-}e}[n] \end{aligned} \tag{80}$$

with

$$n_\mu(\mathbf{r}') = \mu^3 n(\mu \mathbf{r}') \tag{81}$$

(where $\mu > 0$, of course) do *not* hold for T_{kin} of (4) and $H_{\text{e-e}}$ of (5). Instead, one can derive

$$\begin{aligned} (\mu - 1)(E_{\text{kin}}[n_\mu] - \mu^2 E_{\text{kin}}[n]) &\le 0 , \\ (\mu - 1)(E_{e\text{-}e}[n_\mu] - \mu E_{e\text{-}e}[n]) &\ge 0 , \end{aligned} \tag{82}$$

where the equal signs apply only for $\mu = 1$.

It is a simple matter to repeat the arguments of Ref. [25] for the momental functionals $\widetilde{E}_{\text{ext}}$ and $\widetilde{E}_{e\text{-}e}$, and one finds that, for $H_{e\text{-}e}$ of (5) and $V_{\text{ext}} = -Z/r$, the momental functionals *do* scale according to the intuitive laws

$$\begin{aligned} \widetilde{E}_{\text{ext}}[\rho_\mu] &= \mu \widetilde{E}_{\text{ext}}[\rho] , \\ \widetilde{E}_{e\text{-}e}[\rho_\mu] &= \mu \widetilde{E}_{e\text{-}e}[\rho] \end{aligned} \tag{83}$$

with

$$\rho_\mu(\mathbf{p}') = \mu^{-3} \rho(\mathbf{p}'/\mu) . \tag{84}$$

This statement is, unfortunately, no longer true when V_{ext} differs from a pure Coulomb potential.

The intuitive scalings (80) and (83) can be expected to be obeyed approximately to a high accuracy. For instance, a glance at (51)–(53) and (58) suffices to see that the TF functionals scale exactly in the intuitive way.

B. Multiple counting

The quantities

$$E_1[V + \zeta] - \zeta N = \left\langle \psi_0 \left| \sum_j H(\mathbf{r}_j, \mathbf{p}_j) \right| \psi_0 \right\rangle \equiv E_{\text{IP}} \tag{85}$$

and

$$\widetilde{E}_1[T + \zeta] - \zeta N = \left\langle \psi_0 \left| \sum_j \widetilde{H}(\mathbf{r}_j, \mathbf{p}_j) \right| \psi_0 \right\rangle \equiv \widetilde{E}_{\text{IP}} \tag{86}$$

can be regarded as sums of effective independent-particle (IP) energies, once with an effective potential energy, once with an effective kinetic energy.

To obtain the actual energy, one must subtract the amounts

$$\Delta E = \int (d\mathbf{r}') V_{e\text{-}e}(\mathbf{r}') n(\mathbf{r}') - E_{e\text{-}e}[n] \tag{87}$$

or

$$\Delta \widetilde{E} = \int (d\mathbf{p}') T_{e\text{-}e}(\mathbf{p}') \rho(\mathbf{p}') - \widetilde{E}_{e\text{-}e}[\rho] , \tag{88}$$

respectively. In the TF approximation, one finds

$$\Delta E \cong E_{e\text{-}e} , \quad \Delta \widetilde{E} \cong \tfrac{2}{3} \widetilde{E}_{e\text{-}e} \tag{89}$$

with the consequences

$$\begin{aligned} E_{\text{IP}} &\cong E_{\text{kin}} + E_{\text{ext}} + 2E_{e\text{-}e} , \\ \widetilde{E}_{\text{IP}} &\cong \widetilde{E}_{\text{kin}} + \widetilde{E}_{\text{ext}} + \tfrac{5}{3} \widetilde{E}_{e\text{-}e} . \end{aligned} \tag{90}$$

[These are *not* statements about functionals but about their numcerical values for the actual $n(\mathbf{r}'), \rho(\mathbf{p}'), \ldots$]. Thus, the independent-particle energy E_{IP} counts the electron-electron energy $\langle H_{e\text{-}e} \rangle$ (roughly) twice, whereas $\widetilde{E}_{\text{IP}}$ counts $\langle H_{e\text{-}e} \rangle$ (roughly) $\frac{5}{3}$ times. The suggestive intuitive notion of "double" counting the electron pairs, when employing effective independent-particle pictures, does not apply to momentum space formulations. In momentum space, new intuition needs to be built up.

ACKNOWLEDGMENTS

I would like to thank F. Bell, M. Cinal, S. Olszewski, and J. Schwinger for stimulating discussions.

APPENDIX

If we denote the eigenstates of the independent-particle Hamilton operator (21) by $|\varphi_\nu\rangle$ and the corresponding eigenvalues by $\mathcal{E}_\nu$,

$$H|\varphi_\nu\rangle = |\varphi_\nu\rangle \mathcal{E}_\nu , \tag{A1}$$

then Eqs. (19a) and (22) produce

$$n(\mathbf{r}') = \sum_\nu \frac{\partial f(\mathcal{E}_\nu + \zeta)}{\partial \mathcal{E}_\nu} \langle \mathbf{r}' | \varphi_\nu \rangle \langle \varphi_\nu | \mathbf{r}' \rangle . \tag{A2}$$

This has the appearance of Löwdin's sum over natural orbitals [18]. So the question is raised whether the $|\varphi_\nu\rangle$ are identical with the natural orbitals. The answer is no.

