Molecular and Atomic Dipole Moments in Heteronuclear and Homonuclear Diatomics. Density Functional Approach

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In our previous work (Itskowitz, P.; Berkowitz, M. L. *J. Phys. Chem. A* **1997**, *101*, 5687), we showed how in the framework of density functional theory the energy of a molecule can be expressed as a functional of the perturbations on atomic densities. In this work we develop an approximation for these perturbations that assigns two charge distributions to each atom. With the help of this approximation, we obtain the values of the net charges for a number of heteronuclear diatomic molecules with the average error of only 5.4% compared to the experimental data. Our approach also allows us to treat homonuclear diatomics in the same way as heteronuclear. In the limit of a point dipole approximation to the charge distribution on an atom in homonuclear diatomics we obtain results which are in a reasonable agreement with the results from *ab initio* calculations.

I. Introduction

Molecular dynamics and Monte Carlo computer simulations are tools that are used routinely to study the behavior of molecules in clusters, simple fluids, complex fluids, and molecular assemblies.[1] Today, one can perform molecular dynamics simulations by solving the quantum problem for every step of the simulation, although it is computationally very expensive to do this.[2] In fact, it is practically impossible to do this for large systems such as an assembly of biomolecules. In this case one has to resort to the traditional classical molecular dynamics method, where motion of the particles is described by Newton's equations. To move the particles under the influence of the forces one needs to describe these forces (i.e., to have a force field present in the simulations). A very important part of the force field is the electrostatic part, and a lot of work is devoted to its interpretation, representation, and development.[3] In its simplest form, the electrostatic force field is represented as the Coulomb interaction of some net charge monopoles, usually located at the positions of the atomic nuclei. The net charges are configuration independent and as the result in this model the electrostatic energy is pairwise additive. This kind of modeling can be very successful. For example, an SPC/E model of water, where the electrostatic energy is described in a pairwise fashion, is able to reproduce many bulk properties of water.[4] Moreover, the model can reproduce some of the interface properties of water, such as the temperature dependence of the surface tension.[5] But, as was shown recently, simulations done on a water cluster with a simple anion such as Cl^- produced different results when popular pairwise additive potentials were used compared to simulations with nonadditive potentials.[6−8] Comparison with experiments indicated that nonadditive potentials produce a description which is closer to the correct description of the phenomena.[7,8]

The need to use nonadditive electrostatic potentials in simulations including simulations with biomolecules was often expressed in the literature.[9] One can introduce the many-body effects into electrostatic part of the potential by introducing polarizable models or by introducing fluctuating charge models. A fluctuating charge model was recently used by Rick *et al.*[10] to study bulk water and by Stuart and Berne[7] to study Cl^- solvation in water clusters. It was shown that the fluctuation charge model only slightly increases the computational cost compared to simulations with pairwise potentials. The fluctuation charge model is based on the electronegativity equalization principle (eep), which states that the electronegativity of every atom in the molecule is the same.[11] One can consider eep to be an empirical scheme. To apply this scheme one starts with an expression for the energy of a molecule in terms of Taylor series expansion in powers of net charges on atoms:

$$E = E(0) + \sum_i \chi_i q_i + {}^1/_2 \sum_{i,j} \eta_{ij} q_i q_j + ... \qquad (1)$$

To simplify the equations for electronegativities, one stops on the quadratic term of the expansion. In eq 1 χ_i is the electronegativity of atom i, defined as

$$\chi_i = \frac{\partial E}{\partial q_i}\Big|_{q=0} \qquad (2)$$

and η_{ij} is the hardness matrix ij element, defined as

$$\eta_{ij} = \frac{\partial^2 E}{\partial q_i \partial q_j}\Big|_{q=0} \qquad (3)$$

The values of atomic electronegativities and hardness matrix elements may be considered as free parameters to be determined from the experimental information. This was done by Rick et al. in their simulations of water.[10] The eep together with the charge conservation requirement results in a set of linear equations for charges that can be solved on every step of molecular dynamics, thus providing us with fluctuating charges with values depending on environment.

