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Local-density-functional model for atoms in momentum space

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A local-density-functional model in momentum space enabling direct calculations of electron momentum densities for atomic systems is presented. This is based on the coordinate-space local-density-functional model of Parr *et al.* in conjunction with quasiclassical phase-space considerations. Within the model, electron-electron interaction and nuclear-electron attraction energies turn out to be simple local functionals of momentum density while kinetic energy has been treated exactly. The momentum densities obtained through this model have a simple algebraic form. Numerical investigations employing these densities reveal that reasonable estimates of various $\langle p^n \rangle$ expectation values as compared to their Hartree-Fock counterparts can be obtained.

I. INTRODUCTION

There exist two well-known ways for obtaining single-particle momentum density $\chi(\vec{p})$ for a bound N-electron problem:

(i) To solve the Schrödinger equation in coordinate representation yielding a configuration-space wave function $\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ ($\vec{r}$ incorporates the space and spin coordinates), and Fourier transform the wave function thus obtained, to give the momentum-space wave function $\phi(\vec{p}_1,\vec{p}_2,\ldots,\vec{p}_N)$. Consequently, the single-particle momentum density $\chi(\vec{p}_1)$ is extracted from ϕ as

$$\chi(\vec{p}_1)=N\int |\phi(\vec{p}_1,\vec{p}_2,\ldots,\vec{p}_N)|^2 \times d\tau_{\vec{p}_2}d\tau_{\vec{p}_3}\cdots d\tau_{\vec{p}_N}\,, \tag{1}$$

where an integration over $d\tau_{\vec{p}}$ means integration over three momentum components of $\vec{p}$, and the spin coordinate.

(ii) To solve the Schrödinger equation in momentum representation directly and extract the momentum density from the momentum-space wave function using Eq. (1) above. In momentum representation the Schrödinger equation emerges[1] as an integral equation which is difficult to solve, especially for many-electron systems. Hence, by and large, the first of the above approaches has been favored. The earliest study that employs the second approach was carried out by Coulson and McWeeny.[1] They could, however, solve the Schrödinger equation in an approximate way for simple two-electron systems only. Thereafter, no significant progress in this direction seems to have been made. An attractive alternative to the conventional coordinate-space wave function approach is furnished by the density-functional theory[2] wherein the electron density $\rho(\vec{r})$ is treated as a fundamental variable. A momentum-space transcription of the Hohenberg-Kohn formalism has recently been speculated by Henderson[3] based upon the Levy[4] formulation of the density-functional theory. No concrete direct calculation of $\chi(\vec{p})$ has, however, been reported in the literature. The spirit underlying the present work is to report a concrete model which is aimed at achieving such a direct calculation.

II. MODEL

A local-density-functional model in a coordinate space has recently been put forth by Parr *et al.*[5] wherein the total energy of an atomic system, as a functional of electron density, has been modeled as

$$E\equiv E[\rho]=A\int \rho^{5/3}(\vec{r})d\tau + BN^{2/3}\int \rho^{4/3}(\vec{r})d\tau - Z\int \frac{\rho(\vec{r})d\tau}{r}\,, \tag{2}$$

where A and B are constants and N is the number of electrons equal to $\int \rho(\vec{r})d\tau$. This model is local in that each component is represented as an integral of a *function* of the electron density times some function of the electron number. The representation of the electron-electron repulsion energy, V_{ee} by a simple functional

$$BN^{2/3}\int \rho^{4/3}(\vec{r})d\tau$$

is indeed a novel feature of this model.

