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Toward understanding the exchange-correlation energy and total-energy density functionals

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If an accurate ground-state electron density ρ_0 for a system is known, it is shown from calculations on atoms that a strikingly good estimate for the total electronic energy of atoms is provided by the formula $E[\rho_0]=\sum_i \varepsilon_i-(1-1/N)J[\rho_0]$, where N is the number of electrons, $J[\rho_0]$ is the classical Coulomb repulsion energy for ρ_0, and the ε_i are the Kohn-Sham orbital energies determined by the Zhao-Morrison-Parr procedure [Phys. Rev. A 50, 2138 (1994)] for implementation of the Levy-constrained search determination of the Kohn-Sham kinetic energy. The surprising accuracy of this formula is attributed to the fact that the exchange-correlation functional is equal to $-J/N$ plus a functional that behaves as if it were approximately homogeneous, of degree 1 in the electron density. A corresponding exact formula is given, and various approximate models are constructed.

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I. INTRODUCTION

The core problem in the density-functional theory of electronic structure is to obtain a satisfactory specific form of the energy functional in terms of the electron density $\rho(\mathbf{r})$. For an N-electron system characterized by an external potential $v_0(\mathbf{r})$, the Hohenberg-Kohn energy density functional $E_v[\rho]$ can be written as

$$E_v[\rho]=\int d\mathbf{r}\, v_0(\mathbf{r})\rho(\mathbf{r})+J[\rho]+T_s[\rho]+E_{\mathrm{xc}}[\rho]\ , \tag{1}$$

where $J[\rho]$, given by

$$J[\rho]=\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r}')\Big/|\mathbf{r}-\mathbf{r}'|\ , \tag{2}$$

is the classical electrostatic energy, $T_s[\rho]$ represents the kinetic energy of the corresponding noninteracting N-particle system having the same single-particle density $\rho(r)$, and $E_{\mathrm{xc}}[\rho]$ stands for the exchange-correlation energy functional. Minimizing Eq. (1) over all trial densities normalized to N gives the ground-state density ρ_0.

The Kohn-Sham method for solving this problem is to self-consistently solve the single-particle Kohn-Sham orbital equations

$$[-\tfrac{1}{2}\nabla^2+v_{\mathrm{eff}}(\mathbf{r})]=\varepsilon_i\phi_i\ , \tag{3}$$

where the density satisfies

$$\rho(\mathbf{r})=\sum_i|\phi_i|^2 \tag{4}$$

and the effective potential is given by

$$v_{\mathrm{eff}}(\mathbf{r})=v_0(\mathbf{r})+v_J(\mathbf{r})+v_{\mathrm{xc}}(\mathbf{r})\ , \tag{5}$$

where

$$v_J(\mathbf{r})=\int d\mathbf{r}'\rho_0(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| \tag{6}$$

and

$$v_{\mathrm{xc}}(\mathbf{r})=\delta E_{\mathrm{xc}}/\delta\rho(\mathbf{r})\ . \tag{7}$$

At the solution point, where $\rho=\rho_0$, there result

$$T_s[\rho]=-\tfrac{1}{2}\langle\phi_i|\nabla^2|\phi_i\rangle=\sum_i\varepsilon_i-\int d\mathbf{r}\,\rho(\mathbf{r})v_{\mathrm{eff}}(\mathbf{r}) \tag{8}$$

and

$$E[\rho]=\sum_i\varepsilon_i-J[\rho]+\Big[E_{\mathrm{xc}}[\rho]-\int d\mathbf{r}\,\rho(\mathbf{r})v_{\mathrm{xc}}(\mathbf{r})\Big]\ , \tag{9}$$

where $E[\rho]=E_v[\rho_0]$ is the correct ground-state energy for the system of interest. Note that the potentials $v_{\mathrm{eff}}(\mathbf{r})$, $v_J(\mathbf{r})$, and $v_{\mathrm{xc}}(\mathbf{r})$ each depend on the density. To emphasize this, one may write $v_{\mathrm{eff}}[\rho]$, $v_J[\rho]$, and $v_{\mathrm{xc}}[\rho]$.

Calculations with these equations are straightforward. Once we know $v_{\mathrm{xc}}[\rho]$ (or if one can determine the whole $v_{\mathrm{eff}}[\rho]$ directly), one can determine the Kohn-Sham orbitals by solving Eqs. (3)–(8). If in addition one knows $E_{\mathrm{xc}}[\rho]$ [or if one can determine the bracketed term in Eq. (9) by other means], one can then determine the total electronic energy from Eq. (9). There are two problems: determining v_{xc}, and determining E_{xc}.

