J. Phys. Chem. A **1997,** *101,* 5687−5691

Chemical Potential Equalization Principle: Direct Approach from Density Functional Theory

Peter Itskowitz[†] and Max L. Berkowitz*,[‡]

Department of Physics and Astronomy CB 3255 and Department of Chemistry CB 3290,
University of North Carolina, Chapel Hill, North Carolina 27599

Received: December 3, 1996; In Final Form: May 6, 1997[⊗]

In the framework of the density functional theory (DFT) we develop an approximation in which the energy of a molecule is expressed as a functional of perturbations of the atomic electron densities. The result depends on atomic densities, atomic chemical potentials, and hardness kernels that can be found from the solutions of the appropriate atomic DFT problem. A generalized formulation of the chemical potential (electronegativity) equalization principle is suggested. We show how the energy functional can be transformed into a function of the net charges on atoms and discuss the relationship between our approach and the earlier introduced chemical potential (electronegativity) equalization schemes. We present examples where by approximating density perturbations with the squares of Slater orbitals, we obtain values for the net charges that are in reasonable agreement with experiment. This approach can be used for predictions of the transferred charges in the molecules of any size, and its accuracy can be continuously improved by the use of more accurate approximations to the density perturbations.

1. Introduction

The density functional theory (DFT) formulated by Hohenberg and Kohn[1] in 1964 is one of the most powerful tools in modern studies of many-electron systems. The orbital Kohn−Sham approach[2] represents a successful scheme for a practical application of DFT. It yields good results for electronic structure and energy calculations and its accuracy is significantly improving with the development of new corrections to the exchange−correlation functionals.[3] However, the need to solve an equation for every electron of the system makes it difficult to apply this scheme to big molecules and groups of many atoms or molecules. A second look at basic DFT equations stimulates the development of approaches that do not require the decomposition of the electron density into a set of orbitals.

In works of Parr and his collaborators it was shown how to connect DFT with the ideas of structural chemistry (see ref 4a and references therein). First, the Lagrange multiplier μ (we will call it the "chemical potential") that appears in the DFT equation was identified with the negative of the electronegativity,[4b] the quantity often used to explain charge transfer during the process of molecular formation (refs 5 and 6). Second, a definitive scale for the values of the chemical potential was suggested (see refs 4 and 7). Finally, the empirical electronegativity equalization principle was shown to be the consequence of the constrained search for the minimum of the energy functional in DFT.[4b] Later Berkowitz and Parr[8] gave the definitions for hardness and softness kernels and established the hierarchy of the response functions which appear in DFT as the functional derivatives of different orders of the energy functional. Yang and York[9] recently proposed a model for describing the redistribution of the electron density upon perturbation by an applied field. They also gave a prescription for semiempirical numerical calculation of chemical potentials and hardness kernels using the framework of the electronegativity equalization principle. The developments discussed above pave the road to the achievement of two goals. The first goal is to create approximate methods for the calculation of electronic structures and energies of systems too big for direct application of the Kohn−Sham scheme. The idea is that by Volterra-type expansions of the functionals one can obtain the equations for electron density rather than orbitals, thus avoiding the need to solve an equation for every electron.

The other goal is the development of simple models that provide efficient ways for finding the charge distribution in molecules for the purpose of molecular simulations. In this case the energy is often written as a function of the powers of net charges on atoms with the values of the coefficients either taken from a certain scale or considered to be free parameters (Rappe and Goddard,[10] Rick *et al.*[11]). In these models the chemical potential equilization principle was used to calculate charges on the molecules. Rick *et al.*[11] demonstrated that such an approach combined with molecular dynamics leads to a new dynamical model in which the point charges on the atomic sites are allowed to fluctuate in response to the environment. Application of this model to water produced results comparable with the ones obtained from the best polarizable models, while the computational cost increase was very small when compared to the nonpolarizable model. Models introduced by Mortier *et al.*[12] and Nalewajski[13] also used the chemical potential equalization principle for calculations of the transferred charges in the molecules. However, all these models require the use of many empirical corrections to the atomic values of chemical potentials (electronegativities) and hardnesses (idempotentials) in order to get the correct values for the charges. Also, it is not clear what kind of chemical bonds these models can and cannot describe (for example, they fail to explain the bonding in homonuclear molecules). In this article we attempt to provide answers to some of these questions.

