A Generalized Formulation of Electronegativity Equalization from Density-Functional Theory

DARRIN M. YORK

Department of Chemistry, Duke University, Durham, North Carolina, 27708-0354
North Carolina Supercomputing Center MCNC, Research Triangle Park,
North Carolina, 27709-12889

ABSTRACT

A generalized formulation of the electronegativity equalization principle is presented from the perspective of density-functional theory. The resulting equations provide a linear-response framework for describing the redistribution of electrons upon perturbation by an external density or applied field. The equations can be solved using a finite set of basis functions to model the density response. Applications demonstrate the method accurately reproduces dipole moments and chemical potentials obtained from density-functional calculations. The method provides high accuracy in the presence of relatively strong perturbations such as those arising from interactions with other molecules or applied fields, and is "exact" in the limit that these interactions vanish. The method has the advantage that accuracy can be systematically improved by inclusion of more complete basis functions. The present formulation provides the foundation for a promising semiempirical model for polarization and charge transfer in molecular simulations.
© 1995 John Wiley & Sons, Inc.

Introduction

The interaction of atoms and molecules is central to chemistry. Of fundamental importance to understanding and predicting molecular interactions is a reliable description of the electron density. In particular, it is useful to know how the electron density responds to changes in molecular geometry and environment. Density-functional theory (DFT) [1-4] provides a particularly appealing framework for attacking this problem since it treats directly the electron density as the basic variable.

Unfortunately, the computational requirement inherent in conventional ab initio density-functional methods precludes application to very large molecular systems [5], especially when coupled with extensive sampling of configuration or

phase space. Consequently, for these systems, approximate methods that are less computationally demanding are required.

One class of methods that address this difficulty is based on the principle of electronegativity equalization (EE) [6]. Density-functional theory provides a rigorous mathematical definition for many intuitive chemical concepts such as electronegativity [7] and chemical hardness [8, 9], and is the foundation of the EE principle. Parr et al. [10] have identified the electronegativity as the negative of the chemical potential. Analogous to macroscopic thermodynamics, the chemical potential of an equilibrium ground-state electronic system is everywhere equal (a constant) [11]. The idea behind the EE methods, as the name suggests, is that when atoms or molecules interact, the electronegativity (chemical potential) must equalize. From the viewpoint of density-functional theory, this follows directly from the variational condition for the ground-state electron density [1].

Electronegativity equalization was first proposed by Sanderson [6] as a scheme for predicting atomic charges in molecules based on the electronegativity differences of the atoms before and after equalization (molecule formation). However, charges predicted from this method do not distinguish between atoms of the same type. Later, Gasteiger and Marsili [12] introduced an iterative method for determining atomic charges based on partial equalization of orbital electronegativities [13]. A major advance was realized with the development of a rigorous mathematical formalism for electronegativity equalization based on density-functional theory by Nalewajski [14] and Mortier et al. [15]. Methods derived from this formulation predicted atomic charges and other properties that were geometry and connectivity dependent (for a review of these early methods, see refs. [16] and [17]). Following these developments, several variations of the EE method have been proposed [15–29, 45]. For the most part, these methods have been used to determine atomic charges [15–23], model chemical binding [24–26], and analyze charge transfer in chemical bond formation [27–29]. Recently, electronegativity equalization has been used to probe reactivities using charge sensitivity analysis [30–32], and provide a method for determining dynamic charges for molecular simulations [18, 33]. In general, these methods rely on empirical parametrizations of individual atoms, and hence, have the advantage that they can be applied to any

molecule. However, for highly reliable representations of the electron density, as is required for molecular simulations, no single set of atomic parameters appears to be universal in providing sufficient accuracy for a diverse set of molecules.

In this work, we describe a new general formulation of the classic electronegativity equalization principle that can be applied to molecular simulations. The method provides a model of the electron density that gives high accuracy in the presence of relatively large perturbations such as those arising from interactions with other molecules or applied fields, and is "exact" in the limit that these interactions vanish. The method has the additional advantage that it can be systematically improved. The second section gives a general derivation of the electronegativity equalization equations. The third section outlines how the equations can be solved using basis functions for the density response. The fourth section gives formulas for several useful chemical properties derivable from the density. The fifth section applies the method to molecules in the presence of perturbing fields. Finally, the sixth section discusses the advantages and disadvantages of the present method, and its relation with others proposed in the literature. The derivation and implementation of the EE formalism presented here was developed in collaboration with W. Yang.