A particular method of determining $v_{\mathrm{eff}}[\rho_0]$, $v_{\mathrm{xc}}[\rho_0]$, and $T_s[\rho_0]$ has been proposed [1,2], developed [2,3], and successfully applied [3,4]. The idea is to take advantage of the fact that Eqs. (3) and (4) above may be thought of as the constrained search determination of the kinetic energy $T_s[\rho]$ [5,6]. Namely, these are the equations for the minimization of the quantity $\langle D|-(1/2)\sum_i\nabla_i^2|D\rangle$, where D is a Slater determinant composed of the orbitals ϕ_i, subject to the constraint of Eq. (4), with v_{eff} the local position-dependent Lagrange multiplier associated with this constraint. Alternatively, it suffices to attach a single global multiplier to the constraint

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$$C(\lambda)\equiv\tfrac{1}{2}\int\int d\mathbf{r}\,d\mathbf{r}'[\rho^{\lambda}(\mathbf{r}')-\rho_0(\mathbf{r}')]\times[\rho^{\lambda}(\mathbf{r}')-\rho_0(\mathbf{r}')]\Big/|\mathbf{r}-\mathbf{r}'| \tag{10}$$

during minimization of $\langle D|-\frac{1}{2}\sum_i\nabla_i^2|D\rangle$, and to demand that the solution $\rho^{\lambda}(\mathbf{r})$ for a given value of the Lagrange multiplier λ converges to the correct density $\rho_0(\mathbf{r})$ in the limit $\lambda\rightarrow\infty$ at which $C(\lambda)$ goes to zero. More specifically [4], the single-particle equations

$$[-\tfrac{1}{2}\nabla^2+v_0(\mathbf{r})+(1-1/N)v_J(\mathbf{r})+\lambda v_C^{\lambda}(\mathbf{r})]\phi_i^{\lambda}=\varepsilon_i^{\lambda}\phi_i^{\lambda}\ , \tag{11}$$

$$\rho^{\lambda}(\mathbf{r})=\sum_i|\phi_i^{\lambda}(\mathbf{r})|^2\ , \tag{12}$$

with $v_J^{\lambda}=v_J[\rho^{\lambda}]$ and

$$\lambda v_C^{\lambda}(\mathbf{r})=\lambda\int d\mathbf{r}'[\rho^{\lambda}(\mathbf{r}')-\rho_0(\mathbf{r}')]\Big/|\mathbf{r}-\mathbf{r}'|\ , \tag{13}$$

become the Kohn-Sham Eqs. (3) and (4) as $\lambda\rightarrow\infty$. That is to say,

$$v_{\text{xc}}(\mathbf{r})=-(1/N)v_J(\mathbf{r})+\lim_{\lambda\rightarrow\infty}[\lambda v_C^{\lambda}(\mathbf{r})]\ , \tag{14}$$

and

$$v_{\text{eff}}(\mathbf{r})=v_0(\mathbf{r})+(1-1/N)v_J(\mathbf{r})+\lim_{\lambda\rightarrow\infty}[\lambda v_C^{\lambda}(\mathbf{r})]\ . \tag{15}$$

There are a number of reasons why the resolution of v_{xc} as given by Eq. (14) is appropriate. The idea of the first term as a self-interaction correction is 70 years old; it may be called the Fermi-Amaldi term [7]. It guarantees the correct long-range behavior of $v_{\text{xc}}(r)$ and assures that the exchange-correlation hole correctly normalizes to -1. The second term has a relatively short range. Plots of these quantities for the atoms He through Ar may be found in the literature [3,4].

It is important that, with the use of Eq. (14), the solutions of Eqs. (3) and (4) give correct Kohn-Sham eigenvalues without any constant shift [3,4]. The computed highest occupied orbital energy is the negative of the accurate first ionization potential.

A more quantitative argument for the v_J/N term in Eq. (14) is as follows. If the canonical Kohn-Sham orbitals are subjected to the unitary transformation that takes the ε_{ij} matrix (diagonal in the canonical form) to a circulant matrix, the new orbitals, called the circulant orbitals [8], have the property that their densities oscillate about the average total density. In the case of Be there are no oscillations whatever. In the more general case, ignoring the oscillation gives $N\sum_i J_{ii}=J$ exactly, where J_{ii} is the self-repulsion for circulant orbital i.

In the present paper we address the determination of the total electronic energy itself, given only ρ_0 and v_0.

II. APPROXIMATE TOTAL-ENERGY FORMULAS

Should accurate electron densities be available for a species S and its successive positive ions $S^+,S^{2+},\ldots$ down to the one-electron system, successive applications of the method described above will give the accurate total energy as the sum of successively computed highest occupied orbital energies. But we wish to develop ways to calculate the energy without that much information; that is, from ρ_0 and v_0 alone.

The $T_s[\rho_0]$ values themselves already give a good estimate,

$$E[\rho_0]=-T_s[\rho_0]\ . \tag{16}$$

The virial theorem gives $E[\rho_0]=-T[\rho_0]$, where T is the true kinetic energy, so that the error in Eq. (16) is the exchange-correlation contribution to the kinetic energy, usually called T_c. Since $T_s<T$ (Hartree-Fock), this error is less than the conventional correlation energy and so Eq. (16) is a good approximation; see Table I. Note that Eq. (16) clearly cannot provide a basis for a variational determination of ρ_0.