The article has the following structure: in section 2 we obtain the approximation for the energy functional and formulate the generalized chemical potential equalization principle. In section 3 we show how the energy functional can be transformed into the function of charges and compare our equations with the equations in the earlier introduced models. In sections 4 and 5 we present the results of our calculations, and in section 6 we summarize the completed work.

[†] Department of Physics and Astronomy.
[‡] Department of Chemistry.
[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

S1089-5639(96)03962-X CCC: $14.00 © 1997 American Chemical Society

2. Approximation for the Energy Functional

To get the approximate expression for the energy of a molecule in the framework of DFT, we start with the picture of a molecule as a collection of slightly perturbed atoms. As we know, when atoms form a molecule, only valence electrons change their orbitals considerably, while the inner shell electrons remain practically unperturbed. This is why we can expect that the perturbations in the electron probability densities due to formation of the molecule are small compared to the densities of the unperturbed atoms. By using the Volterra expansion for the functionals with these changes of the density on each atom as small parameters, we can obtain different orders of approximation for the molecular energy functional. Application of the variational principle will provide us with a system of equations, the solution of which will yield the ground state electron probability density and the energy of the molecule.

Using this approach, we continue to work with the electron density, the natural variable of DFT, so that the molecular energy remains a functional of the density but not a function of the net charges as in the chemical potential equalization models (refs 10, 12, 13). On the other hand, by taking the density perturbations in the form of some fixed charge distributions, making it a function of the charges, we can expect that we will be able to reproduce and possibly improve the previously obtained results.

We begin the derivation of the expression for the molecular energy by stating the atomic DFT problem. The energy functional for unperturbed atom a with the number of electrons N_a is

$$E[\rho_a(\vec{r})] = \int v_a(\vec{r})\, \rho_a(\vec{r})\, \mathrm{d}\vec{r} + F[\rho_a(\vec{r})] \tag{1}$$

where $v_a(\vec{r})$ is a nuclear potential, $v_a(\vec{r}) = -Z_a/r$, and $\rho_a(\vec{r})$ is the ground state electron density. For a neutral atom it is normalized by the condition

$$\int \rho_a(\vec{r})\, \mathrm{d}\vec{r} = N_a \tag{2}$$

The true ground state electron density $\rho_a(\vec{r})$ satisfies the equation

$$\frac{\delta E[\rho_a(\vec{r})]}{\delta \rho_a(\vec{r})} = v_a(\vec{r}) + \frac{\delta F[\rho_a(\vec{r})]}{\delta \rho_a(\vec{r})} = \mu_a \tag{3}$$

where the atomic chemical potential μ_a appears as a Lagrange multiplier for the condition (2).

Next we state the DFT problem for the molecule. The energy functional is

$$E = E[\rho(\vec{r})] = V_{nn} + \int v(\vec{r})\, \rho(\vec{r})\, \mathrm{d}\vec{r} + F[\rho(\vec{r})] \tag{4}$$

where V_{nn} represents internuclear interactions and $v(\vec{r})$ is the total nuclear potential. Due to its additivity, we can write it as the sum of atomic potentials

$$v(\vec{r}) = \sum_a v_a(\vec{r}) \tag{5}$$

The new charge density for each atom can be written as

$$\rho_{\mathrm{a}}^{\mathrm{new}}(\vec{r}) = \rho_a(\vec{r}) + \rho'_a(\vec{r}) \tag{6}$$

$\rho'_a(\vec{r})$ represents the perturbations of the atomic electron density due to the interaction with the other atoms in the molecule. We hope (see the discussion above) that these perturbations are small compared to atomic densities $\rho_a(\vec{r})$, so that the condition $|\rho'_a(\vec{r})| \ll \rho_a(\vec{r})$ is satisfied everywhere in space.