Derivation of Electronegativity Equalization Equations

Consider a ground-state molecular system characterized by electron density $\rho_o(r)$. From the first Hohenberg–Kohn theorem [1], we know that ρ_o determines all ground-state properties of the system, in particular ρ_o determines (to within a trivial additive constant) the external potential v_o, and total energy E_o. Within the Kohn–Sham [2] (KS) formulation of density-functional theory, the total energy is written:

$$E[\rho] = T_S[\rho] + J[\rho] + E_{XC}[\rho]$$

$$+ \int \rho(r)v_o(r)\, d^3r + V_{NN}$$

$$= F[\rho] + \int \rho(r)v_o(r)\, d^3r + V_{NN} \quad (1)$$

where $T_S[\rho]$ is the Kohn–Sham noninteracting kinetic energy, $J[\rho]$ is the classical electrostatic energy of the electrons, $E_{XC}[\rho]$ is the exchange-correlation energy, and V_{NN} is the nuclear–nuclear repulsion energy. The functional $F[\rho]$ is a universal functional that depends only on the electron density. The second Hohenberg–Kohn theorem establishes a variational principle for the ground-state energy in terms of the electron density,

$$E[\bar{\rho}] \geq E[\rho_o] \equiv E_o \qquad (2)$$

for any N-representable trial density $\bar{\rho}$. Hence, the ground-state electron density satisfies the stationary condition

$$\delta\{E[\rho] - \mu N[\rho]\} = 0 \qquad (3)$$

where the chemical potential μ is the Lagrange multiplier on the normalization constraint $N[\rho] = \int \rho(\mathbf{r}) d^3r$. The Euler–Lagrange equation for the ground-state energy and density is thus

$$\left[\frac{\delta E}{\delta\rho(\mathbf{r})}\right]_{\rho_o} = \left[\frac{\delta F}{\delta\rho(\mathbf{r})}\right]_{\rho_o} + \nu_o(\mathbf{r}) = \mu_o = \text{constant} \qquad (4)$$

Consider now the effect of a perturbation $\delta\nu(\mathbf{r})$ on the ground-state system. The expression for the perturbed energy to second-order is

$$E[\rho_o + \delta\rho, \nu_o + \delta\nu]$$

$$= E_o + \int \left[\frac{\delta E}{\delta\rho(\mathbf{r})}\right]_{\rho_o} \delta\rho(\mathbf{r}) d^3r$$

$$+ \int \rho_o(\mathbf{r})\delta\nu(\mathbf{r}) d^3r$$

$$+ \frac{1}{2} \int \int \delta\rho(\mathbf{r})\left[\frac{\delta^2 F}{\delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}')}\right]_{\rho_o}$$

$$\times \delta\rho(\mathbf{r}') d^3r d^3r' + \int \delta\rho(\mathbf{r}) \delta\nu(\mathbf{r}) d^3r \qquad (5)$$

Note that in the ground-state, the variations $\delta\nu(\mathbf{r})$ and $\delta\rho(\mathbf{r})$ are not independent, but are related through the Euler–Lagrange equation (eq. (4)). The first functional derivative term in eq. (5) is the chemical potential μ_o of the unperturbed system

eq. (4). Thus eq. (5) simplifies to

$$E[\rho_o + \delta\rho, \nu_o + \delta\nu]$$

$$= E_o + \mu_o \int \delta\rho(\mathbf{r})d^3r$$

$$+ \int [\rho_o(\mathbf{r}) + \delta\rho(\mathbf{r})]\delta\nu(\mathbf{r}) d^3r$$

$$+ \frac{1}{2} \int \int \delta\rho(\mathbf{r})\left[\frac{\delta^2 F}{\delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}')}\right]_{\rho_o}$$

$$\times \delta\rho(\mathbf{r}') d^3r d^3r' \qquad (6)$$

The new Euler–Lagrange equation for the perturbed system is given by

$$\int \left[\frac{\delta^2 F}{\delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}')}\right]_{\rho_o} \delta\rho(r')d^3\mathbf{r}' + \delta\nu(\mathbf{r})$$

$$= \mu - \mu_o = \Delta\mu \qquad (7)$$

Equation (7) is the fundamental equation from which the present formulation of electronegativity equalization is based.

Solution of the EE Equations in a Finite Basis

In this section, we show how the EE equations can be solved using basis functions for the density response $\delta\rho(\mathbf{r})$. We further suggest a semi-empirical approximation for the second functional derivative term in eq. (7) that is shown later to give a simple but useful model for polarization and charge transfer.

If we represent variations of the density $\delta\rho(\mathbf{r})$ as a linear combination of L^2 normalized basis functions $\{\varphi_i\}$ such that $\langle \varphi_i \mid \varphi_i \rangle = 1$,

$$\delta\rho(\mathbf{r}) = \sum_i c_i\varphi_i(\mathbf{r}) \qquad (8)$$

where $\{c_i\}$ are coefficients to be determined from matrix analog of the stationary condition eq. (3)

$$\frac{\partial}{\partial c_i}\{E[\underline{c}] - \mu N[\underline{c}]\} = 0 \qquad (9)$$

where $E[\underline{c}]$ and $N[\underline{c}]$ are given in matrix form by

$$E[\underline{c}] = E_o + \langle \rho_o \mid \delta\nu \rangle + \mu_o \underline{c}^T \cdot \underline{d}$$
$$+ \underline{c}^T \cdot \delta\nu + \tfrac{1}{2}\underline{c}^T \cdot \underline{\underline{\eta}} \cdot \underline{c} + V_{NN} \quad (10a)$$

$$N[\underline{c}] = N_o + \underline{c}^T \cdot \underline{d} \quad (10b)$$

where N_o is the number of electrons in the unperturbed system, and the matrix and vector elements are defined by

$$(\underline{d})_i = \int \varphi_i(\mathbf{r})\, d^3r \quad (11a)$$

$$(\underline{\delta\nu})_i = \langle \varphi_i \mid \delta\nu \rangle \quad (11b)$$

$$(\underline{\underline{\eta}})_{ij} = \left\langle \varphi_i \middle| \left[\frac{\delta^2 F}{\delta\rho\,\delta\rho}\right] \middle| \varphi_j \right\rangle \quad (11c)$$