Can the bracketed term in Eq. (9) be constructed from the information provided by Eq. (14)? Not easily, surely, because there is a multitude of $E_{\text{xc}}[\rho]$, the functional derivatives of which are given by Eq. (14). One certainly may write

$$E_{\text{xc}}[\rho]=-(1/N)J[\rho]+G_{\text{xc}}[\rho]\ , \tag{17}$$

where the first term has the first term in Eq. (14) as its functional derivative and $G_{\text{xc}}[\rho]$ has the second term of Eq. (14) as its functional derivative. But what is $G_{\text{xc}}[\rho]$? An exact formula for $G_{\text{xc}}[\rho]$ will be derived in the next section. Here we obtain a simple approximate formula from a single approximation, that $G_{\text{xc}}[\rho]$ *is a homogeneous functional of degree 1 in* ρ. This would mean that

$$G_{\text{xc}}[\rho_0]=\int d\mathbf{r}\,\rho_0(\mathbf{r})\lim_{\lambda\rightarrow\infty}[\lambda v_C^{\lambda}(\mathbf{r})] \tag{18}$$

and

TABLE I. Energy prediction (in a.u.) from approximate virial theorem. The numbers in the third column are calculated values from CI or other accurate wave functions, taken from Refs. [3] and [4]. The numbers in the fourth column are determined in Refs. [3] and [4] by method described in present text.

Atom	Z	E_{exact}	$-T_s$	Error
He	2	-2.904	-2.867	0.037
Li	3	-7.478	-7.440	0.038
Be	4	-14.67	-14.59	0.077
B	5	-24.65	-24.56	0.090
C	6	-37.84	-37.72	0.12
N	7	-54.58	-54.43	0.15
O	8	-75.05	-74.86	0.19
F	9	-99.72	-99.47	0.25
Ne	10	-128.93	-128.63	0.30
Na	11	-162.24	-161.92	0.32
Mg	12	-200.02	-199.69	0.33
Al	13	-242.30	-241.94	0.36
Si	14	-289.28	-288.86	0.42
P	15	-341.17	-340.76	0.41
S	16	-397.99	-397.60	0.39
Cl	17	-460.00	-459.59	0.41
Ar	18	-527.39	-527.18	0.21

$$E_{\mathrm{xc}}[\rho_0] = -(1/N)J[\rho_0] + \int d\mathbf{r}\,\rho_0(\mathbf{r}) \lim_{\lambda\to\infty}[\lambda v_C^{\lambda}(\mathbf{r})] \ . \qquad (19)$$

Hence the total energy is approximately given by

$$E[\rho_0] = \sum_i \varepsilon_i - (1-1/N)J[\rho_0] \ . \qquad (20)$$

With this construction of approximate formulas for E_{xc} and E, the errors in E_{xc} and E will be the same. Note that there is no assumption that G_{xc} is small.

These formulas are readily tested using available data [3,4] for the atoms He through Ar. To test Eq. (18), accurate E values are put into Eq. (9) to give accurate E_{xc} values, and then accurate G_{xc} values are obtained from Eq. (17). In Table II, these values are compared with computed values of the right-hand side of Eq. (18). Results are poor for He and Li but are excellent for Be through Ar. The homogeneity of degree 1 is remarkably accurate for Be through Ar. For the atom H, both sides of Eq. (18) are zero.

To test Eq. (19), accurate E_{xc} values are obtained as just described; then they are compared with computed values of the right-hand side of Eq. (19); see Table II. Errors for He and Li are not small, but they are already obscured by the J/N terms. Again errors for Be through Ar are small. For the atom H, the right-hand side of Eq. (19) reduces to the first term, which is the correct E_{xc} for H.

Table III gives the results for total energy. The results are remarkably good, the errors almost always being of the order of magnitude of the correlation energy and often being less than the errors associated with Eq. (16). For Be through Ar, the average absolute error for Eq. (16) is 0.27 a.u. and for Eq. (20), 0.48 a.u. Note that the errors associated with Eq. (20) are sometimes positive and sometimes negative, with a certain regularity in going from left to right in the periodic table. For the atom H, no error is associated with Eq. (20).

TABLE III. Energy prediction (in a.u.) from new approximate formula. The energies in the third column are for wave functions employed in Refs. [3,4].