Due to additivity, the molecular ground state density is

$$\rho(\vec{r}) = \sum_a (\rho_a(\vec{r}) + \rho'_a(\vec{r})) \tag{7}$$

From the condition $\int \rho(\vec{r})\, \mathrm{d}\vec{r} = \sum N_a$ it follows that $\sum \int \rho'_a(\vec{r})\, \mathrm{d}\vec{r} = 0$.

We now suggest the approximation for the universal functional $F[\rho(\vec{r})]$

$$F[\rho(\vec{r})] = F[\sum_a (\rho_a(\vec{r}) + \rho'_a(\vec{r}))] \simeq \sum_a F[\rho_a(\vec{r}) + \rho'_a(\vec{r})] + \frac{1}{2} \sum_a \sum_{b \neq a} I_{ab} \tag{8}$$

where

$$I_{ab} = \int\int \frac{(\rho_a(\vec{r}_1) + \rho'_a(\vec{r}_1))(\rho_b(\vec{r}_2) + \rho'_b(\vec{r}_2))}{r_{12}} \mathrm{d}\vec{r}_1\, \mathrm{d}\vec{r}_2 \tag{9}$$

It is clear that (8) represents a very strong approximation, since the exchange−correlation and kinetic energies are not additive. The implications of this approximation will be briefly discussed in the conclusion.

Our next step is to expand $F[\rho_a(\vec{r}) + \rho'_a(\vec{r})]$. We stop the expansion at the second-order term because we want to deal with linear equations for $\rho'_a(\vec{r})$ after we apply the variational principle to the energy functional.

$$F[\rho_a(\vec{r}) + \rho'_a(\vec{r})] \simeq F[\rho_a(\vec{r})] + \int \frac{\delta F[\rho_a(\vec{r})]}{\delta \rho_a(\vec{r})} \rho'_a(\vec{r})\, \mathrm{d}\vec{r} + \frac{1}{2} \int\int \frac{\delta^2 F[\rho_a(\vec{r})]}{\delta \rho_a(\vec{r}_1)\, \delta \rho_a(\vec{r}_2)} \rho'_a(\vec{r}_1)\, \rho'_a(\vec{r}_2)\, \mathrm{d}\vec{r}_1\, \mathrm{d}\vec{r}_2 \tag{10}$$

where from (3)

$$\frac{\delta F[\rho_a(\vec{r})]}{\delta \rho_a(\vec{r})} = \mu_a - v_a(\vec{r}) \tag{11}$$

and

$$\frac{\delta^2 F[\rho_a(\vec{r})]}{\delta \rho_a(\vec{r}_1)\, \delta \rho_a(\vec{r}_2)} = \frac{\delta^2 E[\rho_a(\vec{r})]}{\delta \rho_a(\vec{r}_1)\, \delta \rho_a(\vec{r}_2)} = \eta_a(\vec{r}_1, \vec{r}_2) \tag{12}$$

is the hardness kernel, defined in ref 8. The validity of (10) is justified by the condition $|\rho'_a(\vec{r})| \ll \rho_a(\vec{r})$.

We now substitute (5) and (7)−(12) into the expression for the molecular energy (4) and get

