r- and p-space electron densities and related kinetic and exchange energies in terms of s states alone for the leading term in the 1/Z expansion for nonrelativistic closed-shell atomic ions

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As a step towards constructing nonlocal energy density functionals, the leading term in the so-called 1/Z expansion for closed-shell atomic ions is the focus here. This term is characterized by the properties of the bare Coulomb potential $(-Ze^2/r)$, and for an arbitrary number of closed shells it is known that $\partial\rho(r)/\partial r = -(2Z/a_0)\rho_s(r)$, where $\rho(r)$ is the ground-state electron density while $\rho_s(r)$ is the s-state ($l=0$) contribution to $\rho(r)$. Here, the kinetic-energy density $t(r)$ is also derived as a double integral in terms of $\rho_s(r)$ and Z. Although the exchange energy density $\epsilon_x(r)$ is more complex than $t(r)$, a proof is given that, in the Coulomb limit system, ϵ_x is indeed also determined by s-state properties alone. The same is shown to be true for the momentum density $n(p)$, which here is obtained explicitly for an arbitrary number of closed shells. Finally, numerical results are presented that include (a) ten-electron atomic ions ($K+L$ shells), (b) the limit as the number of closed shells tends to infinity, where an appeal is made to the analytical r-space study of Heilmann and Lieb [Phys. Rev. A **52**, 3628 (1995)], and (c) momentum density and Compton line shape for an arbitrary number of closed shells.

I. INTRODUCTION

The search for closed forms of the single-particle kinetic-energy functional $T_s[\rho]$ and the corresponding exchange energy $E_x[\rho]$ continues unabated [1–4]. Such knowledge would bypass the calculation of orbitals presently obtained by solving the Slater-Kohn-Sham equations [5,6] and would greatly facilitate therefore progress in studying, for example, the very large molecules of biological interest. But naturally one must transcend the local density approximation (LDA) to the density functional theory to contribute significantly in this area. Therefore, we have recently been invoking models such as one-dimensional harmonic confinement in order to gain insight into the nature of nonlocality [7] in $T_s[\rho]$. What seems remarkable in this admittedly simple framework is that $T_s[\rho]$ for this model can be completely characterized by the original Thomas-Fermi kinetic-energy functional and the von Weizsäcker inhomogeneity kinetic energy [8]. And this is notwithstanding the genuine nonlocal character of $T_s[\rho]$ in this harmonic model [7].

In a recent paper [9] we have presented both analytical and numerical results for the exchange-energy density $\epsilon_x(r)$ for ten-electron Ne-like atomic ions in the limit of large atomic number Z. Comparison was made between the exact form of $4\pi r^2\epsilon_x(r)$ and the Dirac-Slater $\rho^{4/3}$ LDA equivalent, $\rho(r)$ being the exact electron density. The point-to-point agreement between the two results for $4\pi r^2\epsilon_x(r)$ was excellent but the total LDA exchange energy [10,11,5] was still in error by about 10%.

The present work has a different focus, namely, to handle first of all an arbitrary number of closed shells in the leading term of the 1/Z expansion, which is the bare Coulomb limit [12], in both **r** space and momentum (**p**) space. Second, we shall demonstrate that both kinetic- and exchange-energy densities are determined in this Coulomb-limit case and for an arbitrary number of closed shells $\mathcal{N}$, by $s(l=0)$ states

alone, with atomic number Z. In this latter context, in an earlier work by one of us [13], it was shown that a spatial generalization of Kato's theorem can be established for arbitrary $\mathcal{N}$ as

$$\frac{\partial\rho(r)}{\partial r} = \frac{-2Z}{a_0}\rho_s(r), \quad a_0 = \frac{\hbar^2}{me^2}, \tag{1.1}$$

where $\rho_s(r)$ is the $l=0$ contribution to the total electron density $\rho(r)$. Our initial aim, achieved in Sec. II below, is then to obtain a result for the kinetic-energy density $t(r)$ solely in terms of atomic number Z and s-state density $\rho_s(r)$ for arbitrary $\mathcal{N}$ in this Coulomb-limit system. Section III contains the proof that the corresponding exchange-energy density $\epsilon_x(r)$ is also determined, at least in principle, by Z, $\rho_s(r)$, and physical boundary conditions although the result is less explicit than for the kinetic contribution. In addition to the exchange energy, we treat in Sec. III the momentum density $n(p)$ and show again that s-state properties alone determine this quantity. A complete solution for $n(p)$ for an arbitrary number of closed shells is the content of Sec. IV. As numerical examples, we give in Sec. V explicit results for $t(r)$, both for ten-electron atomic ions for $Z=92$ and for the limit when the number of closed shells is allowed to tend to infinity. Here, we lean heavily on the important analysis of Heilmann and Lieb [14] in this limit when $\mathcal{N}\rightarrow\infty$. After numerical results for $n(p)$ and the associated Compton line shape, some approximate results are also presented for $\epsilon_x(r)$ for $\mathcal{N}\rightarrow\infty$. Section VI constitutes a summary, with some proposals for possible further studies. In one of the appendices, some generalizations are presented that are applicable to any central potential $V(r)$ that confines electrons. In closing this section, we should refer the reader who requires general background for what follows to the review by Benesch and Smith [15] on density matrix methods in x-ray scattering and momentum-space calculations.

II. SECOND DERIVATIVE OF KINETIC-ENERGY DENSITY $t(r)$ IN TERMS OF ATOMIC NUMBER Z AND THE s-STATE DENSITY $\rho(r)$ IN THE LIMIT SYSTEM OF LARGE Z

We generalize below the analysis of Nagy and co-workers [16,17] who treated s and p states only, but dealt with the kinetic-energy density in this case. For independent electrons moving in the general central potential $V(r)$, one can write

$$[r^2 t_s(r)]' = -\tfrac{1}{8}[r^2 \rho_s(r)]''' - \tfrac{1}{2} r^2 \rho_s(r) V'(r), \quad (2.1)$$

where t_s is given by the Laplacian form of the kinetic-energy density, i.e., with the wave function Ψ, $-\tfrac{1}{2}\Psi\nabla^2\Psi$. In this study we shall consistently use the (positive definite) form $\tfrac{1}{2}(\nabla\Psi)^2$ for both total kinetic-energy density $t(r)$ and its s component t_s. The two forms differ, as is well known, by one-quarter of the Laplacian of the electron density $\rho(\mathbf{r})$. Making this change to t_s in Eq. (2.1) yields the equation valid for any central potential $V(r)$, namely,

$$\frac{\partial}{\partial r}[r^2 t_s(r)] - \frac{1}{8}\frac{\partial}{\partial r}(r^2 \rho_s'') + \frac{1}{4}\rho_s' = -\frac{1}{2}r^2 \rho_s V'(r). \quad (2.2)$$

