PHYSICAL REVIEW A VOLUME 24, NUMBER 4 OCTOBER 1981

Sixth-order term of the gradient expansion of the kinetic-energy density functional[*]

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(Received 20 October 1980)

A generalization of Hodges's method of obtaining the gradient expansion is derived and then employed to determine the sixth-order term. The formula for it is as follows: $T_6[\rho]=(3\pi^2)^{-413}/45\,360\int\rho^{-1/3}[13(\nabla\nabla^2\rho/\rho)^2+2575/144(\nabla^2\rho/\rho)^3+249/16(\nabla\rho/\rho)^2(\nabla^4\rho/\rho)+1499/18(\nabla\rho/\rho)^2(\nabla^2\rho/\rho)^2-1307/36(\nabla\rho/\rho)^2(\vec{\nabla}\rho\cdot\vec{\nabla}\nabla^2\rho/\rho^2)+343/18(\vec{\nabla}\rho\cdot\vec{\nabla}\vec{\nabla}\rho/\rho^2)^2+8341/72(\nabla^2\rho/\rho)(\nabla\rho/\rho)^4-1\,600\,495/2592(\nabla\rho/\rho)^6]d^3r$. For atomic densities, $T_6[\rho]$ is divergent near the nucleus and at large distances.

I. INTRODUCTION

The Hohenberg-Kohn[1] proof that the ground-state energy of a system is a universal functional of the ground-state single-particle density forms the theoretical basis of the area of research now known as density functional theory. The Hohenberg-Kohn theorem is an existence proof and does not indicate the form of this universal functional, but certain limiting forms are known.[2-6]

Lieb and Simon[6] have shown that the Thomas-Fermi[7] energy functional is exact in the limit $Z\to\infty$. Some attempts to add corrections to the Thomas-Fermi functional have led to gradient expansions—so named because successive terms in the series involve higher and higher order gradients of the density. Gradient expansions exist for both the kinetic energy[8-10] and the exchange-correlation energy.[3,11] Density functionals for the exchange energy have been successfully employed in the calculation of the orbitals of numerous systems.[12,13]

It follows that if one wishes to perform calculations involving only the density of a system and bypass any reference to orbitals and wave functions, a principal concern must be the functional for the kinetic energy $T[\rho]$. Derivations of the gradient expansion of the kinetic-energy functional show that it can be written in the form[10]

$$T[\rho]=T_0[\rho]+T_2[\rho]+T_4[\rho]+\cdots\,, \tag{1}$$

where $T_0[\rho]$ is given by the well-known Thomas-Fermi kinetic-energy functional

$$T_0[\rho]=\tfrac{3}{10}(3\pi^2)^{2/3}\int\rho^{5/3}d^3r\,, \tag{2}$$

$T_2[\rho]$ is given by one-ninth[8,10] of the correction determined by von Weizsacker,[14]

$$T_2[\rho]=\tfrac{1}{72}\int\frac{(\nabla\rho)^2}{\rho}d^3r\,, \tag{3}$$

and Hodges[10] determined the fourth-order correction to be

$$T_4[\rho]=\frac{(3\pi^2)^{-2/3}}{540}\times\int\rho^{1/3}\left[\left(\frac{\nabla^2\rho}{\rho}\right)^2-\frac{9}{8}\left(\frac{\nabla^2\rho}{\rho}\right)\left(\frac{\nabla\rho}{\rho}\right)^2+\frac{1}{3}\left(\frac{\nabla\rho}{\rho}\right)^4\right]d^3r\,. \tag{4}$$

Empirical studies[15-17] to determine the quality of the kinetic-energy functional defined by Eqs. (1)–(4) have demonstrated that the gradient expansion can reproduce the Hartree-Fock kinetic energy within 1% for most atoms when Hartree-Fock atomic densities are employed.

The present paper presents the theoretical basis of the gradient expansion and a sketch of Hodges's method of evaluating individual terms of the series. An operator is developed which represents a general term generated by Hodges's procedure, and the sixth-order correction to the kinetic-energy functional is explicitly obtained. Finally, some observations are made on the gradient expansion, and its limitations are discussed.

II. BASIS OF THE GRADIENT EXPANSION

Thomas-Fermi theory and the gradient expansion can be derived from the Dirac density matrix. Results to be found elsewhere[18-20] are reviewed here in order to clarify some points.