The matrix $\underline{\underline{\eta}}$ is called the hardness matrix. Application of eq. (9) using eqs. (10) and (11) results in the linear equation

$$\underline{\underline{\eta}} \cdot \underline{c} + \underline{\delta\nu} - \Delta\mu\underline{d} = 0 \quad (12)$$

which, assuming $\underline{\underline{\eta}}$ is nonsingular, has solution

$$\underline{c} = \underline{\underline{\eta}}^{-1} \cdot \{\Delta\mu\underline{d} - \underline{\delta\nu}\} \quad (13)$$

The Lagrange multiplier $\Delta\mu$ is chosen to satisfy the normalization condition $\underline{c}^T \cdot \underline{d} = N - N_o \equiv \Delta N$:

$$\Delta\mu = \frac{\Delta N + \underline{d}^T \cdot \underline{\underline{\eta}}^{-1} \cdot \underline{\delta\nu}}{\underline{d}^T \cdot \underline{\underline{\eta}}^{-1} \cdot \underline{d}} \quad (14)$$

where ΔN is the amount of charge transfer that is allowed. Thus far, we have not explicitly specified the form of the matrix elements $(\eta)_{ij}$. In fact, the form of the two-electron operator

$$\left[\frac{\delta^2 F}{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')}\right] = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \left[\frac{\delta^2 T_S}{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')}\right]$$
$$+ \left[\frac{\delta^2 E_{XC}}{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')}\right] \quad (15)$$

is not known because the kinetic energy and exchange correlation functionals are not known in terms of the density. We are thus inspired to introduce the following extended Hückel-type approximation [35]:

$$(\underline{\underline{\eta}})_{ij} = f_i + \left\langle \varphi_i \middle| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \middle| \varphi_i \right\rangle \quad (16a)$$

$$(\underline{\underline{\eta}})_{ij} = \tfrac{1}{2}\kappa(f_i + f_j)\langle \varphi_i \mid \varphi_j \rangle$$
$$+ \left\langle \varphi_i \middle| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \middle| \varphi_j \right\rangle \text{ for } i \neq j \quad (16b)$$

where the $\{f_i\}$ are empirical parameters, and κ is taken to be unity.

The EE equations (12–16) were derived for any set of normalized basis functions of the form eq. (8), and can be solved to give the density response $\delta\rho(\mathbf{r})$. With the use of density basis functions, there is no built-in constraint that the electron density after equalization be everywhere strictly positive; however, we anticipate that with appropriate parameterization of eqs. (16) this will not be a limitation to obtaining reliable linear-response information for real physical systems. We next outline how other chemical properties can be obtained from this procedure.

Chemical Properties Derivable from the Density

Several useful derivatives can be computed directly from the electronegativity equalization method presented above. Perhaps the simplest is the chemical potential μ, defined from density-functional theory to be the functional derivative of the energy with respect to the electron density (at constant external field ν), or alternatively, the derivative of the energy with respect to the total number of electrons [4]

$$\mu = \left[\frac{\delta E}{\delta\rho(\mathbf{r})}\right]_\nu = \left(\frac{\partial E}{\partial N}\right)_\nu \quad (17)$$

In the EE framework, the chemical potential follows directly from eq. (14). The chemical potential of an atom or molecule has been shown to correspond to minus the electronegativity [10]. Another intuitive chemical property is the hardness η, defined as the second derivative of the energy with respect to the total number of electrons [8], and can be evaluated in the present method from the matrix equation

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_\nu = \left(\underline{d}^T \cdot \underline{\underline{\eta}}^{-1} \cdot \underline{d}\right)^{-1} \quad (18)$$

The Fukui function $f(r)$ is an index of reactivity that measures the response of the chemical potential to a variation in the external field [36]. The Fukui function is computed in the present formalism in the basis of the density response as

$$f(r) = \left[\frac{\delta \mu}{\delta \nu(r)} \right]_N = \left[\frac{\partial \rho(r)}{\partial N} \right]_\nu = \underline{f}^T \cdot \underline{\varphi}(r) \quad (19)$$

where

$$\underline{f} = \left[\frac{\partial \underline{c}}{\partial N} \right]_\nu = \left(\underline{d}^T \cdot \underline{\underline{\eta}}^{-1} \cdot \underline{d} \right)^{-1} \underline{\underline{\eta}}^{-1} \cdot \underline{d} \quad (20)$$

and $\varphi(r)$ is the vector of basis functions $\varphi_i(r)$. Note the Fukui function by this definition is normalized:

$$\int f(r) \, d^3r = 1 \quad (21)$$

Similarly, the two-variable linear response function [4] is defined as

$$\left[\frac{\delta \rho(r)}{\delta \nu(r')} \right]_N = \left[\frac{\delta^2 E}{\delta \nu(r) \, \delta \nu(r')} \right]_N = \left[\frac{\delta \rho(r')}{\delta \nu(r)} \right]_N$$