Atom	Z	E_{exact}	E_{calc} Eq. (20)	Error
He	2	−2.904	−2.903	0.001
Li	3	−7.478	−7.080	0.398
Be	4	−14.667	−14.518	0.149
B	5	−24.650	−24.473	0.177
C	6	−37.841	−37.831	0.010
N	7	−54.581	−54.825	−0.244
O	8	−75.054	−75.074	−0.020
F	9	−99.716	−99.798	−0.082
Ne	10	−128.926	−129.213	−0.287
Na	11	−162.240	−160.631	1.609
Mg	12	−200.024	−198.439	1.585
Al	13	−242.295	−241.194	1.101
Si	14	−289.276	−290.690	−1.414
P	15	−341.172	−341.337	−0.165
S	16	−397.991	−397.975	0.016
Cl	17	−460.004	−460.354	−0.350
Ar	18	−527.388	−527.337	−0.051

III. EXACT TOTAL-ENERGY FORMULA

The results just given show that the stated assumption about homogeneity leads to a good approximation for the exchange-correlation functional and total energy. We now investigate the nature of the terms required to improve upon the simple representations of Eqs. (19) and

TABLE II. Test of approximations for G_{xc}. The numbers in the third column are accurate values, computed using accurate energy as described in Ref. [3]. The numbers in the fifth column are calculated from Eq. (17) of text employing accurate E_{xc} values in first column. The numbers in the last column are from Eq. (49) of text using $\kappa=7.5$ and $A=0.075$.

Atom	Z	$E_{\mathrm{xc,exact}}$	$E_{\mathrm{ex,calc}}$ Eq. (19)	$G_{\mathrm{xc,exact}}$	$G_{\mathrm{xc,calc}}$ Eq. (18)	$G_{\mathrm{xc,calc}}$ Eq. (49)
He	2	−1.068	−0.996	−0.043	0.029	
Li	3	−1.827	−1.431	−0.471	−0.076	−0.318
Be	4	−2.772	−2.624	−0.967	−0.819	−0.603
B	5	−3.870	−3.699	−1.541	−1.369	−0.983
C	6	−5.210	−5.195	−2.234	−2.219	−1.468
N	7	−6.780	−6.936	−3.040	−3.197	−2.072
O	8	−8.430	−8.445	−3.850	−3.866	−2.804
F	9	−10.320	−10.399	−4.783	−4.863	−3.681
Ne	10	−12.490	−12.781	−5.881	−6.173	−4.723
Na	11	−14.440	−12.810	−7.165	−5.534	−5.905
Mg	12	−16.430	−14.854	−8.438	−6.863	−7.241
Al	13	−18.530	−17.409	−9.842	−8.720	−8.726
Si	14	−20.790	−22.464	−11.264	−12.939	−10.370
P	15	−23.150	−23.346	−12.904	−13.100	−12.215
S	16	−25.620	−25.569	−14.543	−14.492	−14.156
Cl	17	−28.190	−28.501	−16.229	−16.541	−16.309
Ar	18	−31.270	−31.604	−18.369	−18.70	−18.627

(20). Can we get the exact E from v_0 and the exact ρ_0?

The methods of Sec. I sufficing to determine the accurate $v_{\rm xc}$ and $\sum \varepsilon_i$ (for a given ρ_0 and v_0), Eq. (9) shows that this problem will be solved if one can carry through some functional integration of the form

$$E_{\rm xc}[\rho_2]=E_{\rm xc}[\rho_1]+\int\int d\mathbf{r}\,\delta\rho_0(\mathbf{r})v_{\rm xc}[\rho]\ , \tag{21}$$

where $E_{\rm xc}[\rho_1]$ is known. The path of integration for ρ can be any path of ground states going from ρ_1 to ρ_2 for which $v_{\rm xc}$ is accurately known for all intermediate states on the path.

Equations (11) and (12) provide a candidate for such a path, parametrized by λ. Namely, these equations may be applied for all densities between the $\lambda=0$ solution of Eqs. (11) and (12) to the $\lambda=\infty$ solution. Call the first the Fermi-Amaldi density $\rho^{\rm FA}=\rho^0$; the second is the true density for the ground state of the system with potential v_0, $\rho_0=\rho^\infty$. Thus, the Fermi-Amaldi density satisfies

$$\begin{gathered}[-\tfrac{1}{2}\nabla^2+v_0(\mathbf{r})+(1-1/N)v_J(\mathbf{r})]\phi_i^{\rm FA}=\varepsilon_i^{\rm FA}\phi_i^{\rm FA}\ ,\\ \sum_i|\phi_i^{\rm FA}|^2=\rho^0=\rho^{\rm FA}(\mathbf{r})\ ;\end{gathered} \tag{22}$$

the intermediate densities satisfy

$$\begin{gathered}[-\tfrac{1}{2}\nabla^2+v_0(\mathbf{r})+(1-1/N)v_J^\lambda(\mathbf{r})+\lambda v_c^\lambda(\mathbf{r})]\phi_i^\lambda=\varepsilon_i^\lambda\phi_i^\lambda\ ,\\ \sum_i|\phi_i^\lambda|^2=\rho^\lambda(\mathbf{r})\ ,\end{gathered} \tag{23}$$