Applying this general equation, valid for any number of filled s-levels and any $V(r)$, to the Coulomb case for which $\partial V/\partial r = Z/r^2$ and using Eq. (1.1) in the right-hand side of Eq. (2.2), one can integrate immediately with respect to r to find

$$t_s(r) = \frac{1}{4}\frac{[\rho'(r) - \rho_s(r)]}{r^2} + \frac{\rho_s''(r)}{8}. \quad (2.3)$$

Here then is a direct route for numerical calculations of the s-wave contribution $t_s(r)$ to the total kinetic-energy density $t(r)$ for the Coulomb-field-limit system under consideration for any chosen number of closed shells $\mathcal{N}$. Such numerical results will be presented in Sec. V below for (a) $K+L$ shells only and (b) for the limit $\mathcal{N}\to\infty$ for which the theory of Heilmann and Lieb gives an explicit (integral) representation of $\rho(r)$, and hence from Eq. (1.1), for $\rho_s(r)$. In passing, we note that integration through the volume of Eq. (2.3) recovers the earlier result [18]

$$T_s = \pi \int_0^\infty \rho(r)dr \quad (2.4)$$

for the total s-state kinetic energy T_s.

Returning to the total kinetic-energy density $t(r)$, Amovilli and March [19] have shown more recently that for the Coulomb-limit system with arbitrary $\mathcal{N}$,

$$\frac{\partial t}{\partial r} = \frac{\rho'''}{8} - \frac{3\rho'}{4r^2} - \frac{3Z}{2r^2}\rho \quad (2.5)$$

and hence, by differentiation and use of Eq. (1.1),

$$\nabla^2 t(r) = -\frac{Z}{a_0}\left[\frac{\rho_s'''}{4} + \frac{\rho_s''}{2r} - \frac{3\rho_s'}{2r^2} - \frac{3Z\rho_s}{r^2}\right] \quad (2.6)$$

or, in terms of the total density $\rho(r)$,

$$\nabla^2 t(r) = \left[\frac{\rho^{IV}}{8} + \frac{\rho'''}{4r} - \frac{3\rho''}{4r^2} - \frac{3Z\rho'}{2r^2}\right]. \quad (2.7)$$

Therefore, $t(r)$ can be written in integral form as

$$t(r) = \frac{-1}{4\pi}\int \frac{[\rho(r')^{IV}/8 + \rho(r')'''/2r' - 3\rho(r')''/4r'^2 - 3Z\rho(r')'/2r'^2]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \quad (2.8)$$

and we note that Z can be determined in terms of the density from Eq. (1.1) as $Z = -(a_0/2)[\rho'(0)/\rho(0)]$. For the Coulomb problem, since $Z = -(a_0/2)[\rho'(0)/\rho(0)]$ from Eq. (1.1), Eq. (2.8) gives $t(r)$ as a functional solely of $\rho(r)$. Of course, it must not be assumed that there is universality from such a result; it is specific to the Coulomb model for $\mathcal{N}$ closed shells. However, the structure of Eq. (2.8) is interesting, and as we shall see when we compare this form with the exchange energy density $\epsilon_x(r)$ to which we now turn, there is remarkable similarity of shape for $t(r)$ and $\epsilon_x(r)$ in this model.

III. PROOF THAT EXCHANGE-ENERGY DENSITY $\epsilon_x(r)$ AND p-SPACE MOMENTUM DENSITY IN THE COULOMB-LIMIT CASE ARE DETERMINED BY s-STATE INFORMATION ALONE

The burden of this section is to demonstrate again that, as shown explicitly for kinetic-energy density $t(r)$ in Eq. (2.7),

the exchange-energy density $\epsilon_x(r)$ derived from the leading term in the $1/Z$ expansion can be characterized by Z and s-state information alone. The proof we have to date is more formal than that in Sec. II for $t(r)$. In particular, we appeal to the investigation of Theophilou and March [20] who generalized Eq. (1.1) to apply to the Dirac density matrix [7] or the "off-diagonal" density $\gamma(\mathbf{r},\mathbf{r}')$, where $\rho(\mathbf{r}) = \gamma(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}$. Their result may be written, using variables discussed by Blinder [21], as

$$\gamma(\mathbf{r},\mathbf{r}') = -(x-y)^{-1}\left[\frac{\partial}{\partial x} - \frac{\partial}{\partial y}\right]\left[xy\,\gamma_s\left(\frac{x}{2},\frac{y}{2}\right)\right] \quad (3.1)$$

where

$$x = r + r' + |\mathbf{r}-\mathbf{r}'|, \quad y = r + r' - |\mathbf{r}-\mathbf{r}'| \quad (3.2)$$

and γ_s is the density matrix for s-states alone. The fact that the (compact) variables x and y suffice to characterize

$\gamma(\mathbf{r},\mathbf{r}')$ in the bare Coulomb field stems from the existence of the Runge-Lenz vector in this case as an additional constant of motion beyond those for a general central potential $V(r)$.

But Dirac's formula [10] for the total exchange energy E_x in terms of $\gamma(\mathbf{r},\mathbf{r}')$, namely,

$$E_x = \frac{-e^2}{4} \int \frac{[\gamma(\mathbf{r},\mathbf{r}')]^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}', \qquad (3.3)$$

allows a definition of the exchange-energy density as [9]

$$\epsilon_x(\mathbf{r}) = \frac{-e^2}{4} \int \frac{[\gamma(\mathbf{r},\mathbf{r}')]^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}', \qquad (3.4)$$

and since $\gamma(\mathbf{r},\mathbf{r}')$ through Eq. (3.1) is characterized by γ_s alone, it follows that s-state information suffices via Eqs. (3.4) and (3.1) to determine $\epsilon_x(r)$. Unfortunately, to date, we have not been able to determine $\gamma_s(r,r')$ in terms of its diagonal element $\rho_s(r)$ the s-state electron density though the theorems of the density-functional theory assure us that $\gamma_s \equiv \gamma_s[\rho_s]$.