$$= \sum_{i,j} \langle r \mid \varphi_i \rangle \langle \varphi_i \mid \left[\frac{\delta \rho}{\delta \nu} \right]_N \mid \varphi_j \rangle \langle \varphi_j \mid r' \rangle$$

$$= \underline{\varphi}^T(r) \cdot \underline{\underline{P}} \cdot \underline{\varphi}(r') \quad (22)$$

and

$$\underline{\underline{P}} = \left[\frac{\underline{\underline{\eta}}^{-1} \cdot \underline{d} \otimes \underline{d}^T \cdot \underline{\underline{\eta}}^{-1}}{\underline{d}^T \cdot \underline{\underline{\eta}}^{-1} \cdot \underline{d}} - \underline{\underline{\eta}}^{-1} \right] \quad (23)$$

where the $\otimes$ indicates the direct product. Note the linear response function satisfies the condition

$$\int \left[\frac{\delta \rho(r)}{\delta \nu(r')} \right]_N d^3r' = 0 \quad (24)$$

A closely related quantity to the linear response function is the static polarizability tensor $\vec{\alpha}$, defined as minus the second derivative of the total energy with respect to components of the electric field [37] $\vec{E} = (e_X, e_Y, e_Z)$

$$(\vec{\alpha})_{\xi\xi'} = -\left(\frac{\partial^2 E}{\partial e_\xi \, \partial e_{\xi'}} \right) \quad (25)$$

In the limit of small uniform electric fields, the interaction of the response density with the field

can be written as the scalar product:

$$-\vec{\mu}_{\text{ind}} \cdot \vec{E} = \left(\int \vec{r} \, \delta\rho(r) \, d^3r \right) \cdot \vec{E} = \underline{c}^T \cdot \underline{R} \cdot \vec{E} \quad (26)$$

where $\vec{\mu}_{\text{ind}}$ is the induced dipole moment, $\vec{r}$ is the position vector $\vec{r} = (x, y, z)$, and $\underline{R}$ is defined by

$$\left(\underline{R} \right)_i = \int \vec{r} \varphi_i(r) \, d^3r \quad (27)$$

It follows directly from eq. (22) that the static polarizability tensor in the EE model is simply

$$\vec{\alpha} = -\underline{R}^T \cdot \underline{\underline{P}} \cdot \underline{R} \quad (28)$$

In this section, it has been shown how the present EE formalism provides a model for the linear density response, and several fundamental properties of the density. In the following section, the reliability of the model is tested.

Numerical Application

In this section we apply the present EE formalism to model the linear density response for a series of molecules in the presence of perturbing external fields, designed to reflect interactions in polar solvents. By expanding the energy about the ground-state density, the model begins with an "exact" representation of the system in the absence of an applied field. The EE parameters for each molecule are chosen to optimize the linear response of perturbations. Results of EE induced dipole moments, polarizabilities, and chemical potentials are compared with corresponding experimental and density-functional derived values.

COMPUTATIONAL PROCEDURE

Density-functional calculations were performed using the Kohn–Sham formulation of density-functional theory [2] implemented in a numerical self-consistent field (SCF) algorithm [38]. Electron correlation was treated using the Vosko–Wilk–Nusair local density approximation (LDA) [39]. Atomic orbital basis functions were generated as numerical LDA solutions of the KS equations for the isolated atoms similar to that of Delley [40]. A basis set of 3s, and 2p (polarization) functions were used for hydrogen atoms, and 4s, 4p, and 2d (polarization) functions for second and third row

atoms. The numerical integration mesh was chosen such that the error in evaluation of the matrix elements was (approximately) less than 10^{-6} Hartree. The convergence criterion for the SCF procedure was 10^{-6} Hartree for the total energy and 10^{-4} Hartree for the classical electrostatic component of the energy. The latter was necessary to achieve convergence of induced dipole moments.

Electronegativity equalization parameters were calculated for molecules by fitting to the LDA induced moments. Dipole moments were induced by introducing a perturbing field at several points outside the molecular surface as follows. A "solvent-accessible surface" was defined as the surface generated by the van der Waals radii of the atoms plus a probe radius of 2.65 a_0 (approximately the radius of a water molecule). Points roughly evenly spaced on the surface were chosen at a density of 0.05 a_0^{-2}. At each surface point R_k a Gaussian probe density was added of the form

$$\rho_{\text{probe}}(r) = \pm Q \cdot \left(\frac{\zeta}{\pi} \right)^{3/2} e^{-\zeta |r - R_k|^2} \qquad (29)$$

where the exponent ζ was 1.0 a_0^{-2}, and the net charge Q was 0.5e. The sign $\pm$ was chosen such that the probe interaction with the molecule was electrostatically favorable. At each surface point, the static potential of the probe was used as an applied field, and the corresponding molecular density was computed from SCF solution of the KS equations. Hence, induced dipole moments and related properties were obtained separately for each applied field.

Basis functions for representation of the EE density response eq. (8) were chosen as normalized atom-centered ns Slater-type functions. The Slater exponents were obtained by optimizing the fit of the quantum mechanically computed induced dipole moments to the corresponding values obtained from the EE procedure without additional parameters [i.e., the $\{f_i\}$ parameters in eqs. (16) set to zero].