The operators used with the density matrix are reduced to normal form, which results in final expressions that have a remarkable classical appearance and interpretation. The normal form of a quantum-mechanical operator, which is a function of the momentum and spatial coordinates of a system, is obtained by commuting functions of momentum $\hat{p}$ to the right of functions of position. For example, if the operator $\hat{O}(\hat{r},\hat{p})$ is given by

$$\hat{O}(\hat{r},\hat{p})=\hat{p}g(\hat{r})\,, \tag{5}$$

where g is any function of $\hat{r}$, then $\tilde{O}(\hat{r},\hat{p})$, the normal form of $\hat{O}(\hat{r},\hat{p})$, is given by

$$\tilde{O}(\hat{r},\hat{p})=-i\nabla g(\hat{r})+g(\hat{r})\hat{p}\,. \tag{6}$$

The density matrix of a system can, in principle, be obtained from the density-matrix operator for that system. The density-matrix operator $\hat{\rho}(\hat{r},\hat{p})$ is defined by

$$\hat{\rho}(\hat{r},\hat{p}) = f(\hat{\mathcal{H}}) , \qquad (7)$$

where f is the Fermi-Dirac distribution function,

$$f(\hat{\mathcal{H}}) = \{1+\exp[(\hat{\mathcal{H}}-\mu)/kT]\}^{-1} . \qquad (8)$$

Here, $\hat{\mathcal{H}}$ is taken to be a single-particle Hamiltonian with potential V,

$$\hat{\mathcal{H}} = \tfrac{1}{2}\hat{p}^2 + \hat{V} , \qquad (9)$$

where V is treated as a local potential, but for a system of interacting electrons, V is the self-consistently determined potential of the system under consideration.

One may write the eigenvalue equation

$$\hat{\rho}(\hat{r},\hat{p})\phi_i = \alpha_i\phi_i , \qquad (10)$$

where ϕ_i is the ith eigenfunction of $\hat{\mathcal{H}}$ and

$$\alpha_i = \{1+\exp[(E_i-\mu)/kT]\}^{-1} , \qquad (11)$$

with E_i being the energy eigenvalue associated with ϕ_i. Notice that in the limit, as the temperature T goes to zero, the value of α_i becomes unity if $E_i < \mu$ and zero if $E_i > \mu$.

The density matrix $\underline{\rho}(\vec{r},\vec{r}\,')$ is usually written as a sum over the occupied orbitals of a system. For the particularly simple case of the ground state of a closed-shell system of $2n$ electrons, the density matrix is

$$\underline{\rho}(\vec{r},\vec{r}\,') = 2\sum_{j=1}^{n}\phi_j^*(\vec{r}\,')\phi_j(\vec{r}) , \qquad (12)$$

where the coefficient 2 indicates that each spatial orbital is doubly occupied.

With an appropriate value for the chemical potential μ of Eq. (8), Eq. (12) may be written

$$\underline{\rho}(\vec{r},\vec{r}\,') = 2\lim_{T\to 0}\hat{\rho}(\hat{r},\hat{p}_r)\sum_j\phi_j^*(\vec{r}\,')\phi_j(\vec{r}) , \qquad (13)$$

where p_r indicates that the momentum operator acts only on functions of $\vec{r}$ and not of $\vec{r}\,'$. However, in Eq. (13), it is not necessary to restrict the summation to the occupied orbitals. Extending the summation to include all the virtual orbitals and continuum functions of the system results in

$$\sum_j\phi_j^*(\vec{r}\,')\phi_j(\vec{r}) = \delta(\vec{r}-\vec{r}\,') , \qquad (14)$$

where $\delta(\vec{r}-\vec{r}\,')$ is the Dirac delta function.

Representing the delta function in terms of the free-particle states, Eq. (13) becomes

$$\underline{\rho}(\vec{r},\vec{r}\,') = 2\lim_{T\to 0}\hat{\rho}(\hat{r},\hat{p}_r)\frac{1}{(2\pi)^3}\int e^{i\vec{p}\cdot(\vec{r}-\vec{r}\,')}d^3p . \qquad (15)$$

Expressing $\hat{\rho}(\hat{r},\hat{p}_r)$ in normal form, taking it under the integral and allowing the momentum operators of $\tilde{\rho}(\hat{r},\hat{p}_r)$ to act on the exponential, one obtains

$$\underline{\rho}(\vec{r},\vec{r}\,') = \frac{1}{4\pi^3}\int\lim_{T\to 0}\tilde{\rho}(\vec{r},\vec{p})e^{i\vec{p}\cdot(\vec{r}-\vec{r}\,')}d^3p . \qquad (16)$$

Here the operators $\vec{r}$ and $\vec{p}_r$ have been replaced by the variable $\vec{r}$ and $\vec{p}$, and $\rho(\vec{r},\vec{p})$ corresponds to a classical phase-space distribution.