A further justification for this form was provided for the major component of V_{ee}, namely, the Coulomb repulsion energy V_c, by Gadre *et al.*[6] in terms of a bound

$$V_c=\int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{2r_{12}}d\tau_1 d\tau_2$$

$$<1.09\,18N^{2/3}\int \rho^{4/3}(\vec{r})d\tau \ . \tag{3}$$

In their work, besides rigorously proving the inequality (3), various fits to the Hartree-Fock V_c and V_{ee} components were also presented for atoms, leading to the representations

$$V_c=A_1N^{2/3}\int \rho^{4/3}(\vec{r})d\tau$$

and

$$V_{ee}=(A_2N^{2/3}-A_3)\int \rho^{4/3}(\vec{r})d\tau \ ,$$

where all A_i's were determined from the fits in a least-squares sense. That the quantity

$$A_1N^{2/3}\int \rho^{4/3}(\vec{r})d\tau$$

represents adequately the Coulomb repulsion energy V_c has been further demonstrated in a recent study[7] on two-electron systems. A further recent work[8] discloses a remarkable proportionality between the $\langle p\rangle$ expectation values and $\int \rho^{4/3}(\vec{r})d\tau$ calculated from the atomic Hartree-Fock wave functions tabulated by Clementi and Roetti.[9] A justification for this is provided by semiclassical phase-space considerations[8] similar to those made by Coulson and March.[10] This enables one to approximately represent the electron-electron interaction energy for atomic systems by a local form

$$V_{ee}=(A_0N^{2/3}-B_0)\int \chi(p)p\,d\tau_p \ . \tag{4}$$

Within the present model, the electron-nuclear attraction energy is also approximated by another local form

$$V_{ne}=-C_0Z\int \chi^{2/3}(p)d\tau_p \ , \tag{5}$$

suggested by the transformations discussed in Ref. 8. In Eqs. (4) and (5) the spherical symmetry of $\chi(\vec{p})$ is implicit. The parameters to be fixed now are A_0, B_0, and C_0. The numbers A_0 and B_0 were determined by independently fitting the Hartree-Fock energy components of Coulomb repulsion, energy, and the exchange energy in a least-squares sense to the form in Eq. (4), yielding $A_0=0.374$ and $B_0=0.312$ (in a.u.). It should be noted that the functionals (4) and (5) are local in the sense of Parr *et al.*[5] That these terms scale correctly as the potential energy of Coulombic interactions, is evident from the scaling arguments akin to those of Szasz *et al.*[11]

If an integral

$$I=f(N)\left[\int \chi^l(p)p^m d\tau_p\right]^n \tag{6}$$

$[f(N)$ being an arbitrary function of $N]$ is to represent the potential energy for Coulombic interactions the numbers l, m, and n must be connected by

$$(3-3l+m)n=1 \ . \tag{7}$$

Thus the representations (4) and (5) become particular cases for $l=m=n=1$ and $l=\frac{2}{3}$, $m=0$, $n=1$, respectively. Having fixed the values of A_0 and B_0, the construction of the total energy functional in momentum space is straightforward since the kinetic energy in momentum space bears an exact simple form

$$T=\int \chi(p)\frac{p^2}{2}d\tau_p \ . \tag{8}$$

Therefore, apart from the number C_0 to be determined later, the total energy within the present model emerges as

$$\begin{aligned}E&\equiv E[\chi]\\&=\int \chi(p)\frac{p^2}{2}d\tau_p\\&\quad+(A_0N^{2/3}-B_0)\int \chi(p)p\,d\tau_p\\&\quad-C_0Z\int \chi^{2/3}(p)d\tau_p \ ,\end{aligned} \tag{9}$$

which is a universal functional of the momentum density χ, for atomic systems. The only unknown, C_0 can be determined by fitting the total energy E [Eq. (8)] to the corresponding Hartree-Fock data (derived from the wave functions of Ref. 9) in a least-squares sense, whence $C_0=0.434$. The momentum densities were obtained by an application of the variational technique to minimize E, subject to the constraint

$$\int \chi(p)d\tau_p=N=\text{const} \tag{10}$$

expressing the constancy of the total number of electrons. This amounts to solving the equation

$$\frac{\delta E}{\delta \chi}-\mu=0\,, \tag{11}$$

where μ, the Lagrange multiplier, can be identified with the chemical potential. Equations (9)–(11) yield

$$\frac{p^2}{2}+(A_0N^{2/3}-B_0)p+\tfrac{2}{3}A_0\langle p\rangle N^{-1/3}-\mu-\frac{2}{3}\frac{ZC_0}{[\chi(p)]^{1/3}}=0\,. \tag{12}$$