For a given basis, each molecule requires 1 parameter $\{f_i\}$ per basis function. The $\{f_i\}$ parameters were determined by least-squares fitting of the LDA and EE induced dipole moments as described in the previous paragraph for the Slater exponents. In all fitting procedures, EE parameters and Slater exponents of topologically equivalent atoms were constrained to be identical (i.e., for methanol, one of the three methyl hydrogens is not

symmetry equivalent, but is topologically equivalent). Evaluation of the total energy in eq. (10(a)), in the case where charge transfer is allowed ($\Delta N = \int \delta \rho(r) \, d^3 r \neq 0$), requires one additional parameter, the molecular chemical potential μ_o. However, if no charge transfer is considered, explicit dependence of this term vanishes, and only the Lagrange multiplier $\Delta \mu$ [eq. (14)] is required. Although we do not consider intermolecular charge transfer explicitly, we do discuss the relative EE and LDA chemical potentials for the perturbed systems. For this purpose, we estimate the LDA chemical potential as the eigenvalue of the highest occupied KS molecular orbital $\varepsilon_{\text{HOMO}}$ [4]. The estimated LDA chemical potential $\varepsilon_{\text{HOMO}}$ for each system in the absence of an applied field perturbation provides the value of μ_o.

Results and Discussion

Table I compares dipole moment, chemical potential, and polarizability results of the present EE procedure with corresponding experimental and LDA density-functional values. Corresponding EE parameters are listed in Table II. Overall, the EE dipole moments agree well with the corresponding LDA values (relative errors of ca. 4–8%). For planar molecules, however, the error in the induced dipole moment is considerably increased. This follows from the use of spherical atom-centered basis functions for the density response, which in the case of a planar molecule, disallows polarization out of the plane. This problem has been pointed out by Dinar [41], who proposed a modified procedure that coupled standard EE methods with a Drude model for atomic dipole polarizabilities. Inclusion of atomic dipolar polarizability is a straight forward extension of the formalism presented here if density basis functions with higher multipolar character are introduced. These possibilities will be explored in future work using Gaussian basis functions, so that analytic evaluation of the appropriate integrals is facilitated [34].

Polarizability is fundamental to atomic and molecular interactions in chemistry. Density-functional theory provides a particularly promising approach for obtaining polarizabilities since it accounts for the effects of electron correlation [42]. Applications using the local density theory [37] have been successful in predicting molecular po-

TABLE I

Comparison of dipole moments D, chemical potentials μ, and polarizabilities α[a].

Molecule	rms D[b]	rel. err D[c]	rms μ[d]	rel. err μ[c]	α[e]	α_{EXP}[f]
H_2O	4.8×10^{-2}	0.10	3.1×10^{-3}	1.1×10^{-2}	0.92	1.45
NH_3	3.2×10^{-2}	7.7×10^{-2}	3.3×10^{-2}	1.3×10^{-2}	2.18	2.81
PH_3	5.0×10^{-2}	0.15	2.7×10^{-3}	1.1×10^{-2}	4.54	4.84
CH_4	1.8×10^{-2}	0.16	3.7×10^{-3}	1.0×10^{-2}	2.20	2.59
CH_3OH	2.4×10^{-2}	5.5×10^{-2}	7.0×10^{-3}	3.3×10^{-2}	2.97	3.29
CH_3F	1.9×10^{-2}	4.1×10^{-2}	4.5×10^{-3}	1.5×10^{-2}	2.42	2.97
CH_3Cl	5.5×10^{-2}	0.10	1.2×10^{-2}	4.1×10^{-2}	4.16	4.72
CH_3NH_2	2.8×10^{-2}	7.2×10^{-2}	8.8×10^{-2}	4.4×10^{-2}	3.70	4.70
CH_3NO	7.3×10^{-2}	7.5×10^{-2}	4.3×10^{-3}	1.7×10^{-2}	3.17	4.08
CH_2O	5.0×10^{-2}	8.6×10^{-2}	5.7×10^{-3}	2.6×10^{-2}	1.87	2.45
CH_3CHO	3.9×10^{-2}	5.3×10^{-2}	1.0×10^{-2}	5.1×10^{-2}	4.15	4.59
CH_3CH_3	3.5×10^{-2}	0.21	1.9×10^{-3}	6.9×10^{-3}	4.31	4.43
CH_3OCH_3	5.4×10^{-2}	0.14	3.2×10^{-3}	1.6×10^{-2}	4.77	5.29
$HCOOH$	4.5×10^{-2}	0.12	2.3×10^{-3}	9.1×10^{-3}	2.31	3.40

[a] Statistical errors for each molecule were derived from data sets consisting of corresponding quantities (dipole moments or chemical potentials) obtained from the EE procedure and from SCF density-functional calculations at each external field perturbation.

[b] Root-mean-square deviations of the dipole moments D (a.u.; 1 au = 2.54 Debye) from SCF density-functional calculations and from EE.

[c] The relative error of data set $\{x\}$ with respect to reference data set $\{y\}$ was computed as $\langle(x - y)^2\rangle^{1/2} / \langle y^2 \rangle^{1/2}$.