Quantities of interest are obtained from the density matrix of Eq. (16) in the usual manner. For example, the single-particle density $\rho(\vec{r})$ is given by the diagonal of the density matrix

$$\rho(\vec{r}) = \underline{\rho}(\vec{r},\vec{r}) = \frac{1}{4\pi^3}\int\lim_{T\to 0}\tilde{\rho}(\vec{r},\vec{p})d^3p . \qquad (17)$$

The explicit form of $\tilde{\rho}(\vec{r},\vec{p})$ is a series involving products of the momentum $\vec{p}$ and gradients of the potential V of the Hamiltonian of Eq. (9). Neglecting all but the zeroth-order term of $\tilde{\rho}(\vec{r},\vec{p})$, i.e., the term involving no gradients of V, and carrying out the integration indicated in Eq. (17), the Thomas-Fermi relationship between the density and potential is obtained,

$$\rho(\vec{r}) = \frac{1}{3\pi^2}\{2[\mu - V(r)]\}^{3/2} . \qquad (18)$$

III. HODGES'S METHOD

Hodges[10] has developed a method, suggested by Kirzhnits,[8] for obtaining the normal form of the density-matrix operator as a series in ascending powers of the gradient operator, in the limit of zero temperature.

First, $f(\hat{\mathcal{H}})$ is expressed as a Fourier integral

$$f(\hat{\mathcal{H}}) = \int C(\tau)\exp(i\tau\hat{\mathcal{H}})d\tau . \qquad (19)$$

The exponential is placed in normal form by writing

$$\exp(i\tau\hat{\mathcal{H}}) = \exp(i\tau\hat{V})\hat{K}\exp(i\tau\hat{P}^2/2) , \qquad (20)$$

and a differential equation for the normal form of K is obtained,

$$\frac{\partial K}{\partial\lambda} = (O_1+O_2)K . \qquad (21)$$

Here

$$O_1 = i\vec{p}\cdot(\vec{\nabla}+\lambda\vec{\nabla}V) , \qquad (22)$$

$$O_2 = -[\nabla^2/2 + \lambda(\nabla^2V/2 + \vec{\nabla}V\cdot\vec{\nabla}) + (\lambda^2/2)(\nabla V)^2] , \qquad (23)$$

and

$$\lambda = i\tau . \qquad (24)$$

In Eqs. (21)–(23), P, V, and K are written as variables rather than operators because all quantities are now in normal form.

An expression for K is obtained by iteration of Eq. (21); the leading term of $K=1$ may be obtained by taking the classical limit of Eq. (20). The resulting expression is a series of terms of various orders in ∇, which can be arranged into a series in ascending order of the gradient operator by making use of O_1 being first order in ∇, while O_2 is second order. For example, the second-order term in the expansion for K, $\delta_2 K$, is given by

$$\delta_2 K=\int O_2+\int O_1\int O_1\,, \tag{25}$$

and the fourth-order term is given by

$$\delta_4 K=\int O_2\int O_2+\int O_2\int O_1\int O_1+\int O_1\int O_2\int O_1+\int O_1\int O_1\int O_2+\int O_1\int O_1\int O_1\int O_1\,. \tag{26}$$

Quantities of interest are obtained by averaging $\tilde{\rho}(\vec{r},\vec{p})$ over $\vec{p}$ [Eqs. (10) and (17)], which results in there being no contribution from the terms of $\tilde{\rho}(\vec{r},\vec{p})$ involving odd powers of $\vec{p}$ and ∇, so only the even order terms of $\tilde{\rho}(\vec{r},\vec{p})$ and K need be calculated. Once the normal form of K has been determined, $\tilde{\rho}(\vec{r},\vec{p})$ is obtained from Eq. (19) by noticing that each power of λ in the expansion of K introduces a factor of $\partial/\partial E$ acting on $f(E)$.

In general, the integral of the corrections to the density are not zero, so that if the chemical potential μ remains constant then the normalization of the density changes as quantum corrections are added to ρ. This requires that corrections to the free energy

$$\langle\mathcal{H}\rangle-\mu N=\frac{1}{4\pi^3}\int\left(\frac{p^2}{2}+V-\mu\right)\tilde{\rho}(\vec{r},\vec{p})\,d^3p\,d^3r\,, \tag{27}$$

be calculated in order to determine the change in the total energy with the number of particles fixed.