The rigorous justification of the eep principle follows from the density functional theory (DFT) of atoms and molecules.[12] One can also derive eq 1, starting from basic postulates of the

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DFT. This approach was taken by Mortier *et al.*,[13] Winkler and Pantelidis,[14] and by us.[15] The derivation of eq 1 that we reported previously illustrated that the coefficients in Taylor expansion are not the electronegativities and hardnesses of isolated atoms as sometimes is indicated. We showed that values of atomic electronegativities in a molecule depend on the atom partners and therefore are not fixed once and forever. This point was also previously mentioned in the work of Cioslowski and Mixon.[16] In our recent work we obtained the expression for the molecular energy as a functional of perturbations on atomic densities. This expression contained only atomic parameters which in principle can be calculated from the atomic DFT problem. A generalized chemical potential (electronegativity) equalization principle was proposed. The use of density perturbations in the form of spherically symmetric fixed charge distributions led to a quadratic model with respect to net charges on the atoms. Calculations with all the parameters evaluated from the first principles yielded a reasonable agreement with the experiment. It was also suggested that the use of a physically more accurate approximation to the perturbations on atomic densities could lead to better results.

Below we will show how one can significantly improve the description of molecules compared to our previous model while still remaining in the framework of simple quadratic expression for the energy with respect to atomic charges. We will develop a new approximation which can be viewed as the next step in the "multipole" expansion for the perturbations on atomic densities. We will show that the application of this approximation to atoms in diatomic molecule can provide very good results for charge transfer and can be used to explain the bonding in homonuclear molecules.

II. Approximation

As we showed earlier,[15] the energy of a molecule can be expressed as a functional of the perturbations on the atomic densities:

$$\begin{aligned} E[\rho(\vec r)] = E[\rho_1'(\vec r),\rho_2'(\vec r),...] = V_{nn} + \sum_a E_a[\rho_a(\vec r)] + \\ \sum_a\sum_{b\neq a}\int v_a(\vec r)\rho_b(\vec r)\mathrm{d}r + \\ {}^1\!/_2\sum_a\sum_{b\neq a}\int\int\frac{\rho_a(\vec r_1)\rho_b(\vec r_2)}{r_{12}}\mathrm{d}\vec r_1\,\mathrm{d}\vec r_2 + \sum_a\mu_a\int\rho_a'(\vec r)\mathrm{d}\vec r + \\ \sum_a\sum_{b\neq a}\int\left[v_b(\vec r_1) + \int\frac{\rho_b(\vec r_2)}{r_{12}}\mathrm{d}\vec r_2\right]\rho_a'(\vec r_1)\mathrm{d}\vec r_1 + \\ {}^1\!/_2\sum_a\int\int\eta_a(\vec r_1,\vec r_2)\rho_a'(\vec r_1)\rho_a'(\vec r_2)\mathrm{d}\vec r_1\,\mathrm{d}\vec r_2 + \\ {}^1\!/_2\sum_a\sum_{b\neq a}\int\int\frac{\rho_a'(\vec r_1)\,\rho_b'(\vec r_2)}{r_{12}}\mathrm{d}\vec r_1\,\mathrm{d}\vec r_2 \quad (4)\end{aligned}$$

where V_{nn} represents the internuclear repulsion, $E_a[\rho_a(\vec r)]$ is the energy of unperturbed atom a, $v_a(\vec r)$ are the nuclear potentials, $\rho_a(\vec r)$ are the atomic densities and $\rho_a'(\vec r)$ are the perturbations on the atomic densities. Also atomic chemical potential μ_a and atomic hardness kernels $\eta_a(\vec r_1, \vec r_2)$ enter eq 4. They are respectively the first and the second functional derivatives of the energy at the point where the density is equal to the true atomic density $\rho_a(\vec r)$. Equation 4 can be a reasonable approximation when the perturbations $\rho_a'(\vec r)$ are small compared to unperturbed atomic densities.