To see this, first observe that (37a) and (40) imply, quite analogously,

$$\rho(\mathbf{p}') = \sum_\nu \frac{\partial \widetilde{f}(\widetilde{\mathcal{E}}_\nu + \zeta)}{\partial \widetilde{\mathcal{E}}_\nu} \langle \mathbf{p}' | \widetilde{\varphi}_\nu \rangle \langle \widetilde{\varphi}_\nu | \mathbf{p}' \rangle \tag{A3}$$

with

$$\widetilde{H}|\widetilde{\varphi}_\nu\rangle = |\widetilde{\varphi}_\nu\rangle \widetilde{\mathcal{E}}_\nu . \tag{A4}$$

Thus, if (A2) sums over natural orbitals then (A3) does the same. And because the natural orbitals are unique, the set of states $|\varphi_\nu\rangle$ must be identical with the set $|\tilde{\varphi}_\nu\rangle$. In short, H and $\tilde{H}$ have their eigenstates in common, which is to say that they commute. Consequently,

$$[T(\mathbf{p}), V(\mathbf{r})] = [T_{\text{kin}}(\mathbf{p}), V_{\text{ext}}(\mathbf{r})] \tag{A5}$$

must be true. This, however, is only possible if V is a numerical multiple of V_{ext} and T_{kin} is the same multiple of T. Since V and V_{ext} as well as T and T_{kin} are in fact very different functions of $\mathbf{r}$ or $\mathbf{p}$, respectively, Eq. (A5) does not hold. So the $|\varphi_\nu\rangle$ and $|\tilde{\varphi}_\nu\rangle$ are not the same and neither set of states is identical with the natural orbitals.

---

*Also at the Max-Planck-Institut für Quantenoptik, Ludwig-Prandtl-Strasse 10, D-8046 Garching, Germany.

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[2] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).

[3] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer-Verlag, Berlin, 1990).

[4] G. I. Plindov and I. K. Dmitrieva, Phys. Lett. **64A**, 348 (1978).

[5] J. Schwinger, Phys. Rev. A **24**, 2353 (1981).

[6] B.-G. Englert and J. Schwinger, Phys. Rev. A **32**, 47 (1985).

[7] B.-G. Englert and J. Schwinger, Phys. Rev. A **32**, 26 (1985).

[8] G. A. Henderson, Phys. Rev. A **23**, 19 (1981).

[9] R. K. Pathak, P. V. Panat, and S. R. Gadre, Phys. Rev. A **26**, 3073 (1982).

[10] G. P. Das, S. K. Ghosh, and V. C. Sahni, Solid State Commun. **65**, 719 (1988).

[11] V. D. Smith, Jr., in *Local Density Approximations in Quantum Chemistry and Solid State Physics,* edited by J. P. Dahl and J. Avery (Plenum, New York, 1984), pp. 1–19.

[12] *Density Functional Methods in Physics,* Vol. 123 of *NATO Advanced Study Institute, Series B: Physics,* edited by R. M. Dreizler and J. da Providencia (Plenum, New York, 1985).

[13] G. P. Das, K. V. Bhagwat, and V. C. Sahni, Phys. Rev. A **36**, 2984 (1987).

[14] Experimental methods are reviewed in *Momentum Distributions,* edited by R. N. Silver and P. E. Sokol (Plenum, New York, 1989).

[15] For example, C. A. Coulson and N. H. March, Proc. Phys. Soc. London Sect. A **63**, 367 (1950); L. Lam and P. U. Platzman, Phys. Rev. B **9**, 5122 (1974); S. R. Gadre and R. K. Pathak, Phys. Rev. A **24**, 2906 (1981); S. R. Gadre and S. J. Chakravorty, *ibid.* **33**, 1374 (1986).

[16] K. Buchwald and B.-G Englert, Phys. Rev. A **40**, 2738 (1989).

[17] M. Cinal and B.-G. Englert, following paper, Phys. Rev. A **44**, 135 (1991).

[18] P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955).

[19] B.-G. Englert, *Semiclassical Theory of Atoms,* Vol. 300 of *Lecture Notes in Physics,* edited by J. Ehlers *et al.* (Springer-Verlag, Berlin, 1988).

[20] As an illustration, for the TF functionals these eliminations are explicitly performed in Ref. [19], p. 110.

[21] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[22] This procedure—momental density calculated from Fourier transformed spatial KS orbitals—has, of course, been used repeatedly. See, for example, G. E. W. Bauer and J. R. Schneider, Solid State Commun. **47**, 673 (1983); Z. Phys. B **54**, 17 (1983); or H. Reinisch, dissertation (Dr. rer. nat.), Universität München, 1990.

[23] B.-G. Englert, Phys. Rev. A **33**, 2146 (1986).

[24] For the analogous improvements of the spatial description, consult B.-G. Englert and J. Schwinger, Phys. Rev. A **29**, 2339 (1984), or Ref. [19], Chap. 4.

[25] M. Levy and J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).