while the true density satisfies

$$\left[-\tfrac{1}{2}\nabla^2+v_0(\mathbf{r})+(1-1/N)v_J^\infty(\mathbf{r})+\lim_{\lambda\to\infty}[\lambda v_c^\lambda(\mathbf{r})]\right]\phi_i^\infty=\varepsilon_i^\infty\phi_i^\infty\ , \tag{24}$$

$$\sum_i|\phi_i^\infty|^2=\rho^\infty(\mathbf{r})=\rho_0\ .$$

As has by now been amply demonstrated, the ϕ_i^∞ and ε_i^∞ are accurate Kohn-Sham orbitals and orbital energies for the ground state of the system with external potential v_0 and electron density ρ_0.

Equation (23), for any λ, also is an exact Kohn-Sham equation, because it is the constrained search procedure [5,6] for generating the Kohn-Sham $T_s[\rho^\lambda]$ that the present series of papers has been exploiting [1–4]. However, one must take care in identifying the exchange-correlation component of the effective potential

$$v_{\rm eff}^\lambda(\mathbf{r})=v_0(\mathbf{r})+(1-1/N)v_J^\lambda(\mathbf{r})+[\lambda v_C^\lambda(\mathbf{r})]\ . \tag{25}$$

The problem is that, except for $\lambda=\infty$, $\rho^\lambda(\mathbf{r})$ is the ground state not for the external potential v_0, but for a different external potential $v_{\rm ext}^\lambda$,

$$v_{\rm ext}^\lambda=v_0(\mathbf{r})+w_0^\lambda(\mathbf{r})\ ,\quad w_0^\infty=0\ . \tag{26}$$

That is,

$$v_{\rm eff}^\lambda=v_0(\mathbf{r})+w_0^\lambda(\mathbf{r})+v_J^\lambda(\mathbf{r})+v_{\rm xc}^\lambda(\mathbf{r})\ , \tag{27}$$

where

$$v_{\rm xc}^\lambda(\mathbf{r})=-v_J/N+\lambda v_C^\lambda-w_0^\lambda(\mathbf{r})\ . \tag{28}$$

Note that $(\lambda v_C^\lambda)^0=0$ and $w_0^0=w_0^{\rm FA}$.

From Eq. (28) follow

$$\langle\rho^\infty|v_{\rm xc}^\infty\rangle=-(1/N)2J^\infty-\left\langle\rho^\infty\left|\lim_{\lambda\to\infty}[\lambda v_C^\lambda]\right.\right\rangle \tag{29}$$

and

$$\langle\rho^0|v_{\rm xc}^0\rangle=-(1/N)2J^0-\langle\rho^0|w_0^0\rangle\ . \tag{30}$$

Also, inserting Eq. (28) in Eq. (21) with $d\rho^\lambda(\mathbf{r})=(\partial\rho^\lambda(\mathbf{r})/\partial\lambda)d\lambda$,

$$E_{\rm xc}^\infty-E_{\rm xc}^0=\int d\lambda\int d\mathbf{r}[\partial\rho^\lambda(r)/\partial\lambda][-v_J^\lambda/N+\lambda v_C^\lambda-w_0\lambda]\ . \tag{31}$$

On integration by parts this gives

$$\begin{aligned}E_{\rm xc}^\infty={}&-(1/N)J^\infty+\left\langle\rho^\infty\left|\lim_{\lambda\to\infty}[\lambda v_C^\lambda]\right.\right\rangle+\langle\rho_0^0|w_0^0\rangle\\ &+E_{\rm xc}^0+(1/N)J^0+\int d\lambda\int d\mathbf{r}\,\rho^\lambda(\mathbf{r})(\partial/\partial\lambda)\\ &\times[w_0^\lambda-\lambda v_C^\lambda]\ ,\end{aligned} \tag{32}$$

and the resultant-energy formula

$$\begin{aligned}E^\infty={}&\sum_i\varepsilon_i^\infty-(1-1/N)J^\infty\\ &+\left[\langle\rho^0|w_0^0\rangle+E_{\rm xc}^0+(1/N)J^0\right.\\ &\left.+\int d\lambda\int d\mathbf{r}\,\rho^\lambda(\mathbf{r})(\partial/\partial\lambda)[w_0^\lambda-\lambda v_C^\lambda]\right]\ .\end{aligned} \tag{33}$$

These are exact formulas, for which Eqs. (19) and (20) are good approximations. Recall that the superscript 0 here denotes Fermi-Amaldi quantities; superscript ∞ denotes quantities for the ground state of the external potential v_0.