$$E[\rho(\vec{r})] = E[\rho'_1(\vec{r}),\rho'_2(\vec{r}),...] = V_{nn} + \sum_a E_a[\rho_a(\vec{r})] + \sum_a \sum_{b\neq a} \int v_a(\vec{r})\, \rho_b(\vec{r})\, \mathrm{d}\vec{r} + \frac{1}{2}\sum_a \sum_{b\neq a} \int\int \frac{\rho_a(\vec{r}_1)\, \rho_b(\vec{r}_2)}{r_{12}} \mathrm{d}\vec{r}_1\, \mathrm{d}\vec{r}_2 + \sum_a \mu_a \int \rho'_a(\vec{r})\, \mathrm{d}\vec{r} + \sum_a \sum_{b\neq a} \int \left[v_b(\vec{r}_1) + \int \frac{\rho_b(\vec{r}_2)}{r_{12}} \mathrm{d}\vec{r}_2 \right] \rho'_a(\vec{r}_1)\, \mathrm{d}\vec{r}_1 + \frac{1}{2}\sum_a \int\int \eta_a(\vec{r}_1,\vec{r}_2)\, \rho'_a(\vec{r}_1)\, \rho'_a(\vec{r}_2)\, \mathrm{d}\vec{r}_1\, \mathrm{d}\vec{r}_2 + \frac{1}{2}\sum_a \sum_{b\neq a} \int\int \frac{\rho'_a(\vec{r}_1)\, \rho'_b(\vec{r}_2)}{r_{12}} \mathrm{d}\vec{r}_1\, \mathrm{d}\vec{r}_2 \quad (13)$$

with the constraint for $\rho'_a(\vec{r})$

$$\sum_a \int \rho'_a(\vec{r})\, \mathrm{d}\vec{r} = 0 \quad (14)$$

In (13) the atomic characteristics such as atomic densities $\rho_a(\vec{r})$, chemical potentials μ_a, and hardness kernels $\eta_a(\vec{r}_1,\vec{r}_2)$ which themselves can be calculated from the atomic DFT problem are the parameters. The variables are the perturbations of the electron probability density $\rho'_a(\vec{r})$.

A constrained search for the set of $\rho'_a(\vec{r})$'s that minimizes (13) yields the system of equations

$$\frac{\delta E[\rho]}{\delta \rho'_a(\vec{r})} = \mu \quad (15)$$

for every a, where μ is the Lagrange multiplier for condition (14).

As we can see, (15) provides a generalized formulation of the chemical potential (electronegativity) equalization principle: *The functional derivatives of the energy functional with respect to the perturbations of the density on each atom, constituting a molecule, equalize.*

This statement now is a direct consequence of the constrained search for a functional minimum. The system of equations (15) must be solved for every $\rho'_a(\vec{r})$ to give the molecular electron density and the energy of the system.

3. Application

In order to further simplify the problem, we suggest that the perturbations of the atomic density $\rho'_a(\vec{r})$ can be written in the form

$$\rho'_a(\vec{r}) = Q_a f_a(\vec{r}) \quad (16)$$

where $f_a(\vec{r})$'s are some known functions, normalized to unity, and Q_a's are the net charges transferred to atoms in the process of formation of a molecule. Because of the fixed form of $f_a(\vec{r})$'s, energy in (13) becomes a simple function of the net charges Q_a

$$E(Q_a) = E_0 + \sum_a \mu^*_a Q_a + \frac{1}{2}\sum_a \tilde{\eta}_a {Q_a}^2 + \frac{1}{2}\sum_a \sum_{b\neq a} J_{ab} Q_a Q_b \quad (17)$$

where E_0 is the collection of terms independent of Q_a and

$$\mu^*_a = \mu_a + \sum_{b\neq a} \int \left[v_b(\vec{r}_1) + \int \frac{\rho_b(\vec{r}_2)}{r_{12}} \mathrm{d}\vec{r}_2 \right] f_a(\vec{r}_1)\, \mathrm{d}\vec{r}_1 \quad (18)$$

$$\tilde{\eta}_a = \int\int \eta_a(\vec{r}_1,\vec{r}_2)\, f_a(\vec{r}_1)\, f_a(\vec{r}_2)\, \mathrm{d}\vec{r}_1\, \mathrm{d}\vec{r}_2 \quad (19)$$

and

$$J_{ab} = \int\int f_a(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} f_b(\vec{r}_2)\, \mathrm{d}\vec{r}_1\, \mathrm{d}\vec{r}_2 \quad (20)$$

Here we need to stress that (16) must be viewed as another strong approximation because it cannot reproduce all the complexity of the real perturbation of the density. For example, it is absolutely not valid for homonuclear molecules, as it yields the bonding energy equal to zero because no charge is transferred from one atom to another. For this case general equations (15) must be solved.