[d] Root-mean-square deviations of the chemical potentials μ (Hartree) from SCF density-functional calculations and from EE. The chemical potentials from the DF calculations were taken as the eigenvalues of the highest occupied molecular orbitals (ε_{HOMO}).

[e] Effective polarizabilities ($\mathring{A}^3$) calculated from EE parameters fit to LDA dipole moments.

[f] Experimental polarizabilities ($\mathring{A}^3$) (ref. [44]).

larizabilities [43]. Here we focus on obtaining effective molecular polarizabilities (higher order hyperpolarizabilities included implicitly) by fitting the EE parameters to dipole moments induced in fairly large nonuniform fields, designed to reflect a highly polar solvent environment.

The effective EE polarizabilities parametrized from the LDA calculations (Table I) are fairly well correlated with experimental values. In all cases, the calculated polarizability slightly underestimates the corresponding experimental value. This is mainly attributed to the error introduced by the finite orbital basis sets used in the LDA calculations [43], which tend to underestimate the polarizability, especially for large fields (for example, in the case of NH_3, if a much larger 5442/333 basis set is used, the EE/LDA polarizability increases from 2.18 $\mathring{A}^3$ to 2.40 $\mathring{A}^3$). Further error is introduced due to the limited basis set used for the density response, as illustrated in the extreme case of planar molecules described above. Presumably, this can be corrected by inclusion of more complete basis functions with higher multipolar character. In addition, strong perturbing fields outside the molecular surface have polarization effects that

are nonlinear. The EE procedure, being intrinsically a linear response theory, must therefore implicitly account for nonlinear effects. Although the effective EE polarizabilities parametrized for the "strong fields" here underestimate the experimental polarizabilities, the close agreement between the EE and LDA induced dipole moments indicates the model is adequate.

In addition to the induced moments, it is interesting to consider the EE and LDA predicted chemical potentials. We have estimated the LDA chemical potential from the highest occupied KS eigenvalue ε_{HOMO} [4]. The EE chemical potential was calculated via eq. (14). These two quantities are remarkably well correlated (Fig. 1). The maximum relative error in the chemical potential of all the molecules considered is 5.1% (CH_3CHO). The striking agreement of the EE and estimated LDA chemical potentials, which were not considered explicitly in the EE parameterization, is intriguing. Moreover, it is suggestive that coupling of the EE procedure with density-functional methods, for example in hybrid quantum mechanical/molecular mechanical simulation force fields, may be possible.

TABLE II

Electronegativity equalization parameters.[a]

Molecule	Atom	ζ	f	Molecule	Atom	ζ	f
H_2O	O	1.825	0.0	CH_3NO	C	1.524	−0.141
	H	2.396	0.0		H_C	1.839	−0.011
NH_3	N	1.538	−4.0		O	2.391	−0.008
	H	1.938	−0.095		N	3.118	0.018
PH_3	P	1.589	0.048		H_N	2.820	0.0
	H	1.642	−0.002	CH_2O	C	1.315	−4.0
CH_4	C	1.980	−0.088		H	2.074	0.0
	H	2.042	0.0		O	2.576	0.017
CH_3OH	C	1.526	0.056	CH_3CHO	C_1	1.405	−0.593
	H_C	1.967	0.010		H_{C_1}	1.865	−0.045
	O	2.784	−0.043		C_2	8.0	4.0
	H_O	3.901	−0.050		H_{C_2}	2.990	0.024
CH_3F	C	4.002	−0.001		O	3.588	0.019
	H	2.068	0.0	CH_3CH_3	C	1.976	−0.133
	F	3.179	0.0		H	2.315	−0.040
CH_3Cl	C	1.114	−4.0	CH_3OCH_3	C	2.964	−0.187
	H	1.658	−0.007		H	2.985	−0.014
	Cl	2.997	0.155		O	1.419	0.276
CH_3NH_2	C	1.530	0.671	HCOOH	C	1.795	0.116
	H_C	1.856	0.054		H_C	2.699	0.023
	N	2.477	−0.320		O_1	2.345	0.010
	H_N	3.433	−0.103		O_2	3.355	−0.074
					H_O	2.668	−0.033

[a] Electronegativity equalization parameters: Slater exponents ζ for ns Slater-type density basis functions, and f parameters of eq. (16). All units are atomic units.

Relation to Other EE Models

Two related methods based on electronegativity equalization have been proposed by Mortier et al. [15], and later by Rappé and Goddard [18]. The former has been employed mainly as a method for estimating atomic charges in molecules based on parameterization to STO-3G Mulliken charges [15, 16], and more recently for probing reactivity using sensitivity coefficients from density-functional theory [31, 32]. The latter method [18] has been developed to provide a dynamic charge for molecular simulations. Both methods are based on the approximation of the molecular energy as a second-order Taylor expansion about the neutral atoms. The molecular charge distribution and energy are obtained as solutions to the EE equations of the neutral atoms assembled to form a molecule. The methods require two parameters per atom: an effective electronegativity (negative of the chemical potential), and hardness (in the latter method, the hardness appears as the atomic electrostatic self-energy). These atomic parameters are assumed

to be transferable for all molecules. Mortier et al. [17] have demonstrated that this approximation is remarkably robust, and gives useful qualitative, and sometimes even quantitative insight to a variety of chemical problems. Nonetheless, the representation of the molecular energy and charge distribution as an expansion about the neutral atoms is considerably limited in its ability to give high accuracy. Consequently, a new method that provides high accuracy and can be systematically improved is required for reliable molecular simulations.