However, in Appendix A, $\epsilon_x(r)$ is written for heavy Ne-like atomic ions explicitly in terms of $\rho(r)$ and $t(r)$. But $\rho(r)$ from Eq. (1.1) is determined by $\rho_s(r)$ and Z. From Eq. (2.4), $t(r)$ is characterized by these same two quantities. Hence in Appendix A we have an explicit, though somewhat complicated, characterization of the exchange-energy density $\epsilon_x(r)$ by $\rho_s(r)$, $t(r)$, and Z for ten-electron atomic ions at large Z.

To conclude this section, we briefly sketch the proof that the momentum density $n(p)$, calculated explicitly in the following section, is also determined completely by s-state information alone. The counterpart of $\gamma(\mathbf{r},\mathbf{r}')$ in momentum space is given by

$$\tilde{\gamma}(\mathbf{p},\mathbf{p}') = \int \gamma(\mathbf{r},\mathbf{r}')\exp(i\mathbf{p}\cdot\mathbf{r})\exp(-i\mathbf{p}'\cdot\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' \qquad (3.5)$$

and by definition the momentum density $n(p)$ is given, to within a normalization factor, by the diagonal element of $\tilde{\gamma}$, i.e.,

$$n(\mathbf{p}) = \tilde{\gamma}(\mathbf{p},\mathbf{p}')|_{\mathbf{p}'=\mathbf{p}}. \qquad (3.6)$$

But Eq. (3.1) shows that $\gamma(\mathbf{r},\mathbf{r}')$ is completely determined by the density matrix γ_s for s states alone. Hence it follows that for an arbitrary number of closed shells in a bare Coulomb field, the momentum density $n(\mathbf{p})$ is determined by s-state information only.

IV. COMPLETE SOLUTION FOR MOMENTUM DENSITY $n(p)$ FOR AN ARBITRARY NUMBER OF CLOSED SHELLS

Having given a formal proof in Sec. III above that $n(p)$ is determined, at least in principle, by s-state information alone, we shall in this section obtain explicit analytical results for $n(p)$ for an arbitrary number of closed shells. Fock [22] has

shown that the momentum density for the mth closed shell can be written as

$$n_m(p) = \frac{16m^2 p_m^5}{\pi^2(p^2+p_m^2)^4}, \qquad p_m = Z/m. \qquad (4.1)$$

Summing this expression over $\mathcal{N}$ closed shells, we find

$$\begin{aligned}
n_{\mathcal{N}}(p) = \sum_{m=1}^{\mathcal{N}} n_m(p) = \frac{Z^5}{2\pi^2}\bigg\{ &\frac{iZ}{3p^9}[\Psi_3(\mathcal{N}+1+iZ/p) \\
&-\Psi_3(\mathcal{N}+1-iZ/p)+\Psi_3(1-iZ/p) \\
&-\Psi_3(1+iZ/p)]+\frac{3}{p^8}[\Psi_2(\mathcal{N}+1-iZ/p) \\
&+\Psi_2(\mathcal{N}+1+iZ/p)-\Psi_2(1+iZ/p) \\
&-\Psi_2(1-iZ/p)]+\frac{5i}{Zp^7}[\Psi_1(\mathcal{N}+1-iZ/p) \\
&-\Psi_1(\mathcal{N}+1+iZ/p)+\Psi_1(1+iZ/p) \\
&-\Psi_1(1-iZ/p)]\bigg\}, \qquad (4.2)
\end{aligned}$$

where

$$\Psi_n(x) = \frac{\partial^{n+1}\ln\Gamma(x)}{\partial x^{n+1}} \qquad (4.3)$$

is the polygamma function [23]. We may also take the limit of Eq. (4.2) as $\mathcal{N}\to\infty$ to find the momentum density in the limit of an infinite number of closed shells,

$$\begin{aligned}
n_\infty(p) \equiv \lim_{\mathcal{N}\to\infty}[n_{\mathcal{N}}(p)] = \frac{-Z^2}{6\pi^2 p^9}\{&-3ip^4-2iZ^4\pi^4 \\
&+15i\pi^2 Z^2 p^2-30ip^2\Psi_1(iZ/p)+18pZ^3\Psi_2(iZ/p) \\
&+2iZ^4\Psi_3(iZ/p)-18ipZ^3\pi^3\coth(\pi Z/p) \\
&+8iZ^4\pi^4\coth^2(\pi Z/p)-15ip^2 Z^2\pi^2\coth^2(\pi Z/p) \\
&+18ipZ^3\pi^3\coth^3(\pi Z/p)-6iZ^4\pi^4\coth^4(\pi Z/p)\}.
\end{aligned}$$
$$(4.4)$$

This is the **p**-space analog of the Heilmann-Lieb result [14] for the **r**-space electron density $\rho_\infty(r)$. However, whereas $\rho_\infty(r)$ is everywhere finite though its volume integral diverges, $n_\infty(p)$ diverges as p tends to zero. Some numerical results for $n(p)$ are presented in Sec. V C below.

V. SOME NUMERICAL APPLICATIONS

A. Ten-electron atomic ions: Large-Z limit

Using the ground-state electronic density given in Ref. [24], we have calculated the radial kinetic-energy density $4\pi r^2 t(r)$ from Eq. (B2); the result is shown in the solid curve of Fig. 1. For comparison the s-state contribution $4\pi r^2 t_s(r)$ is shown in the broken curve. One sees that the
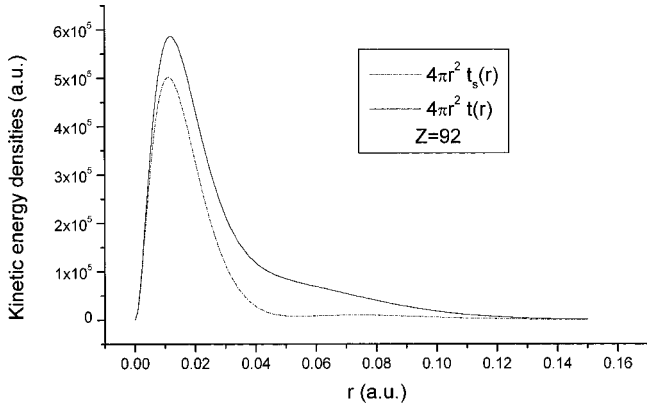
FIG. 1. Radial kinetic-energy density $4\pi r^2 t(r)$ for the ten-electron atom for $Z=92$ (solid curve) and radial s-state kinetic-energy density $4\pi r^2 t_s(r)$ for the same case (broken curve).

position of the maximum in the two curves is approximately the same for the case $Z=92$, which we have examined, though the p-state contribution is quantitatively important in the region from ~ 0.005–0.12 a.u.