Next, the kinetic-energy functional $T[\rho]$ is written as a series

$$T[\rho]=T_0[\rho]+T_2[\rho]+T_4[\rho]+\cdots\,, \tag{28}$$

where $T_j[\rho]$ indicates a functional involving j powers of ∇. The density ρ is written as

$$\rho=\rho_0+\delta\rho\,, \tag{29}$$

where ρ_0 is the Thomas-Fermi density given by Eq. (18). Equation (29) is substituted into Eq. (28), which is then expanded about ρ_0. Using the fact that

$$\left.\frac{\delta T_0[\rho]}{\delta\rho}\right|_{\rho=\rho_0}=\mu-V(r)\,, \tag{30}$$

where $T_0[\rho]$ is given by Eq. (2), the relation

$$\begin{aligned}T+\int(V-\mu)\delta\rho\,d^3r={}&T_0[\rho_0]+\tfrac{1}{2}\int\left(\frac{\delta^2T_0}{\delta\rho^2}\right)_{\rho=\rho_0}(\delta\rho)^2d^3r+\tfrac{1}{3!}\int\left(\frac{\delta^3T_0}{\delta\rho^3}\right)_{\rho=\rho_0}(\delta\rho)^3d^3r+\cdots+T_2[\rho_0]\\&+\int\left(\frac{\delta T_2}{\delta\rho}\right)_{\rho=\rho_0}(\delta\rho)d^3r+\tfrac{1}{2}\int\left(\frac{\delta^2T_2}{\delta\rho^2}\right)_{\rho=\rho_0}(\delta\rho)^2d^3r+\cdots+T_4[\rho_0]+\int\left(\frac{\delta T_4}{\delta\rho}\right)_{\rho=\rho_0}\delta\rho\,d^3r+\cdots\end{aligned} \tag{31}$$

is obtained. By writing $\delta\rho=\delta_2\rho+\delta_4\rho+\cdots$, where $\delta_i\rho$ is the ith-order correction to the density, and equating terms of order j in ∇, an expression for $T_j[\rho_0]$ is obtained. For example,

$$T_4[\rho_0]=\delta_4(\langle\mathcal{H}\rangle-\mu N)-\tfrac{1}{2}\int\left(\frac{\delta^2T_0}{\delta\rho^2}\right)_{\rho=\rho_0}(\delta_2\rho)^2d^3r-\int\left(\frac{\delta T_2}{\delta\rho}\right)_{\rho=\rho_0}\delta_2\rho\,d^3r\,. \tag{32}$$

Any gradients of the potential present on the right-hand side of Eq. (32) can be related to gradients of the density through the use of Eq. (18).

IV. GENERALIZATION

Hodges's method shows that the correction to K of order $2l$, $\delta_{2l}K$, is given by the sum of all possible products of O_1 and O_2 operators which have an overall order of $2l$. A typical term involving nO_2 operators, located at the positions $q(1)$, $q(2),\ldots,q(n)$ in the product, may be represented by $P_n(q(1),q(2),\ldots,q(n))$,

$$\begin{aligned}P_n(q(1),q(2),\ldots,q(n))={}&\int O_1^{(2l-n)}\int O_1^{(2l-n-1)}\cdots\int O_1^{[q(n)+1]}\int O_2^{[q(n)]}\int O_1^{[q(n)-1]}\cdots\int O_1^{[q(1)+1]}\\&\times\int O_2^{[q(1)]}\int O_1^{[q(1)-1]}\cdots\int O_1^{(1)}\,.\end{aligned} \tag{33}$$

Evaluation of the integrals indicated in Eq. (33) is facilitated by expressing Q and O_2 in terms of simpler operators. The operator O_1 may be written

$$O_1 = i\sum_{k=1}^{3} p(k) \sum_{j=1}^{2} \lambda^{j-1}\phi(j,k) = i\lambda^{j-1}p(k)\phi(j,k)\,, \tag{34}$$

where the index k indicates the kth vector component of a quantity

$$\phi(1,k) = \frac{\partial}{\partial x_k} \tag{35}$$

and

$$\phi(2,k) = \frac{\partial V}{\partial x_k}\,. \tag{36}$$

For brevity, the summations over j and k have been made implicit in the last step of Eq. (34). Similarly,

$$O_2 = -\tfrac{1}{2}\delta(k(1),k(2))\lambda^{j(1)+j(2)-2}\phi(j(2),k(2))\phi(j(1),k(1))\,. \tag{37}$$