The present EE formulation accommodates these difficulties. Since the total molecular energy is expanded about the ground-state molecular density, the exact energy and charge distribution are recovered in the absence of an applied field. For a system of interacting molecules, the present method provides a model for the linear density response of each molecule in the field of the other molecules, with the possibility of charge transfer. As demonstrated in the previous section, this method reproduces well the density response, even with a very simple spherical atom-centered basis.
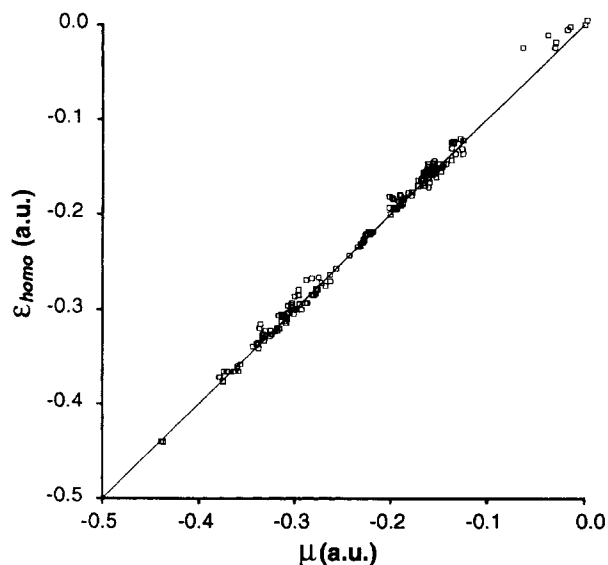
FIGURE 1. Linear regression of the chemical potential obtained from EE procedure (μ) and estimated from the eigenvalue of the KS-LDA highest occupied molecular orbital (ε_{HOMO}). Data shown is for all molecules listed in Table I for each applied field perturbation. Note: the EE parameters were fit to induced dipoles moments only; hence, the observed correlation of the chemical potentials is not a result of explicit fitting.

More importantly, systematic improvement of the methodology is straightforward by inclusion of more complete density basis functions, not necessarily atom-centered or spherical. Exploration of such possibilities are currently underway [34].

The methods proposed by Mortier et al. [15], and Rappé and Goddard [18] are in fact particular cases of the general formalism developed here. To illustrate this, consider the integral Taylor expansion eq. (5) to be chosen about the neutral-atom ground-state densities. If the density basis functions are chosen to be delta functions at the atomic positions (neglecting the infinite electrostatic self-energy term in the diagonal elements of the hardness matrix), the present model reduces to that proposed by Mortier [15]. In this case, the empirical parameters are the effective atomic chemical potentials and hardnesses. Alternately, if atom-centered ns Slater-type functions are used as basis functions, and the empirical parameters $\{f_i\}$ of eq. (16) are set to zero, the present model reduces to that proposed by Rappé and Goddard [18]. The latter method parameterizes the diagonal elements of the hardness matrix by adjusting the Slater exponents of the density basis functions. The cor-

responding electrostatic self-energies play the same role as the atomic hardness parameters of Mortier [15]. Note both of these methods treat the off-diagonal elements of the hardness matrix as being purely Coulombic in nature.

The present electronegativity equalization method provides a particularly convenient framework for modeling polarization in molecular simulations. Electrostatic fields in molecular simulations are typically modeled by static charge distributions obtained from fitting to gas-phase electrostatic potentials. For such models that do not attempt to take into account polarization implicitly, the present method is ideal. This derives from the fact that the static charge distribution is chosen to directly reflect the zero order term in the Taylor expansion eq. (5) corresponding to the ground-state electron density in the absence of a perturbing field. Hence, parameters for the density response are uncorrelated with parameters used to represent the static charge distribution. In this way, improvement of force field models by inclusion of additional polarization terms does not require reparameterization of existing static terms.

It should be pointed out that the present model has been introduced specifically as an empirical model for polarization and charge transfer, derived from the physics of density-functional theory. The use of basis functions for the linear density response illustrates that one should be careful in interpreting the parameters of this model as having any well defined "atomic" character, since there has been no effort here to rigorously define an atom in a molecule. If such an interpretation is sought, for example, in the analysis of wavefunctions from electronic structure calculations, one must adopt a rigorous definition of an atom in a molecule, and employ appropriate constraints. Such work has been explored extensively by Cioslowski [27–29].

Conclusion

A general formulation of the electronegativity equalization principle has been presented, and cast in a form that can be solved using basis functions for the linear density response. A simple semi-empirical representation of the hardness matrix is suggested that requires only one parameter per basis function. Numerical application using a basis set of atom-centered ns Slater-type functions

demonstrates that the method reproduces well induced dipole moments and chemical potentials derived from LDA density-functional calculations. The method has the advantages that it recovers the "exact" ground-state density in the absence of an applied field, provides high accuracy in the presence of relatively strong perturbations, and can be systematically improved by inclusion of more complete basis functions for the density response. The present formulation generalizes many of the EE methods that have been proposed in the literature, and forms the foundation for future work to model polarization and charge transfer effects in molecular simulations.