Though not plotted, we have also examined the von Weizsäcker inhomogeneity kinetic-energy density $t_W(r)$ defined by

$$t_W(r) = \frac{1}{8} \frac{[\rho'(r)]^2}{\rho(r)} \qquad (5.1)$$

with the same exact Coulomb density $\rho(r)$. Though it is, of course, different from $t(r)$, there is increasing accord between the two quantities for larger r. We stress in the present context that all three kinetic energies can be constructed directly from the s-state density, because of the spatial generalization (1.1) of Kato's theorem.

B. Kinetic-energy densities: limit as number $\mathcal{N}$ of closed shells tends to infinity in bare Coulomb potential

The result (2.5) is applicable for an arbitrary number of closed shells $\mathcal{N}$, and therefore can be used in conjunction with the Heilmann-Lieb (HL) limit [14] $\mathcal{N} \to \infty$. Using the series representation given by these authors [their equations (1.20) and (1.29)] for this limiting case of the bare Coulomb problem, one can construct numerically $\rho(r)$ and also, via the relation (1.1), the s-state density $\rho_s(r)$. These two quantities are plotted, using the HL scaling, in Fig. 2 from the HL formula. [In all our HL results of Figs. 2, 3, and 4 below, summation over the series representation of HL's Eq. (1.29) up to principal quantum number $n=50$ has been carried out.]

Hence, by insertion of $\rho(r)$ in Eq. (2.5), the limit $\partial t/\partial r|_{\mathcal{N}\to\infty}$ can be obtained and, by numerical integration of this result, $t(r)|_{\mathcal{N}\to\infty}$ can be plotted. The radial kinetic-energy density $4\pi r^2 t(r)|_{\mathcal{N}\to\infty}$ corresponding to the HL limit is shown in Fig. 3, where it is compared with the Thomas-Fermi approximation (LDA)

$$t_{\mathrm{TF}}(r) = c_k [\rho(r)]^{5/3} \qquad (5.2)$$

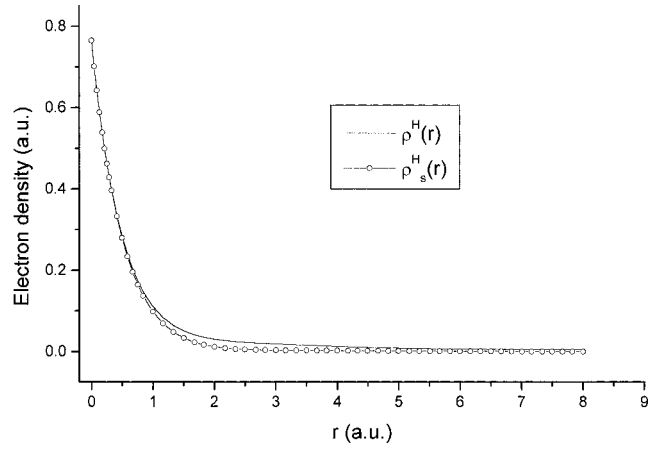with the same exact density, c_k having the electron-gas value

FIG. 2. Total charge density $\rho^H(r)$ (solid curve) and s-state charge density $\rho_s^H(r)$ (circles) for the sum over $\mathcal{N}=50$ closed shells with $Z=1$.

$$c_k = \frac{3h^2}{10m} \left(\frac{3}{8\pi} \right)^{2/3} \qquad (5.3)$$

with $h=2\pi$ and $m=1$ in atomic units.

The two curves $4\pi r^2 t(r)$ and $4\pi r^2 t_{\mathrm{TF}}(r)$, both decaying as $r^{-1/2}$, have identical forms for sufficiently large r, since

$$t(r) \to t_{\mathrm{TF}}(r) \to \frac{A}{r^{5/2}}, \quad A = c_k \left[\frac{\sqrt{2}}{3\pi^2} \right]^{5/3}. \qquad (5.4)$$

To obtain $t_s(r)$ is less straightforward in this limit $\mathcal{N} \to \infty$. It can be calculated from radial wave functions $R_{n0}(r)$ via an infinite series (see Appendix C), but in parts of r space this is only slowly convergent. However, if we calculate $t_s(r)$ using Eq. (2.3) for 50 closed shells, then the curve denoted by circles in Fig. 3 results.
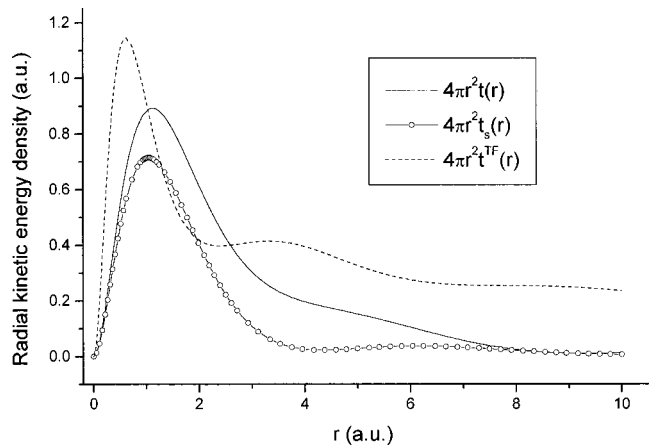