Expressing Eq. (33) in terms of the ϕ operators and evaluating the indicated integrals, one finds

$$p_n(q(1),q(2),\ldots,q(n)) = (-1)^l\left(\frac{1}{2}\right)^n \prod_{i=1}^{n+1}\left(A(q(i))\prod_{\gamma=q(i-1)+i}^{q(i)-2+i} p(k(\gamma))\right)\lambda^{J-n}\Phi\,, \tag{38}$$

where

$$A(q(i)) = \delta[k(q(i)+i),k(q(i)+i-1)][B(q(i)+i)-i]^{-1}\prod_{\gamma=q(i-1)+i}^{q(i)-2+i}[B(\gamma)-i+1]^{-1}\,, \tag{39}$$

$$A(q(n+1)) = \prod_{\gamma=q(n)+n+1}^{2l}[B(\gamma)-n]^{-1}\,, \tag{40}$$

$$B(\gamma) = \sum_{\alpha=1}^{\gamma} j(\alpha)\,, \tag{41}$$

$$J = B(2l)\,, \tag{42}$$

$$q(0) \equiv 0\,, \tag{43}$$

$$q(n+1) \equiv 2l+1-n\,, \tag{44}$$

and Φ is the product of ϕ operators given by

$$\Phi = \phi(j(2l),k(2l))\,\phi(j(2l-1),k(2l-1))\cdots\phi(j(1),k(1))\,. \tag{45}$$

Since the ϕ operators do not in general commute, the product in Eq. (45) must be maintained in the stated order. Here the convention is being used that

$$\prod_{\gamma=a}^{b<a} g(\gamma) = 1\,. \tag{46}$$

One can more easily understand the structure of the right-hand side of Eq. (38) by noticing that the factor $A(i)$ contains information about the products of O_1 and O_2 operators of Eq. (33) occupying the positions $q(i-1)+1$ to $q(i)$. The Kronecker delta occurring in Eq. (39) originated in $O_2^{[q(i)]}$, while factors such as $[B(\gamma)-n]^{-1}$ result from the integration of λ raised to the power $j(1)+j(2)+\cdots+j(\gamma)-n-1$. The values of the indices of the Kronecker delta, and the other factors making up Eq. (39), are shifted from what one might first expect; this results from taking into account that a single O_2 operator is replaced by two ϕ operators.

The task now at hand is to sum $P_n(q(1),\ldots,q(n))$ over all allowable values of the q's. Since $q(i)$ is the position of the ith O_2 operator in Eq. (33), then necessarily $q(i) > q(i-1)$. Also, the largest value $q(i)$ may obtain is $2l-2n+i$, so that the allowed range of $q(i)$ is

$$q(i-1)+1 \leqslant q(i) \leqslant 2l-2n+i\,. \tag{47}$$

Equation (38) shows that the part of $P_n(q(1),\ldots,q(n))$, which is dependent on the values of the $q(i)$, may be written as a product of factors, each of which depends on a single $q(i)$. Summations over such a product may be written

$$\sum_{g(1)}\sum_{g(2)}\cdots\sum_{g(n)}\prod_{i=1}^{n} f(g(i)) = \sum_{g(1)} f(g(1))\sum_{g(2)} f(g(2))\cdots\sum_{g(n)} f(g(n)) = \prod_{i=1}^{n}\sum_{g(i)} f(g(i))\,. \tag{48}$$

Finally, summing $P_n(q(1),q(2),\ldots,q(n))$ over all values of n, one obtains

$$\delta_{2l}K=(-1)^l\sum_{n=0}^{l}\left(\tfrac{1}{2}\right)^n\prod_{i=1}^{n+1}\left(\sum_{q(i)}A(q(i))\prod_{\gamma=q(i-1)+i}^{q(i)-2+i}p(k(\gamma))\right)\lambda^{J-n}\Phi\,, \tag{49}$$

where the range of $q(i)$ is given by Eqs. (43)–(47).

As mentioned in Sec. III, $\delta_{2l}\tilde{\rho}(\vec{r},\vec{p})$ is obtained from $\delta_{2l}K$ by replacing λ^n by $\partial^n f(E)/\partial E^n$. The $2l$th-order correction to the density $\delta_{2l}\rho(\vec{r})$ is obtained by integrating $\delta_{2l}\tilde{\rho}(\vec{r},\vec{p})$ over the momentum. The only factors of $\delta_{2l}\tilde{\rho}(\vec{r},\vec{p})$ which depend on the momentum are the derivatives of f and the components of momentum which are explicitly present in the expression for $\delta_{2l}\tilde{\rho}(\vec{r},\vec{p})$. The required integrals are given by[21]

$$\frac{1}{4\pi^3}\int\left(\prod_{i=1}^{n+1}\prod_{\gamma=q(i-1)+i}^{q(i)-2+i}p(k(\gamma))\right)\frac{\partial^{J-n}f(E)}{\partial E^{J-n}}d^3p=\frac{(-1)^{l-n}}{\pi^2}(2J-2l-5)!!\,\Delta(\{k\})\kappa_F^{2l+3-2J}\,, \tag{50}$$