ACKNOWLEDGMENT

References

1. P. Hohenberg and W. Kohn, Phys. Rev. B, 186, 864 (1964).

2. W. Kohn and L. Sham, Phys. Rev. A, 140, 1133 (1965).

3. M. Levy and J. Perdew, in Density-Functional Methods in Physics, R. H. Dreizler and J. da Providencia, Eds., Plenum Press, New York, 1985.

4. R. G. Parr and W. Yang, Density-Functional Theory of Atoms and Molecules, Oxford University Press, 1989.

5. T. Ziegler, Chemical Reviews, 91, 651 (1991).

6. R. T. Sanderson, Chemical Bonds and Bond Energy, Academic Press, New York, 1976.

7. R. P. Iczkowski and J. L. Margrave, J. Am. Chem. Soc., 83, 3547 (1961).

8. R. G. Parr and R. G. Pearson, J. Am. Chem. Soc., 105, 7512 (1983).

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

10. R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, J. Chem. Phys., 68, 3801 (1978).

11. P. Politzer and H. Weinstein, J. Chem. Phys., 71, 4218 (1979).

12. J. Gasteiger and M. Marsili, Tetrahedron, 36, 3219 (1980).

13. J. Hinze and H. H. Jaffé, J. Am. Chem. Soc., 84, 540 (1962).

14. R. F. Nalewajski, J. Am. Chem. Soc., 106, 944 (1984).

15. W. J. Mortier, S. K. Ghosh, and S. Shankar, J. Am. Chem. Soc., 108, 4315 (1986).

16. W. J. Mortier, K. V. Genechten, and J. Gasteiger, J. Am. Chem. Soc., 107, 829 (1985).

17. W. J. Mortier, Structure and Bonding: Electronegativity, 66, 125 (1987).

18. A. K. Rappé and W. A. Goddard, J. Phys. Chem., 95, 3358 (1991).

19. L. V. Szentpály, J. Mol. Struct. (THEOCHEM), 233, 71 (1991).

20. Z.-Z. Yang, E.-Z. Shen, and L.-H. Wang, J. Mol. Struct. (THEOCHEM), 312, 167 (1994).

21. K. T. No, J. A. Grant, and H. A. Scheraga, J. Phys. Chem., 94, 4732 (1990).

22. K. T. No, J. A. Grant, M. S. Shik, and H. A. Scheraga, J. Phys. Chem., 94, 4740 (1990).

23. J. M. Park, K. T. No, M. S. Jhon, and H. A. Scheraga, J. Comp. Chem., 14, 1482 (1993).

24. S. K. Ghosh and R. G. Parr, Theor. Chim. Acta, 72, 379 (1987); T. K. Ghanty and S. K. Ghosh, J. Phys. Chem., 95, 6512 (1991).

25. T. K. Ghanty and S. K. Ghosh, J. Phys. Chem., 98, 1840 (1994).

26. T. K. Ghanty and S. K. Ghosh, J. Am. Chem. Soc., 116, 3943 (1994).

27. J. Cioslowski and B. B. Stefanov, J. Chem. Phys., 99, 5151 (1993).

28. J. Cioslowski and S. T. Mixon, J. Am. Chem. Soc., 115, 1084 (1993).

29. J. Cioslowski and M. Martinov, J. Chem. Phys., 101, 366 (1994).

30. R. F. Nalewajski, Int. J. Quant. Chem., 40, 265 (1991).

31. B. G. Baekelandt, W. J. Mortier, and R. A. Schoonheydt, Structure and Bonding, 80, 187 (1993).

32. B. G. Baekelandt, W. J. Mortier, J. L. Lievens, and R. A. Schoonheydt, J. Am. Chem. Soc., 113, 6730 (1991).

33. S. W. Rick, S. J. Stuart, and B. J. Berne, J. Chem. Phys., 101, 6141 (1994).

34. D. York and W. Yang, in preparation.

35. R. Hoffman, J. Chem. Phys., 39, 1397 (1963).

36. R. G. Parr and W. Yang, J. Am. Chem. Soc., 106, 4049 (1984).

37. G. D. Mahan and K. R. Subbaswamy, Local Density Theory of Polarizability, Plenum Press, New York, 1990.

38. W. Yang, J. Chem. Phys., 94, 1208 (1991).

39. S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys., 58, 1200 (1980).

40. B. Delley, J. Chem. Phys., 92, 508 (1990).

41. U. Dinar, J. Phys. Chem., 97, 7984 (1993).

42. P. G. Jasien and G. Fitzgerald, J. Chem. Phys., 93, 2554 (1990).

43. D. P. Chong, J. Chin. Chem. Soc., 39, 375 (1992).

44. CRC Handbook of Chemistry and Physics, 74th Ed., CRC Press, Boca Raton, 1993.

45. W. Yang and W. Mortier, J. Am. Chem. Soc., 108, 5708 (1986).