FIG. 3. Radial kinetic-energy density $4\pi r^2 t(r)$ (solid curve), radial s-state kinetic-energy density $4\pi r^2 t_s(r)$ (circles), and Thomas-Fermi radial kinetic-energy density $4\pi r^2 t^{\mathrm{TF}}(r)$ (broken curve) for the sum over $\mathcal{N}=50$ closed shells using the scaling of Heilmann and Lieb [14].
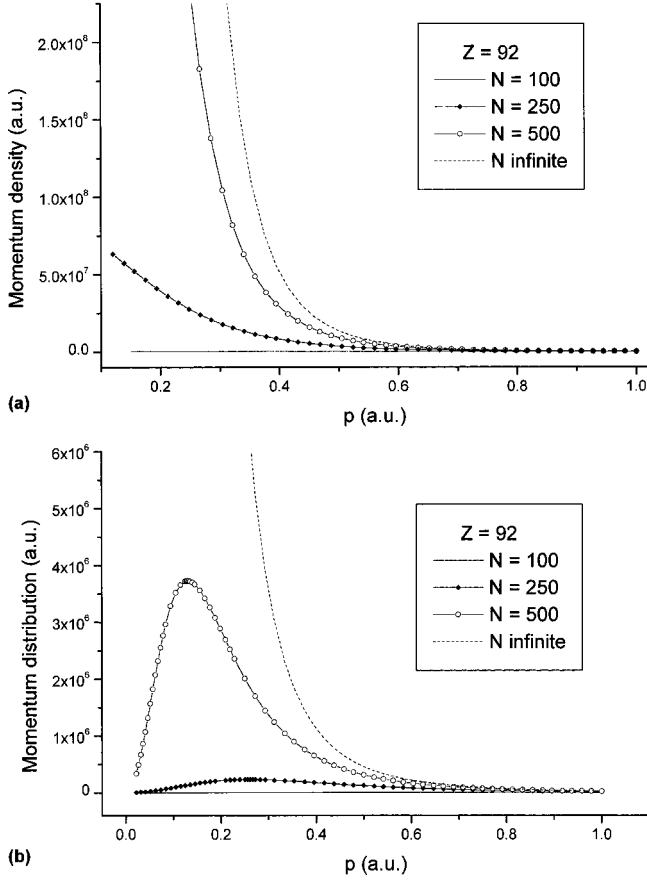
(a)

(b)

FIG. 4. (a) Momentum density $n_{\mathcal{N}}(p)$ for $\mathcal{N}=100$, 250, 500, and an infinite number of closed shells with $Z=92$, (b) momentum distribution $I(p)=4\pi p^2 n(p)$ for the same cases.

C. Momentum-space density and Compton profile

Equations (4.2) and (4.4) give the momentum density $n(p)$ for an arbitrary number of closed shells; this is plotted in Fig. 4(a) for $\mathcal{N}=100$, 250, and 500 shells, and for an infinite number of shells, with $Z=92$. We also plot, in Fig. 4(b), the momentum distribution function $I(p)=4\pi p^2 n(p)/Z$ for the same cases. Note that for an infinite number of shells, $n(p)$ and $I(p)$ are singular at the origin. Finally, the Compton profile $J(q)$, given by

$$J(q)=\frac{1}{2}\int_q^\infty \frac{I(p)}{p}\,dp,$$

is shown for the cases $\mathcal{N}=250$ and 500 and for an infinite number of shells in Fig. 5.

D. Local-density approximation to exchange-energy density

To close this section, we show in Fig. 6 the local-density approximation $4\pi r^2 \epsilon_x^{\text{LDA}}(r)$, where

$$\epsilon_x^{\text{LDA}}(r)\big|_{\mathcal{N}\to\infty}=-c_x[\rho_\infty(r)]^{4/3}, \quad c_x=\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \quad (5.5)$$

with the HL density $\rho_\infty(r)$. So far, we have not achieved a calculable form for $\epsilon_x(r)\big|_{\mathcal{N}\to\infty}$ beyond the local-density ap-
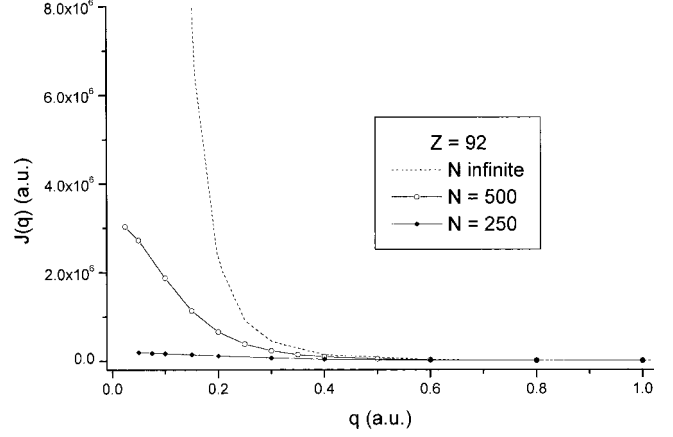

FIG. 5. Compton profile $J(q)$ for $\mathcal{N}=250$, 500, and an infinite number of closed shells with $Z=92$.

proximation. Since $\rho_\infty(r)\propto r^{-3/2}$ as $r\to\infty$ from the HL study, $\epsilon_x(r)\big|_{\mathcal{N}\to\infty}\propto 1/r^2$ at large r, and hence $4\pi r^2 \epsilon_x^{\text{LDA}}(r)\big|_{\mathcal{N}\to\infty}$ tends to a finite, nonzero value as $r\to\infty$. As for the total kinetic energy $T=\int t(r)d\mathbf{r}$, the total exchange energy $E_x=\int\epsilon_x(r)d\mathbf{r}$ diverges as $\mathcal{N}\to\infty$.

VI. SUMMARY AND FUTURE DIRECTIONS

The main results of the present study are to determine, for the leading term in the $1/Z$ expansion of the atomic theory for nonrelativistic atomic ions with N electrons. (i) The nonlocal form (2.8) of the kinetic-energy density $t(r)$ solely in terms of the electron density $\rho(r)$, since the atomic number Z appearing there can also be expressed in terms of ρ using Kato's theorem. Equation (2.8), it is to be stressed, is valid for an arbitrary number $\mathcal{N}$ of closed shells for the bare Coulomb field. We should also stress that, through Eq. (2.6), $t(r)$ is determined completely by the s-state density $\rho_s(r)$, the atomic number Z, and two physical boundary conditions. (ii) The s-state kinetic energy $t_s(r)$ in Eq. (2.3) that is the appropriate spatial generalization of the earlier integral result (2.4)
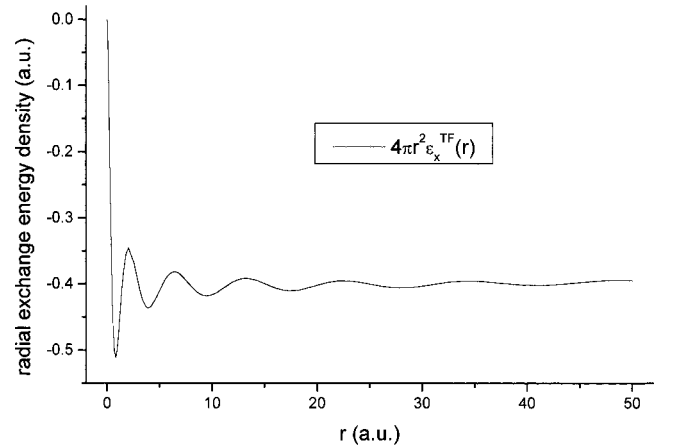

FIG. 6. Local-density approximation to radial exchange-energy density $4\pi r^2 \epsilon_x^{\text{TF}}(r)$ for the sum over $\mathcal{N}=50$ closed shells calculated with exact electron density using the scaling of Heilmann and Lieb [14].