However, approximation (16) allows us to discuss the relation of our approach to the earlier introduced chemical potential (electronegativity) equalization schemes, and, as we show below, with a good choice of functions $f_a(\vec{r})$ it can provide reliable results for the net charge distributions in many cases.

The search for the energy minimum results in a system of linear equations for Q_a's and Lagrange multiplier μ

$$\frac{\partial E(Q_a)}{\partial Q_a} = \mu^*_a + \tilde{\eta}_a Q_a + \sum_{b\neq a} J_{ab} Q_b = \mu \quad (21)$$

for all a and

$$\sum_a Q_a = 0 \quad (22)$$

Equations 21 have a form similar to the equations of the Mortier–Ghosh–Shankar (MGS) model,[12] but there are some important differences: in the MGS approach μ^*_a and $\tilde{\eta}_a$ are treated as independent of the neighbors, whereas in our case μ^*_a depends upon the neighboring atoms through the second term in (18) and $\tilde{\eta}_a$ depends upon the choice of f_a's as can be seen from (19). Also in (21) $J_{ab}(r)$ represents a shielding correction to the Coulomb point charge interaction, which is not used in ref 12. As we show in the next sections, these differences lead to substantial improvements in numerical results compared to MGS scheme.

4. Results

In order to use (21) for calculations of the net charges, we first need to specify the form of the functions $f_a(\vec{r})$. Following Rappe and Goddard,[10] we choose them to be the squares of the spherically symmetric Slater orbitals (we cannot use the point-charge approximation in which the functions $f_a(\vec{r})$ in (16) are substituted by delta-functions because it yields the values of $\tilde{\eta}_a = \infty$ in (19))

$$f_a(\vec{r}) = {\phi_a}^2(\vec{r} - \vec{r}_a) \quad (23)$$

where $\vec{r}_a$ is a vector to the position of nucleus a and

$$\phi_a(r) = A_n r^{n_a - 1} \mathrm{e}^{-\zeta_a r} \quad (24)$$

where n_a is a principal quantum number of the valent orbital of atom a and A_n is a normalization constant.

The major difference of our approach compared to the Rappe–Goddard scheme[10] is that the values of μ^*_a in our case are dependent on the environment through the second term in (18), which allows us to obtain correct results for the charges without making any modifications to the accepted scale of

TABLE 1: Charges on Halides[a]

	Q^{exp}	Q^{cpe}
LiF	0.837	0.731
LiCl	0.731	0.619
LiBr	0.694	0.549
LiI	0.647	0.441
NaF	0.879	0.697
NaCl	0.792	0.697
NaBr	0.757	0.684
NaI	0.708	0.634
KF	0.821	0.706
KCl	0.800	0.742
KBr	0.783	0.752
KI	0.740	0.734
RbF	0.781	0.728
RbCl	0.784	0.760
RbBr	0.768	0.766
RbI	0.753	0.749

[a] The values of experimental charges Q^{exp} were taken from ref 10. The values of the calculated charges Q^{cpe} were obtained using the chemical potential equalization principle.

atomic chemical potentials $\mu_a = -(I_a + A_a)/2$. Also, we use atomic hardness kernels defined in (12) for calculations of $\tilde{\eta}_a$.