Reverting to the more perspicuous notations, Eqs. (32) and (33) read

$$E_{\rm xc}[\rho_0]=-(1/N)J[\rho_0]+\int d\mathbf{r}\,\rho_0\lim_{\lambda\to\infty}[\lambda v_C^\lambda(\mathbf{r})]+\Delta\ , \tag{34}$$

and

$$E[\rho_0]=\sum_i\varepsilon_i-(1-1/N)J[\rho_0]+\Delta\ , \tag{35}$$

where

$$\begin{aligned}\Delta={}&\langle\rho^{\rm FA}|w_0^{\rm FA}\rangle+E_{\rm xc}[\rho^{\rm FA}]+(1/N)J[\rho^{\rm FA}]\\ &+\int d\lambda\langle\rho^\lambda(\mathbf{r})|(\partial/\partial\lambda)[w_0^\lambda-\lambda v_C^\lambda]\rangle\ .\end{aligned} \tag{36}$$

Note that no homogeneity assumption has been made in the derivation of these formulas.

Values of Δ can be read from Tables II and III. In fact they generally are small—of the order of the correlation energy. There must be much cancellation among the several components of Δ. Thinking intuitively about the Fermi-Amaldi model [7], one suspects that

$$w_0^{\mathrm{FA}} \approx 0 \text{ or at least } \langle \rho^{\mathrm{FA}} | w_0^{\mathrm{FA}} \rangle \approx 0 \tag{37}$$

and

$$E_{\mathrm{xc}}[\rho^{\mathrm{FA}}] \approx -(1/N) J[\rho^{\mathrm{FA}}] \ , \tag{38}$$

which would imply

$$\Delta \approx \int d\lambda \langle \rho^{\lambda}(\mathbf{r}) | (\partial/\partial\lambda)[w_0^{\lambda} - \lambda v_C^{\lambda}] \rangle \text{ (small) .} \tag{39}$$

Further work is necessary to assess the Fermi-Amaldi properties. It would be particularly valuable to have a method for determining w_0^{λ}. But note that the whole Δ would be zero in any case if the homogeneity property postulated after Eq. (17) were to hold true.

Various formulas alternative to Eqs. (34)–(36) are readily derived. Useful in this connection are the identities

$$\langle \rho^{\mathrm{FA}} | w_0^{\mathrm{FA}} \rangle + \int d\lambda \langle \rho^{\lambda}(\mathbf{r}) | (\partial w_0^{\lambda}/\partial\lambda) \rangle = -\int d\lambda \langle w_0^{\lambda} | (\partial \rho^{\lambda}(\mathbf{r})/\partial\lambda) \rangle \tag{40}$$

and

$$\left\langle \rho_0 \middle| \lim_{\lambda \to \infty} [\lambda v_C^{\lambda}(\mathbf{r})] \right\rangle - \int d\lambda \langle \rho^{\lambda}(\mathbf{r}) | (\partial/\partial\lambda)[\lambda v_C^{\lambda}] \rangle = \int d\lambda \langle [\lambda v_C^{\lambda}] | (\partial \rho^{\lambda}(\mathbf{r})/\partial\lambda) \rangle = \int d\lambda \, C(\lambda) \ , \tag{41}$$

where $C(\lambda)$ is the constraint as a function of λ as defined in Eq. (10). Thus Eq. (36) may be rewritten

$$\Delta = \int d\lambda \langle (\partial \rho^{\lambda}(\mathbf{r})/\partial\lambda) | [\lambda v_C^{\lambda} - w_0^{\lambda}] \rangle + \int d\lambda \, C(\lambda) - \left\langle \rho_0 \middle| \lim_{\lambda \to \infty} [\lambda v_C^{\lambda}(r)] \right\rangle + E_{\mathrm{xc}}[\rho^{\mathrm{FA}}] + (1/N) J[\rho^{\mathrm{FA}}] \ . \tag{42}$$

The foregoing analysis only formally solves the problem of finding $E[\rho_0]$ from ρ_0, because the quantity Δ of Eq. (36) or Eq. (42) is not exactly calculable without an accurate knowledge of the quantities w_0^{λ} and $E_{\mathrm{xc}}[\rho^{\mathrm{FA}}]$. Other paths of integration of Eq. (21) might do the job. For example, there is the path defined by coordinate scaling of $\rho_0(\mathbf{r})$ or the path leading to the bare-nuclear (hydrogenlike) reference state for which the electron-electron repulsion by definition is identically zero. There also is the possibility of using Hellmann-Feynman theorems [6] as an alternative to or in addition to Eq. (21) [9].