TABLE I. Moments $\langle p^m \rangle$ of the momentum distribution for $Z = 92$ and $\mathcal{N} = 50$ closed shells.

m	$\langle p^m \rangle$ (a.u.)
-2	0.895
-1	0.699[a]
0	1
1	2.320[b]
2	9.859[c]
3	138.56
4	13561.2

[a]This result checks with $\langle p^{-1} \rangle = 8\mathcal{N}(\mathcal{N}+1)/Z\pi(2\mathcal{N}+1)$ in Ref. [25].
[b]This result reproduces $\langle p \rangle = 8Z/\pi(2\mathcal{N}+1)$.
[c]This result is the total kinetic energy, which is Z^2 per shell.

for the total kinetic energy T_s for s states for a general number of closed shells $\mathcal{N}$. (iii) The momentum density $n_{\mathcal{N}}(p)$ in Eq. (4.2), together with its limiting form $n_{\infty}(p)$ in Eq. (4.4). As mentioned above, Eq. (4.4) is the **p**-space counterpart of the Heilmann-Lieb result [14] for the **r**-space electron density $\rho_{\infty}(r)$. Various moments of momentum have been calculated numerically for $\mathcal{N} = 50$, $Z = 92$, and are listed in Table I. In particular, $\langle p \rangle$ and $\langle p^{-1} \rangle$ have been checked against the closed forms obtained earlier [25].

As to possible future directions, it has not to date proved possible for an arbitrary number of closed shells to evaluate the exchange-energy density $\epsilon_x(r)$ exactly (though this has been achieved earlier in Ref. [9] for K and L shells only). The most promising approach to this appears to lie in endeavoring to construct the off-diagonal generalization of Eq. (4.2), especially $\tilde{\gamma}(\mathbf{p}, \mathbf{p}')$ in Eq. (3.5). Further progress seems feasible here, since Fock [22] has given an off-diagonal generalization of his diagonal result (4.1) for a particular closed shell in terms of Tschebyscheff polynomials (see also the later study of May [26]). By Fourier inversion of Eq. (3.5), if the sum over shells can be achieved eventually, insertion of the resulting $\gamma(\mathbf{r}, \mathbf{r}')$ into the Dirac form (3.4) of the exchange-energy density $\epsilon_x(r)$ would allow the LDA plot in Fig. 6 to be transcended.

APPENDIX A: CHARACTERIZATION OF EXCHANGE-ENERGY DENSITY FOR Ne-LIKE IONS BY s-WAVE DENSITY $\rho_s(r)$

From Eq. (6.2) of March and Santamaria [24], we have for the ten-electron ion

$$\gamma(\mathbf{r}, \mathbf{r}') = \rho\left(\frac{r+r'}{2}\right) + |\mathbf{r} - \mathbf{r}'|^2$$

$$\times \left[\frac{1}{24}\rho''\left(\frac{r+r'}{2}\right) - \frac{m}{3\hbar^2}t\left(\frac{r+r'}{2}\right)\right] \quad \text{(A1)}$$

so that the exchange-energy density $\epsilon_x(r)$ is given by

$$\epsilon_x(r) = -\frac{e^2}{4}\int \frac{[\rho((r+r')/2)]^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' - \frac{e^2}{4}\int 2\rho\left(\frac{r+r'}{2}\right)$$

$$\times |\mathbf{r}-\mathbf{r}'|\left[\frac{1}{24}\rho''\left(\frac{r+r'}{2}\right) - \frac{m}{3\hbar^2}t\left(\frac{r+r'}{2}\right)\right]d\mathbf{r}' - \frac{e^2}{4}$$

$$\times \int |\mathbf{r}-\mathbf{r}'|^3\left[\frac{1}{24}\rho''\left(\frac{r+r'}{2}\right) - \frac{m}{3\hbar^2}t\left(\frac{r+r'}{2}\right)\right]^2 d\mathbf{r}'. \quad \text{(A2)}$$

Since we know $t(r)$ in terms of $\rho_s(r)$ and $\rho(r)$ for this case [see Eq. (B3) below], we can substitute it in the expression (A2) and write

$$\epsilon_x(r) = -\frac{e^2}{4}\int\left[\rho\left(\frac{r+r'}{2}\right)\right]^2\left\{\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{|\mathbf{r}-\mathbf{r}'|}{(r+r')^2}\right.$$

$$\left.+ \frac{1}{4}\frac{|\mathbf{r}-\mathbf{r}'|^3}{(r+r')^4}\right\}d\mathbf{r}' + \frac{e^2}{4}\int \rho\left(\frac{r+r'}{2}\right)\rho_a\left(\frac{r+r'}{2}\right)$$

$$\times \left\{\frac{|\mathbf{r}-\mathbf{r}'|}{(r+r')^2} + \frac{1}{2}\frac{|\mathbf{r}-\mathbf{r}'|^3}{(r+r')^4}\right\}d\mathbf{r}'$$

$$- \frac{e^2}{16}\int\left[\rho_s\left(\frac{r+r'}{2}\right)\right]^2\frac{|\mathbf{r}-\mathbf{r}'|^3}{(r+r')^4}d\mathbf{r}' \quad \text{(A3)}$$

so that $\epsilon_x(r)$ can be entirely determined for the ten-electron ion (in the $1/Z$ limit) in terms of integrals over $\rho_s(r)$ and $\rho(r)$ or, since Eq. (1.1) relates $\rho_s(r)$ to $\rho'(r)$ through the atomic number Z, in terms of integrals over $\rho(r)$ and $\rho'(r)$.