The only free parameter left is ζ_a. In general, its value probably should be found individually for every atom with the help of some numerical fitting procedure. However, for this moment we accept the idea of Rappe and Goddard[10] and suggest that ζ_a be chosen in such a way that $\phi_a(r)$ yields the expectation value of r equal to the covalent radius of the atom (half of the bond distance for the appropriate homonuclear diatomic molecule)

$$R_a = \langle \phi_a(\vec{r})|r|\phi_a(\vec{r})\rangle = \frac{2n_a + 1}{2\zeta_a} \tag{25}$$

Sixteen alkali-metal halide molecules were studied on the basis of the described approach. For diatomic molecule the solution of (21) for the net charges is

$$Q_1 = -Q_2 = \frac{\mu_2^* - \mu_1^*}{\tilde{\eta}_1 + \tilde{\eta}_2 - 2J_{12}(r_{12})} \tag{26}$$

where r_{12} is the appropriate bond distance, and μ_1^*, μ_2^*, $\tilde{\eta}_1$, $\tilde{\eta}_2$, and J_{12} are found from (18), (19), and (20), respectively. The value for μ_a in (18) was taken as $-(I_a + A_a)/2$, where I_a is an ionization potential and A_a is an electron affinity of atom a, and atomic densities entering (18) were calculated through the atomic DFT program. We used the Coulomb part of the hardness kernel to calculate the values of $\tilde{\eta}_1$ and $\tilde{\eta}_2$. The calculated results are shown in Table 1 together with the experimental values of the charges Q^{exp} which were obtained from the experimental dipole moments.

The importance of these results is that all the coefficients in (26) are calculated from first principles with no fitting parameters used. The results are better for heavier atoms because for them the condition $|\rho_a'(\vec{r})| \ll \rho_a(\vec{r})$ is satisfied better. Considering all the approximations made, we can conclude that (21) can be successfully used for net charge calculations. The improvement of numerical results can be achieved by consideration of kinetic and exchange−correlation energy terms in hardness kernels as it is suggested in ref 9 and also by a more "personalized" choice of ζ_a.

5. Hydrogen

Besides the fact that the expansion (10) is the least accurate for the hydrogen atom, there are other reasons why the approach described in the previous section cannot be applied directly to hydrogen. First, for atoms that have valence electrons with $n \geq 2$ the excessive charge must be located at some distance away from the nuclei. Equation 25 establishes the correspondence of this distance to the covalent radius of the atom. However, for $n = 1$ the maximum of the extra density is at the position of the nucleus, and therefore ζ_a in (24) simply defines the width of the charge distribution. This is why a covalent radius is not a correct scale for the determination of ζ_a for hydrogen. Also, the hardness kernel for H is a differential operator (this follows from the Weizsacker kinetic energy term) which is very sensitive to the form of $\rho_a'(\vec{r})$. Still, as we show below, if $\tilde{\eta}_{\text{H}}$ and ζ_{H} are treated as free parameters, we can obtain reasonable results for molecules containing hydrogen using (21).

TABLE 2: Charges on Hydrogen[a]

	Q^{exp}	Q^{cpe}
LiH	0.768	0.617
CH_4	−0.150	−0.191
NH_3	−0.267	−0.300
H_2O	−0.325	−0.282[b]
HF	−0.415	−0.395

[a] The values of experimental charges Q^{exp} were taken from ref 10. [b] We used the value $\zeta_{\text{O}} = 1.61$ au recommended by Rick *et al.*[11] for oxygen. For $\zeta_{\text{O}} = (2n + 1)/(2R_{\text{O}}) = 2.19$ au the charge on H is $Q_{\text{H}} = -0.120$.

In Table 2 we present the results of calculations of the charges on hydrogen for five molecules with $\tilde{\eta}_{\text{H}} = 14.98$ eV and $\zeta_{\text{H}} = 1.602$ au. Positive values of Q_a signify the presence of the extra electron density on the atom. Again, only the Coulomb parts of hardness kernels were used to calculate $\tilde{\eta}_a$ for all other atoms.

It is remarkable that we can successfully predict a dual behavior of hydrogen: in the case of LiH it is an acceptor, while in other cases it is a donor.