IV. FURTHER EXAMINATION OF THE EXCHANGE CORRELATION

The central conclusion of the previous papers in this series has been that one can now compute accurate exchange-correlation potentials from accurate electron densities. Furthermore, the calculational scheme is built on a natural and exact partitioning

$$v_{\mathrm{xc}}[\rho] = -(1/N) v_J[\rho] + v_C[\rho] \ , \tag{43}$$

where $v_C[\rho]$ is given by

$$v_C[\rho] = \lim_{\lambda \to \infty} (\lambda v_C^{\lambda}[\rho^{\lambda}]) = \delta G_{\mathrm{xc}}[\rho]/\delta\rho \ , \tag{44}$$

where λv_C^{λ} is the potential defined by Eq. (13) and $G_{\mathrm{xc}}[\rho]$ is the universal functional defined by Eq. (17). In view of the origin of v_C as a potential arising from the constraint of Eq. (10), it may be called the *constraint potential.* Note that it is capital *C* and not lower case *c*. The constraint potential is trivially computed from v_{xc}; graphs of it for the atoms have already been given [3,4].

As argued and demonstrated in Sec. III above, $G_{\mathrm{xc}}[\rho]$ is approximately homogeneous, of degree 1, in the density. In this section we undertake learning more about G through a detailed study of the functions $v_C[\rho(r)]$ for atoms. Note that while v_C is the functional derivative of G, there are many functionals for which it is the functional derivative.

A glance at the published [3,4] plots of $v_C(r)$ and $r^2\rho(r)$ reveals that these quantities show complementary shell structures: a minimum in one tends to correspond to a maximum in the other. This prompts the hope that the quantity $\rho(r)v_C(r)$ would be simply related to $\rho(r)$. Indeed this is so. Except for He, the relationship is almost linear. This is demonstrated in Fig. 1, where, for the atoms He to Ar, the quantity

$$\Gamma[\rho] \equiv \rho(r) v_C(r) / \rho(0) v_C(0) \tag{45}$$

is graphed versus the quantity

$$R[\rho] \equiv \rho(r)/\rho(0) \ . \tag{46}$$

Each of these varies monotonically from 0 to 1 as r varies from ∞ to 0. According to the first Hohenberg-Kohn theorem, Γ must be a universal *functional* of R: $\Gamma[R]$. From Fig. 1, it is clear that in fact Γ is close to a universal *function* of R: $\Gamma(R)$. For R near unity (near the nucleus) Γ is quite accurately linear in R; for R near zero (far from the nucleus) Γ deviates from linearity, apparently having $\Gamma'(0)=0$. A simple analytical formula

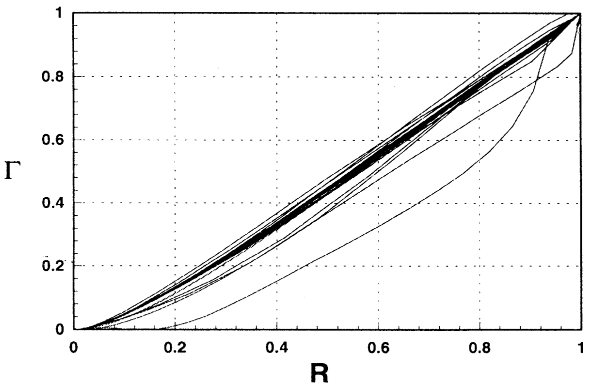

FIG. 1. Plot of $\Gamma(R)$ versus R for the atoms He to Ar. See Eqs. (45) and (46) of the text for definitions of Γ and R. The irregular behavior of several of the curves near $R=1$ (near the nucleus) probably is due to numerical errors. The curve for He is the curve that shows the largest departure from the others.

that fits the data admirably is

$$\Gamma(R)=[\kappa R-1+\exp(-\kappa R)]/[\kappa-1+\exp(-\kappa)]\ , \tag{47}$$

where κ is a parameter. Best values of κ vary from atom to atom, but a single (universal) κ value does nearly as well: $\kappa=7.5$. Figure 1 shows just how good this representation is.

For a given $\rho(r)$ and a given universal (or other) $\Gamma(R)$, such as Eq. (47), how would one calculate $v_C(r)$ from these formulas? For each r, one could determine $R(r)$ from Eq. (46) and $\Gamma(r)$ from Eq. (47) (or other formula). From Eq. (45) would follow

$$v_C(r)=[\Gamma(r)/R(r)]v_C(0)\ , \tag{48}$$

so that $v_C(r)$ would be determined up to a constant. To reasonable accuracy, the data show that $v_C(0)$ is proportional to Z^2, where Z is the atomic number and the proportionality constant is universal. Further, as is well known, $\rho(0)$ is approximately proportional to Z^3. Accordingly, a reasonable approximation is

$$v_C(r)=AZ[\rho(0)]^{1/3}[\Gamma(r)/R(r)]\ , \tag{49}$$

where A is a constant. Table II presents the results of a simple test of this formula, with $A=0.075$: Calculate $\langle\rho_0(r)|v_C(r)\rangle$ and compare with the accurate values previously calculated

V. RECAPITULATION AND DISCUSSION

In this research, taking advantage of the fact that there now exists a procedure for obtaining an accurate v_{xc} from an accurate ground-state density [1–4], we have learned a great deal about v_{xc}. The calculations we have carried out are calculations on atoms only, and our results are not perfectly accurate. To a certain extent, therefore, our conclusions are tentative. However, extensions to molecules and to higher accuracy should be straightforward, and we believe that the conclusions we draw now will not be substantially affected.