APPENDIX B: s-WAVE DENSITY MATRIX $\gamma_s(r,r')$ AND KINETIC-ENERGY DENSITY $t_s(r)$ FOR TEN-ELECTRON ATOMIC IONS IN THE COULOMB-LIMIT SYSTEM

The s-wave density matrix $\gamma_s(r,r')$ consists of the spherically symmetric part of Eq. (A1) above, that is,

$$\gamma_s(r,r') = \rho\left(\frac{r+r'}{2}\right) + (r^2+r'^2)\left[\frac{1}{24}\rho''\left(\frac{r+r'}{2}\right)\right.$$

$$\left.- \frac{1}{3}t\left(\frac{r+r'}{2}\right)\right]. \quad \text{(B1)}$$

The first result of this decomposition is that, from the diagonal element of Eq. (B1), one finds

$$t(r) = \frac{3}{2}\left[\frac{\rho(r) - \rho_s(r)}{r^2}\right] + \frac{\rho''}{8}. \quad \text{(B2)}$$

It is worth emphasizing that the use of this result (B2) for the quantity within the square brackets of both Eqs. (A1) and (B1) allows the off-diagonal matrices to be rewritten solely in terms of the densities $\rho(r)$ and $\rho_s(r)$. Thus, for the full Dirac density matrix γ one has

$$\gamma(\mathbf{r},\mathbf{r}') = \rho\left(\frac{r+r'}{2}\right) + 2|\mathbf{r}-\mathbf{r}'|^2 \left[\frac{\rho_s\left(\frac{r+r'}{2}\right) - \rho\left(\frac{r+r'}{2}\right)}{(r+r')^2}\right]$$

(B3)

giving the off-diagonal behavior solely in terms of the diagonal densities. One can still use the spatial generalization of Kato's theorem in Eq. (B3) to remove ρ_s in terms of ρ', but then the atomic number Z enters. However, since

$$Z = -\frac{1}{2}\frac{\rho'(0)}{\rho(0)}$$

(B4)

one can still view the result thus obtained as giving the first-order density matrix γ as a functional of its diagonal element $\rho(r)$. This is related to, of course, but is somewhat more general than the problem of the single-particle kinetic-energy functional $T_s[\rho]$. Reverting to this, one can return to Eq. (B2) and differentiate it with respect to r to find

$$t'(r) = -3\frac{[\rho(r)-\rho_s(r)]}{r^3} + \frac{3}{2r^2}[\rho'(r)-\rho_s'(r)]$$
$$+ p'''(r)/8.$$

(B5)

But for an arbitrary number of closed shells, Amovilli and March obtain Eq. (2.5) [19]. Comparing Eqs. (B5) and (2.5), it follows for the ten-electron ions considered in this appendix that

$$-\frac{3\rho'(r)}{4r^2} - \frac{3Z}{2r^2}\rho(r) = -3\frac{[\rho(r)-\rho_s(r)]}{r^3} + \frac{3\rho'(r)}{2r^2}$$
$$- \frac{3\rho_s'(r)}{2r^2}.$$

(B6)

1. Differential equation for ground-state electron density $\rho(r)$

Introducing again the spatial generalization (1.1) of Kato's theorem to remove $\rho_s(r)$ from Eq. (B6), one finds a differential equation for the ground-state density $\rho(r)$, namely,

$$\frac{3}{4Zr^2}\rho''(r) + \left[-\frac{3}{2Zr^3} + \frac{9}{4r^2}\right]\rho'(r) + \left[\frac{3Z}{2r^2} - \frac{3}{r^3}\right]\rho(r) = 0.$$

(B7)

It is noteworthy that for this example, $t(r)$ can be calculated directly by combining Eq. (B2) with Eq. (1.1) to find

$$t(r) = \frac{3}{2}\frac{\rho(r)}{r^2} + \frac{\rho''(r)}{8} + \frac{3}{4Z}\rho'(r).$$

(B8)

2. Calculation of *s*-state kinetic-energy density $t_s(r)$

From the *s*-wave density matrix (B1) we have

$$t_s(r) = \frac{1}{2}\frac{\partial^2}{\partial r\,\partial r'}\gamma_s(r,r')|_{r'=r},$$

(B9)

which results in the *s*-wave kinetic-energy density of

$$t_s(r) = \frac{1}{8}\rho''(r) + \frac{r}{24}\rho''' + \frac{r^2}{96}\rho^{IV}(r) - \frac{r}{3}t'(r) - \frac{r^2}{12}t''(r).$$

(B10)

One can now use Eq. (2.5) and its derivative to eliminate t' and t'' and hence find $t_s(r)$ in terms of ρ, its derivative, and atomic number Z. Equation (B11) then becomes

$$t_s(r) = \frac{3}{16}\rho''(r) + \frac{\rho'(r)}{8}\left(\frac{1}{r}+Z\right) + \frac{Z\rho(r)}{4r}.$$

(B11)

By volume integration of Eq. (B11), the earlier result of one of us [18] (see also Ref. [16]) for the total *s*-state kinetic energy given in Eq. (2.4) is then regained after some modest manipulation. The result (B11) as derived here for $K+L$ shells is readily verified to be true also for the K shell alone.

APPENDIX C: *s*-WAVE DENSITY MATRIX $\gamma_s(r,r')$ FOR THE GENERAL COULOMB PROBLEM

The *s*-wave density matrix $\gamma_s(r,r')$ may be written for $\mathcal{N}$ closed shells as

$$\gamma_s(r,r') = \sum_{n=1}^{\mathcal{N}} R_{n0}(r)R_{n0}(r')$$

(C1)

with $R_{n0}(r)$ as the radial wave functions for $l=0$. The Theophilou-March relation, Eq. (3.1), may be used to get $\gamma(\mathbf{r},\mathbf{r}')$ by first expressing $\gamma_s(r,r')$ in terms of the variables x and y,

$$\gamma_s(x/2,y/2) = \sum_{n=1}^{\mathcal{N}} R_{n0}(x/2)R_{n0}(y/2).$$

(C2)

Then, since

$$\frac{\partial}{\partial x}(x\gamma_s) = \gamma_s + x\frac{\partial\gamma_s}{\partial x}$$

(C3)

and

$$\frac{\partial}{\partial y}(y\gamma_s) = \gamma_s + y\frac{\partial\gamma_s}{\partial y}$$