where κ_F is the local Fermi momentum

$$\kappa_F=[2(\mu-V)]^{1/2}\,, \tag{51}$$

for a positive integer C:

$$(2C-1)!!=(2C-1)(2C-3)(2C-5)\cdots(3)(1)\,, \tag{52}$$

and $\Delta(\{k\})$ is a function of the set of k's present in the integrand of Eq. (50),

$$\begin{aligned}\{k\}=\{&k(1),k(2),\ldots,k(q(1)-1),k(q(1)+2),\ldots,k(q(i)-2+i)\\ &\times k(q(i)+i+1),\ldots,k(q(n)-2+n),k(q(n)+n+1),\ldots,k(2l)\}\,.\end{aligned} \tag{53}$$

One may represent $\Delta(\{k\})$ by the sum of all possible products of Kronecker deltas, which can be formed from the $2l-2n$ elements of $\{k\}$. When $\Delta(\{k\})$ is a function of only two arguments, it is the Kronecker delta, $\Delta(a,b)=\delta(a,b)$, while

$$\Delta(a,b,c,d)=\delta(a,b)\delta(c,d)+\delta(a,c)\delta(b,d)+\delta(a,d)\delta(b,c)\,. \tag{54}$$

In general, when $\Delta(\{k\})$ is a function of $2a$ arguments, it consists of a sum of $(2a-1)!!$ terms. For the case of $\{k\}$ being the null set, i.e., when $n=l$, $\Delta(\{\,\})$ is set equal to 1.

The final result obtained for $\delta_{2l}\rho(\vec{r})$ is

$$\delta_{2l}\rho(\vec{r})=\frac{1}{\pi^2}\left[\sum_{n=0}^{l}\left(-\tfrac{1}{2}\right)^n\left(\prod_{i=1}^{n+1}\sum_{q(i)}A(q(i))\right)\Delta(\{k\})\right](2J-2l-5)!!\,\kappa_F^{2l+3-2J}\Phi\,. \tag{55}$$

In an analogous manner, $\delta_{2l}(\langle\mathcal{H}\rangle-\mu N)$ may be evaluated, and an expression similar to that for $\delta_{2l}\rho(\vec{r})$ is obtained. In fact, the expression for $\delta_{2l}(\langle\mathcal{H}\rangle-\mu N)$ may be obtained from the right-hand side of Eq. (55) by multiplying the factor $(-\frac{1}{2})^n$ by $(1+n-J)$, replacing $(2J-2l-5)!!$ with $(2J-2l-7)!!$ and replacing $\kappa_F^{2l+3-2J}\Phi$ with $\int\kappa_F^{2l+5-2J}\Phi\,d^3r$.

The expressions obtained here for $\delta_{2l}\rho(\vec{r})$ and $\delta_{2l}(\langle\mathcal{H}\rangle-\mu N)$ must be treated as operators for the quantities indicated because of the pending operations in Φ. Expressions involving derivatives of the potential are obtained by applying these operators to the constant 1, the leading term in the expansion of K. Also, $\delta_{2l}\rho(\vec{r})$ consists of more terms than are explicitly present in Eq. (55), because of the implicit summations over the j's and k's present in $A(q(i))$, $\Delta(\{k\})$, J, and Φ.

In the derivations of $\delta_{2l}\rho(\vec{r})$ and $\delta_{2l}(\langle\mathcal{H}\rangle-\mu N)$, the quantities $(2J-2l-5)$ and $(2J-2l-7)$ were assumed to always be positive. This assumption is valid for $l\geq 2$ for corrections to $\rho(\vec{r})$ and for $l\geq 3$ for corrections to $\langle\mathcal{H}\rangle-\mu N$. Equation (55) can be made valid for all $l(\geq 1)$ by replacing the factor $(2J-2l-5)!!$ with $(2J-2l-3)!!/(2l+3-2J)$. Similarly, the expression for $\delta_{2l}(\langle\mathcal{H}\rangle-\mu N)$ is correct for all l when $(2J-2l-7)!!$ is replaced by $(2J-2l-3)!!/(2l+5-2J)(2l+3-2J)$.