The most important conclusion would appear to be that it may be well to eschew the traditional resolution of exchange correlation into exchange plus correlation, in favor of a resolution into an Amaldi term plus a constraint term:

$$v_{\mathrm{xc}}[\rho]=-(1/N)v_J+v_C\ . \tag{50}$$

Here N is a parameter (not a functional) that is the number of electrons, v_J is the classical electrostatic potential due to the whole electron distribution, and v_C is the potential arising from the constraint of Eq. (10). The constraint potential enters in order to assure that the Kohn-Sham equations are the proper Kohn-Sham equations for the problem at hand; that is, that they are the proper variational equations for providing the correct T_s for the ground state in question—all as have been described in some detail in the present text.

While v_{xc} is equal to $\delta E_{\mathrm{xc}}[\rho]/\delta\rho$, knowledge of v_C in Eq. (50), which our method gives us, is not sufficient to accurately determine E_{xc} and the total energy. However, Eq. (50) implies

$$E_{\mathrm{xc}}[\rho]=-(1/N)J+G_{\mathrm{xc}}[\rho]\ , \tag{51}$$

where $\delta G_{\mathrm{xc}}[\rho]/\delta\rho=v_C$. We have demonstrated that an excellent approximation results if one assumes that $G_{\mathrm{xc}}[\rho]$ is homogeneous, of degree 1, in ρ. There then results

$$E_{\mathrm{xc}}[\rho]=-(1/N)J+\langle\rho|v_C\rangle \tag{52}$$

and

$$E=\sum_i \varepsilon_i-(1-1/N)J\ , \tag{53}$$

where the ε_i are the Kohn-Sham orbital energies, calculable from the density as we have shown [3,4]. Errors in these formulas are on the order of the correlation energy, so that the procedure thus defined is close to a complete procedure for determining the total energy from the density. A procedure for determining the exact energy from the true ground-state density ρ_0 so far has escaped us (and also we have failed to solve the problem of determining the energy variationally starting only from N and the ground-state external potential).

The Amaldi terms in these formulas provide the correct normalization of the exchange-correlation hole and the correct long-range behavior of the exchange-correlation potential. [It is notable that plots of the two components in Eq. (49) [3,4] clearly show that the first is long range and the second is short range.] Errors in Eqs. (51)–(53) do not escalate as N increases; rather, they appear to decrease. The implication of all of this is that the separation of $-(1/N)v_J$ out of v_{xc}, as in Eq. (50), may be a very natural separation indeed. One might be able to understand this better by taking a fresh look at the density-matrix formulation of the whole exchange-correlation problem. Examination of accurate actual $v_C[\rho]$ curves for neutral atoms reveals that to a good approximation there is a universal formula for $v_C[\rho]$, Eq. (47), which states that ρv_C is an almost linear local functional of ρ.

Among the many problems slated for further work, we mention the following: (a) a careful, very accurate study of regions near nuclei (which are vital for high accuracy with this method); (b) a study of the potential v_C at long range (low density limit); (c) positive ions; (d) spin-polarized theory and open shell systems; (e) corresponding studies using Hartree-Fock densities as input (one may be able to find a simple formula for the correlation energy); (f) refinement of the extrapolation procedures; (g) a study of whole "fixed λ" chemistries (first do a lot of calculations on many systems and many properties taking $\lambda=100$, say; then repeat for $\lambda=200$, etc.); (h) accurate virtual Kohn-Sham orbitals and orbital energies, and their use in the theory of excited electronic states; (i) the $Z=N=\infty$ limit; (j) finding a theoretical derivation of the value of the empirical constants κ and A in Eqs. (47) and (49); and (k) a study of size—extensivity questions.

We conclude with a note of optimism, coming from addressing a point that at first might seem to be a weak point of the present paper. The Levy constrained search procedure for determining T_s that we have employed makes no use whatever of the specific form of the two-body potential u_{12} (in fact, $1/r_{12}$ for our cases of interest). How then, could we ever hope to generate the correct total energy, without inserting, somewhere, the explicit form for this potential (which we have not done)? To guess how to do it is an acceptable procedure, but only if we guess correctly. But there is a more satisfactory answer. The quantities $\rho_0(r)$ and $v_0(r)$ in fact uniquely determine the Hohenberg-Kohn functional $F[\rho_0]$ that goes with them. It will be different for different u_{12}, but u_{12} is not needed to determine it. Proof of this interesting result follows from the fact that the Kohn-Sham effective potential given by the Levy procedure is unique. So we are justified in pursuing the goal of finding $E[\rho_0, v_0]$ starting from the Levy search for $T_s[\rho_0]$. That is what this paper has been about.

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