Here, the abbreviation $\langle p\rangle$ means $\int \chi(p)p\,d\tau_p$. Now for the exact solution $\chi(p)$, i.e., that minimizes E and satisfies Eq. (10), $\langle p\rangle$ turns out to be a number, which is fixed for a given system. The chemical potential μ is also a constant for a given system rendering the quantity

$$\lambda=\left[\frac{2}{3}\frac{A_0\langle p\rangle}{N^{1/3}}-\mu\right]\,,$$

a positive constant for a given atomic system. Hence, Eq. (12) gives the momentum density $\chi(p)$ as

$$\chi(p)=\frac{(\frac{2}{3}ZC_0)^3}{\left[\frac{p^2}{2}+(A_0N^{2/3}-B_0)p+\lambda\right]^3}\,. \tag{13}$$

Employing the form (13) of the electron-momentum density, the only unknown parameter λ can at once be determined with the normalization condition (10). The atomic-momentum densities thus obtained will be investigated for numerical tests in the next section.

III. RESULTS AND DISCUSSION

It may be noticed that the form (13) for $\chi(p)$ is a simple algebraic function of p. This makes it possible to evaluate the $\langle p\rangle$ expectation values analytically. Numerical investigations to obtain these for neutral as well as singly ionized atomic species were carried out for $Z=3-36$. Since the energy components scale appropriately as kinetic and potential energies, the fulfillment of the virial theorem is automatically guaranteed, independent of the actual values of the parameters A_0, B_0, and C_0. It was ensured numerically that the normalization condition (10) was satisfied extremely accurately. Also, the virial criterion

$$V=-2T\,, \tag{14}$$

where V is the total potential energy and T, the total kinetic energy was satisfied exactly to eight decimal places by the solutions $\chi(p)$ for atoms and the corresponding singly ionized ions. Table I displays the values $\langle p^{-1}\rangle$, $\langle p\rangle$, and the total energies along with the energy components V_{ne} and V_{ee} for a few randomly selected neutral atoms. The corresponding Hartree-Fock values have also been displayed for a comparison. A mean deviation of about 5% can be seen between these total energies and the corresponding Hartree-Fock energies. The errors in V_{ne} and V_{ee} from the corresponding Hartree-Fock values are typically ~20% for low-Z atoms and decreases to ~2% for high-Z atoms. As may be seen from Table I, expecially the $\langle p\rangle$ expectation values agree extremely well with their Hartree-Fock counterparts, a typical error being 0.5%. The $\langle p^{-1}\rangle$ values, however, are not predicted with this much accuracy, the typical error in these values is 20%.

TABLE I. Total energies E, energy components V_{ne} and V_{ee}, and $\langle p\rangle$ and $\langle p^{-1}\rangle$ expectation values for a few atoms within the present model in comparison with their Hartree-Fock counterparts[a] (all values in a.u.).

		$-E$		$-V_{ne}$		V_{ee}		$\langle p\rangle$		$\langle p^{-1}\rangle$	
Z	Atom	Present model	Hartree-Fock[b]	Present model	Hartree-Fock[b]	Present model	Hartree-Fock[b]	Present model	Hartree-Fock[b]	Present model	Hartree-Fock[b]
3	Li	9.29	7.43	20.93	17.14	2.36	2.88	5.06	4.91	3.29	5.19
8	O	84.35	74.81	197.3	178.1	28.6	28.5	23.72	23.72	5.20	5.55
13	Al	255.5	241.9	604.1	578.6	93.1	94.8	53.05	52.72	6.37	10.29
18	Ar	539.0	526.8	1281.0	1255.0	203.5	202.9	90.18	88.70	7.26	10.13
23	V	947.5	942.9	2261.0	2237.0	365.4	351.5	134.7	134.6	7.98	14.77
28	Ni	1491.3	1506.9	3566.0	3601.0	583.5	587.1	186.0	173.8	8.61	13.97
36	Kr	2664.6	2752.0	6388.0	6583.0	1059.0	1078.5	281.2	268.9	9.46	14.40

[a] See text for further details.