The result for CH_4 deserves a special discussion. The solution of (21) for this case is

$$Q_{\text{H}} = -\frac{1}{4}Q_{\text{C}} = \frac{\mu_{\text{C}}^* - \mu_{\text{H}}^*}{4\tilde{\eta}_{\text{C}} + \tilde{\eta}_{\text{H}} + 3J_{\text{HH}}(r_{\text{HH}}) - 8J_{\text{CH}}(r_{\text{CH}})} \tag{27}$$

The sign of Q_{H} is determined by the numerator of (27) (the denominator must be positive; this follows from the condition that the energy extremum must be a minimum). The atomic value for μ_{C} is −6.27 eV, and for μ_{H} it is −7.18 eV. Therefore on the basis of these values one can expect that the charge moves from carbon to hydrogen. But due to the presence of the second term in (18), the values become $\mu_{\text{C}}^* = -11.43$ eV and $\mu_{\text{H}}^* = -9.66$ eV and the charge is drawn from hydrogen to carbon, in agreement with experiment.

The above results clearly show that the form of coefficients in (21) does not need to be changed when hydrogen atoms are present in the problem. Such a change was proposed by Rappe and Goddard in ref 10. Also the same scale for the atomic value of the chemical potential for hydrogen $\mu_{\text{H}} = -(I_{\text{H}} + A_{\text{H}})/2 = -7.18$ eV can be used, consistent with the scale used for the other atoms.

6. Conclusion

Let us summarize the major points of this paper. We derived the expression for the energy of a molecule which is a functional of the perturbations on the atomic densities. The parameters in this energy expression are the atomic densities, atomic chemical potentials (electronegativities), and atomic hardness kernels. Application of the variational principle to the energy functional results in the generalized formulation of the chemical potential equalization principle. Second, we showed how the energy functional can be transformed into an energy function. The minimization of this energy function results in a system of linear equations for the net charges on atoms (see (21)).

Two strong approximations were made in deriving (21). One was done in (8) by leaving out a term due to the nonadditive character of exchange−correlation energy (incidentally, a similar approximation was made in the paper of Mortier *et al.*[12]). Our results show that approximation (8) can be used to study charge transfer in heterogeneous molecules. The second approximation was to choose a form of the perturbation of the density as the one given by (16).

Considering the severity of these approximations, it is encouraging that by using no free parameters we were able to obtain the values for the net charges that are in reasonable agreement with experiment.

Previously, a system of equations like (21) was sometimes written as a result of a Taylor series expansion. In such an approach it was not clear what the connection was between (21) and DFT; moreover, it was not obvious what the meaning of the expansion coefficients was. Our present systematic development showed how this system of equations can be related to DFT and how the parameters in these equations should be determined.

Acknowledgment. We are grateful to Dr. L. Bartolotti for providing us with the program that performs calculations of atomic densities and for his help in making the program work. We thank Prof. R. G. Parr for very useful conversations. Partial support of the Office of Naval Research is acknowledged.

References and Notes

(1) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *B136*, 864.

(2) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *A140*, 1133.

(3) Kohn, W.; Becke, A. D.; Parr, R. G. *J. Phys. Chem.* **1996**, *100*, 12974.

(4) (a) Parr, R. G.; Yang, W. *Density functional theory of atoms and molecules*; Oxford University Press: New York, 1989. (b) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *69*, 4431.

(5) Iczkowski, R. P.; Margrave, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 3547.

(6) Sanderson, R. T. *Science* **1951**, *114*, 670.

(7) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734.

(8) Berkowitz, M.; Parr, R. G. *J. Chem. Phys.* **1988**, *88*, 2554.

(9) Yang, W.; York, D. M. *J. Chem. Phys.* **1996**, *104*, 159.

(10) Rappe, A. K.; Goddard, W. A. *J. Phys. Chem.* **1991**, *95*, 3358.

(11) Rick, S. W.; Stuart, S. J.; Berne, B. J. *J. Chem. Phys.* **1994**, *101*, 6141.

(12) Mortier, W. J.; Ghosh, S. K.; Shankar, S. *J. Am. Chem. Soc.* **1986**, *108*, 4315.

(13) Nalewajski, R. *J. Phys. Chem.* **1985**, *89*, 2831.