V. THE SIXTH-ORDER CORRECTIONS

The operators described in the last section were employed to determine $\delta_6\rho(\vec{r})$ and $\delta_6(\langle\mathcal{H}\rangle-\mu N)$. The sixth-order correction to the density is given by

$$\delta_6\rho(\vec{r}) = -\frac{1}{\pi^2}\Bigg[\kappa_F^{-5}\frac{\nabla^6 V}{2240} + \kappa_F^{-7}\left(\frac{17}{2688}(\nabla\nabla^2 V)^2 + \frac{\nabla^2 V\nabla^4 V}{192} + \frac{3}{448}\vec{\nabla}V\cdot\vec{\nabla}\nabla^4 V + \frac{(\nabla_i\nabla_j\nabla_k V)^2}{448} + \frac{(\vec{\nabla}_i\vec{\nabla}_j V)\cdot(\vec{\nabla}_i\vec{\nabla}_j\nabla^2 V)}{112}\right)$$

$$+\kappa_F^{-9}\left(\frac{7}{384}(\nabla V)^2\nabla^4 V + \frac{17}{192}(\vec{\nabla}_i\nabla^2 V)\cdot(\nabla V\cdot\vec{\nabla}\vec{\nabla}_i V) + \frac{7}{192}\vec{\nabla}V\cdot\vec{\nabla}(\nabla^2 V)^2 + \frac{7}{288}\nabla^2 V(\nabla_i\nabla_j V)^2\right.$$

$$\left. + \frac{(\vec{\nabla}_i\vec{\nabla}_j V)\cdot[(\vec{\nabla}_j\vec{\nabla}_k V)\cdot(\vec{\nabla}_i\vec{\nabla}_k V)]}{54} + \frac{\vec{\nabla}V\cdot\vec{\nabla}(\nabla_i\nabla_j V)^2}{32} + \frac{3}{64}\vec{\nabla}_i V\cdot[\vec{\nabla}V\cdot\vec{\nabla}(\vec{\nabla}_i\nabla^2 V)] + \frac{35}{3456}(\nabla^2 V)^3\right)$$

$$+\kappa_F^{-11}\left(\frac{35}{256}(\nabla^2 V)^2(\nabla V)^2 + \frac{21}{64}(\nabla V)^2\vec{\nabla}V\cdot\vec{\nabla}\nabla^2 V + \frac{7}{64}(\nabla V)^2(\nabla_i\nabla_j V)^2 + \frac{51}{128}(\vec{\nabla}V\cdot\vec{\nabla}\vec{\nabla}V)^2\right.$$

$$\left. + \frac{21}{128}\nabla^2 V\vec{\nabla}V\cdot\vec{\nabla}(\nabla V)^2 + \frac{9}{64}(\vec{\nabla}_i V\vec{\nabla}_j V)\cdot(\vec{\nabla}V\cdot\vec{\nabla}\vec{\nabla}_i\vec{\nabla}_j V)\right)$$

$$+\kappa_F^{-13}\left(\frac{385}{512}\nabla^2 V(\nabla V)^4 + \frac{231}{256}\vec{\nabla}V\cdot\vec{\nabla}(\nabla V)^4\right) + \frac{5005}{3072}\kappa_F^{-15}(\nabla V)^6\Bigg]. \tag{56}$$

The expression for $\delta_6(\langle\mathcal{H}\rangle - \mu N)$, obtained directly from application of the operator for $\delta_6(\langle\mathcal{H}\rangle - \mu N)$, is analogous to the expression for $\delta_6\rho(\vec{r})$. However, utilizing Green's identity this may be reduced to

$$\delta_6(\langle\mathcal{H}\rangle - \mu N) = \frac{1}{\pi^2}\int\Bigg[-\kappa_F^{-5}\frac{(\nabla\nabla^2 V)}{4480} + \kappa_F^{-7}\left(\frac{11}{16\,128}(\nabla^2 V)^3 + \frac{(\nabla V)^2\nabla^4 V}{1792}\right)$$

$$+\kappa_F^{-9}\left(\frac{31}{6912}(\nabla V)^2(\nabla^2 V)^2 + \frac{11}{3456}(\nabla V)^2\vec{\nabla}V\cdot\vec{\nabla}\nabla^2 V - \frac{5}{3456}(\vec{\nabla}V\cdot\vec{\nabla}\vec{\nabla}V)^2\right)$$

$$+\frac{5}{512}\kappa_F^{-11}\nabla^2 V(\nabla V)^4 + \frac{11}{1024}\kappa_F^{-13}(\nabla V)^6\Bigg]d^3r. \tag{57}$$

This assumes all surface terms vanish for the V under consideration.