(C4)

we have

$$\gamma(\mathbf{r},\mathbf{r}') = \gamma_s\left(\frac{x}{2},\frac{y}{2}\right) - (x-y)^{-1}[xy]\left(\frac{\partial\gamma_s}{\partial x} - \frac{\partial\gamma_s}{\partial y}\right).$$

(C5)

Now from Eq. (C2),

$$\frac{\partial \gamma_s}{\partial x} = \sum_{n=1}^{\mathcal{N}} \frac{1}{2} R'_{n0}(x/2) R_{n0}(y/2) \qquad \text{(C6)}$$

and

$$\frac{\partial \gamma_s}{\partial y} = \sum_{n=1}^{\mathcal{N}} \frac{1}{2} R_{n0}(x/2) R'_{n0}(y/2) \qquad \text{(C7)}$$

so that with

$$x = r + r' + |\mathbf{r} - \mathbf{r}'|, \quad y = r + r' - |\mathbf{r} - \mathbf{r}'| \qquad \text{(C8)}$$

we can write

$$\gamma(\mathbf{r}, \mathbf{r}') = \gamma_s \left(\frac{x}{2}, \frac{y}{2} \right) - \frac{1}{2} \left[\frac{(r+r')^2}{|\mathbf{r} - \mathbf{r}'|} - |\mathbf{r} - \mathbf{r}'| \right]$$
$$\times \left[\sum_{n=1}^{\mathcal{N}} \frac{1}{2} \{ R'_{n0}(x/2) R_{n0}(y/2) \right.$$
$$\left. - R_{n0}(x/2) R'_{n0}(y/2) \} \right] \qquad \text{(C9)}$$

or

$$\gamma(\mathbf{r}, \mathbf{r}') = \gamma_s \left(\frac{r+r'+|\mathbf{r}-\mathbf{r}'|}{2}, \frac{r+r'-|\mathbf{r}-\mathbf{r}'|}{2} \right)$$
$$- \frac{1}{2} \left[\frac{(r+r')^2}{|\mathbf{r}-\mathbf{r}'|} - |\mathbf{r}-\mathbf{r}'| \right]$$
$$\times \sum_{n=1}^{\mathcal{N}} \frac{1}{2} \left[R'_{n0} \left(\frac{r+r'+|\mathbf{r}-\mathbf{r}'|}{2} \right) \right.$$
$$\times R_{n0} \left(\frac{r+r'-|\mathbf{r}-\mathbf{r}'|}{2} \right)$$
$$\left. - R_{n0} \left(\frac{r+r'+|\mathbf{r}-\mathbf{r}'|}{2} \right) R'_{n0} \left(\frac{r+r'-|\mathbf{r}-\mathbf{r}'|}{2} \right) \right], \qquad \text{(C10)}$$

which is the desired result for the Dirac matrix in terms purely of the *s*-state information.

APPENDIX D: EXCHANGE-ENERGY DENSITY $\epsilon_x(r)$ FOR AN ARBITRARY NUMBER OF CLOSED SHELLS IN A CENTRAL FIELD

For the full first-order density matrix $\gamma(\mathbf{r}, \mathbf{r}')$ in the presence of a central field potential, we can write

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_{(n,l)} \rho_{nl}^{1/2}(r) \rho_{nl}^{1/2}(r') P_l(\cos \Omega) \qquad \text{(D1)}$$

where $\cos \Omega = (\mathbf{r} \cdot \mathbf{r}')/rr'$, and the summations over n and l are over all principal quantum numbers and allowed angular momentum quantum numbers, respectively. Here $\rho_{nl}^{1/2}(r) \equiv [(2l+1)/2\pi] R_{nl}(r)$ is the square root of the density associated with the (n,l)th subshell, and thus proportional to the (n,l)th radial wave function $R_{nl}(r)$. If we take $\mathbf{r} \| \mathbf{z}$, the exchange energy density $\epsilon_x(r)$ then becomes, from Eq. (3.4),

$$\epsilon_x(r) = -(e^2 \pi/2) \sum_{(n,l)} \sum_{(p,q)} \rho_{nl}^{1/2}(r) \rho_{pq}^{1/2}(r)$$
$$\times \int_{r'=0}^{\infty} \rho_{nl}^{1/2}(r') \rho_{pq}^{1/2}(r') r'^2$$
$$\times \int_{\theta=0}^{\pi} \frac{P_l(\cos \theta') P_0(\cos \theta')}{|\mathbf{r}-\mathbf{r}'|} d(\cos \theta') dr'. \qquad \text{(D2)}$$

We can then expand $1/|\mathbf{r}-\mathbf{r}'|$ in Legendre polynomials as

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \sum_{t=0}^{\infty} \frac{r_<^t}{r_>^{t+1}} P_t(\cos \theta')$$

so that

$$\epsilon_x(r) = -(\epsilon^2 \pi/2) \sum_{(n,l)} \sum_{(p,q)} \sum_{t=0}^{\infty} \rho_{nl}^{1/2}(r) \rho_{pq}^{1/2}(r)$$
$$\times \int_{r'=0}^{\infty} \rho_{nl}^{1/2}(r') \rho_{pq}^{1/2}(r') r'^2 \frac{r_<^t}{r_>^{t+1}} dr'$$
$$\times \int_{\theta=0}^{\pi} P_l(\cos \theta') P_q(\cos \theta') P_t(\cos \theta') d(\cos \theta'). \qquad \text{(D3)}$$

But the angular integral is just $(4\pi/2l+1)|\langle tq00|tql0 \rangle|^2$, where the $\langle tq00|tql0 \rangle$ are the Clebsch-Gordon coefficients. Altogether then, we can write

$$\epsilon_x(r) = -(2e^2 \pi^2) \sum_{(n,l)} \sum_{(p,q)} \rho_{nl}^{1/2}(r) \rho_{pq}^{1/2}(r)$$
$$\times \int_{r'=0}^{\infty} \rho_{nl}^{1/2}(r') \rho_{pq}^{1/2}(r') r'^2$$
$$\times \sum_{t=0}^{\infty} \frac{r_<^t}{r_>^{t+1}} \frac{|\langle tq00|tql0 \rangle|^2}{2l+1} dr' \qquad \text{(D4)}$$

so that the exchange-energy density is expressed entirely in terms of radial integrals. We note that the Clebsch-Gordon coefficients are zero *unless*

$$|t-q| \leq l \leq (t+q).$$

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