[b] Derived from the wave functions of Ref. 9.

From the nature of $\chi(p)$, it is evident that $\chi(p)$ decreases monotonically and falls off to zero asymptotically as $\sim p^{-6}$ as do the momentum densities derived from the Thomas-Fermi model. Benesch and Smith[12] have established the exact asymptotic behavior of momentum densities to be $\sim p^{-8}$.

The $\chi(0)$ values obtained within the present model decrease monotonically with increasing Z for neutral atoms, whereas the near Hartree-Fock $\chi(0)$'s oscillate[13] with Z. The $\chi(0)$ values for oxygen, neon, and argon atoms within the present model are 0.99, 0.87, and 0.59, respectively, as compared to the corresponding Hartree-Fock values of 0.51, 0.25, and 0.76. Also, the $\chi(p)$'s within the present model fall off rather slowly in comparison with their Hartree-Fock counterparts.

When applied to ionic systems, the present model deems all positive ions stable, which is a desirable feature, but it rules out the existence of any stable negative ions. These features are also similar to those exhibited by the Thomas-Fermi atomic model. This similarity may be attributed to the quasiclassical considerations that are exact within the Thomas-Fermi realm. Yet another artifact of the present model is that the radial momentum density $I(p)=4\pi p^2\chi(p)$ exhibits only a single maximum as has been portrayed for the case of neon in Fig. 1. It may be noticed from Fig. 1 that the present model leads to $I(p)$ which closely resembles the corresponding Hartree-Fock one[13] for the case of the neon atom. Both the Hartree-Fock and the present $I(p)$ show a single maximum around $p \sim 1.4$ a.u. A recent study[13] of shell structure of atoms in momentum space employing near Hartree-Fock wave functions[9] reveals that most atoms show more than one maximum in their $I(p)$'s with the notable exceptions of helium, carbon, and neon atoms which show a single peak. Within the present model, however, only one peak in $I(p)$ is discernible for *all* the atoms. Thus the present model denies the shell structure for atoms in momentum space. Incidentally, the chemical potential, which is, magnitudewise, a small number compared to the total energy of a system, cannot be reliably estimated from this simple model.

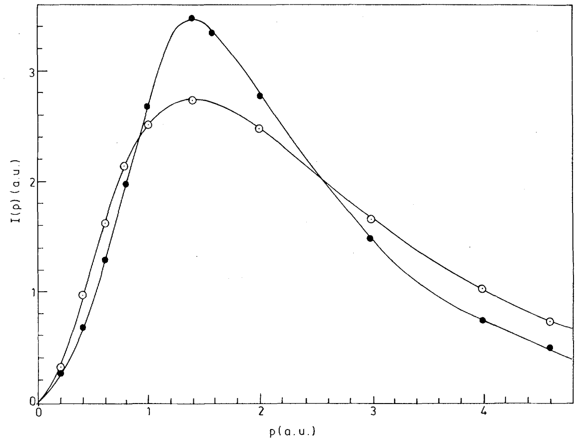

FIG. 1. Plot of the radial momentum density $I(p)$ vs p within the present model (○—○) compared with that within the Hartree-Fock theory (Ref. 13) (●—●) for the ground state of the neon atom.

It is gratifying that this model ascribes a closed form to the atomic electron-momentum density and also has a potential to provide quick and fairly accurate estimates of various gross atomic properties. The atomic electron-momentum densities and properties computed for $Z=3-36$ were worked out within less than 10 sec on the ICL 1904 S computer. This exercise, which aims at constructing a *first ever* concrete density-functional model in momentum space is expected to impart an impetus for more exhaustive considerations in this direction.

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