Equating terms of order 6 in Eq. (31) results in

$$T_6[\rho_0] = \delta_6(\langle\mathcal{H}\rangle - \mu N) - \int\left(\frac{\delta^2 T_0}{\delta\rho^2}\right)_{\rho_0}\delta_2\rho\,\delta_4\rho\,d^3r - \tfrac{1}{6}\int\left(\frac{\delta^3 T_0}{\delta\rho}\right)_{\rho_0}(\delta_2\rho)^2 d^3r$$

$$-\int\left(\frac{\delta T_2}{\delta\rho}\right)_{\rho_0}\delta_4\rho\,d^3r - \tfrac{1}{2}\int\left(\frac{\delta^2 T_2}{\delta\rho^2}\right)_{\rho_0}(\delta_2\rho)^2 d^3r - \int\left(\frac{\delta T_4}{\delta\rho}\right)_{\rho_0}\delta_2\rho\,d^3r. \tag{58}$$

Substituting for $\delta_6(\langle\mathcal{H}\rangle - \mu N)$, $\delta_2\rho^8$, and $\delta_4\rho^{10}$ and employing Eq. (18), one obtains the final formula

$$T_6[\rho] = \frac{(3\pi^2)^{-4/3}}{45\,360}\int\rho^{-1/3}\Bigg[13\left(\frac{\nabla\nabla^2\rho}{\rho}\right)^2 + \frac{2575}{144}\left(\frac{\nabla^2\rho}{\rho}\right)^3 + \frac{249}{16}\left(\frac{\nabla\rho}{\rho}\right)^2\left(\frac{\nabla^4\rho}{\rho}\right) + \frac{1499}{18}\left(\frac{\nabla\rho}{\rho}\right)^2\left(\frac{\nabla^2\rho}{\rho}\right)^2$$

$$-\frac{1307}{36}\left(\frac{\nabla\rho}{\rho}\right)^2\left(\frac{\nabla\rho\cdot\nabla\nabla^2\rho}{\rho^2}\right) + \frac{343}{18}\left(\frac{\nabla\rho\cdot\nabla\nabla\rho}{\rho^2}\right)^2 + \frac{8341}{72}\left(\frac{\nabla^2\rho}{\rho}\right)\left(\frac{\nabla\rho}{\rho}\right)^4 - \frac{1\,600\,495}{2592}\left(\frac{\nabla\rho}{\rho}\right)^6\Bigg]d^3r. \tag{59}$$

Again following Hodges,[10] we note that the sixth-order term predicted by linear response theory is

$$T_6[\rho] = \frac{13(3\pi^2)^{-4/3}}{45\,360}\int\rho^{-1/3}\left(\frac{\nabla\nabla^2\rho}{\rho}\right)^2 d^3r. \tag{60}$$

VI. DISCUSSION

For atomic densities, $T_6[\rho]$ becomes divergent at both large distances and near the nucleus. This behavior seems to be a result of employing the local density approximation in the derivation and is predictable from scaling arguments.[22,23] However, Eq. (59) is still valid in the limit of slowly varying densities and may be useful in certain problems of solid-state physics.

Other functions that could serve just as well in the integrand are related to the ones given here through Green's identity, although surface terms may contribute in particular cases. Of course, the value of $T_4[\rho]$ or $T_6[\rho]$ is unique in any problem in which the functional is fully applicable.

Although Eq. (59) may be of limited applicability, the density matrix from which it is derived would at first appear to be quite general, and some interesting results may be obtained with it. Starting with Eq. (16), the Thomas-Fermi theory is recovered by retaining only the lowest-order term of $\tilde{\rho}(\vec{r},\vec{p})$.[20] This term corresponds to treating the $\hat{p}$ and $\hat{V}$ operators of Eq. (9) as commuting operators and thus shows the classical nature of Thomas-Fermi theory. Insertion of the Thomas-Fermi result $\mu=0$ into $\hat{\rho}$ in Eq. (13) results in a density matrix which indicates that all bound states of the system are occupied. For an atom, such a result can be correct only in the limit $Z\rightarrow\infty$ and this is where Thomas-Fermi theory has been shown to be exact.[6]

A sometimes undesirable property of the density matrix, defined by Eqs. (7) and (8), is that it requires all the states of a degenerate set to be completely occupied or completely vacant. Therefore, the density-matrix operator employed here is sufficient to describe only closed-shell[8,18] (or, more precisely, closed-subshell) systems.

This feature of Thomas-Fermi theory and the gradient expansion could help explain the anomalous behavior observed in the error curves of some very recent studies of the gradient expansion.[17,24] This problem is less severe, but still present, in a spin-polarized formulation of the gradient expansion.[23,24] Although the higher-order terms of the gradient expansion appear to be divergent in certain applications, a closer examination of the boundary conditions employed may alleviate these difficulties.[25]

ACKNOWLEDGMENTS

I wish to thank Professor R. G. Parr and Dr. L. J. Bartolotti for many helpful discussions and encouragement throughout the course of this work. This work was aided by a research grant to The University of North Carolina at Chapel Hill from the National Science Foundation.

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