The variables $\rho_a'(\vec r)$ are constrained by the condition

$$\sum_a\int\rho_a'(\vec r)\,\mathrm{d}\vec r = 0 \quad (5)$$

which follows from the charge conservation considerations.

In this work we will concentrate at the studies of diatomic molecules containing nuclei A and B (not restricted to cases when $A \neq$ B). Each atom will be characterized by a set of parameters that enter eq 4, with subscripts a and b, respectively.

We begin with a simple approach when the density perturbations are taken in the form

$$\begin{aligned} \rho_a'(\vec r) &= Q_a f_a(\vec r - \vec r_a) \\ \rho_b'(\vec r) &= Q_b f_b(\vec r - \vec r_b) \quad (6)\end{aligned}$$

where $\vec r_a$ and $\vec r_b$ are the position vectors of nuclei A and B. The known positive functions $f_a(\vec r)$ and $f_b(\vec r)$ are normalized to unity. Substitution of eq 6 into eq 4 transfers the energy functional into a function of the net charges Q_a and Q_b:

$$E(Q_a,Q_b) = E_0 + \mu_a^* Q_a + \mu_b^* Q_b + {}^1\!/_2\tilde\eta_a Q_a^2 + {}^1\!/_2\tilde\eta_b Q_b^2 + J_{ab}Q_aQ_b \quad (7)$$

where E_0 is the collection of terms independent of the charges. The coefficients in eq 7 are defined as follows:

$$\begin{aligned} \mu_a^* &= \mu_a + \int\left[v_b(\vec r_1 - \vec r_b) + \int\frac{\rho_b(\vec r_2 - \vec r_b)}{|r_1 - r_2|}\mathrm{d}\vec r_2\right]f_a(\vec r_1 - \vec r_a)\mathrm{d}\vec r_1 \\ \mu_b^* &= \mu_b + \int\left[v_a(\vec r_1 - \vec r_a) + \int\frac{\rho_a(\vec r_2 - \vec r_a)}{|r_1 - r_2|}\mathrm{d}\vec r_2\right]f_b(\vec r_1 - \vec r_b)\mathrm{d}\vec r_1 \quad (8)\end{aligned}$$

and

$$\begin{aligned} \tilde\eta_a &= \int\int\eta_a(\vec r_1, \vec r_2)f_a(\vec r_1)f_a(\vec r_2)\mathrm{d}\vec r_1\,\mathrm{d}\vec r_2 \\ \tilde\eta_b &= \int\int\eta_b(\vec r_1, \vec r_2)f_b(\vec r_1)f_b(\vec r_2)\mathrm{d}\vec r_1\,\mathrm{d}\vec r_2 \quad (9)\end{aligned}$$

Finally,

$$J_{ab}(R_{ab}) = \int\int f_a(\vec r_1 - \vec r_a)\frac{1}{|\vec r_1 - \vec r_2|}f_b(\vec r_2 - \vec r_b)\mathrm{d}\vec r_1\,\mathrm{d}\vec r_2 \quad (10)$$

where $R_{ab} = |\vec r_a - \vec r_b|$ is the distance between the nuclei A and B.

The constraint (eq 5) will now read

$$Q_a + Q_b = 0 \quad (11)$$

As we can see, all the parameters defined by eqs 8−10 depend on our choice of functions $f(\vec r)$ which in principle should not remain the same for different molecules. It is interesting that the first of the two terms in eq 8 is indeed a quantity describing an isolated atom (absolute atomic chemical potential). The second term in eq 8 accounts for the influence of the environment and, clearly, is not an atomic quantity. In some cases this term may become very important for the understanding of the correct physical picture, especially for the studies of homonuclear molecules.

Our calculations show that usually the first term in equation 8 contributes dominantly to the value of μ_a^*. This leads us to an interesting conclusion: the major part of the first order correction to the energy in eq 4 is dependent on the amounts of the transferred charges but not on the shapes of the perturbations $\rho_a'(\vec{r})$. Such an observation provides an explanation for a considerable success of the electronegativity approach in chemistry which tends to describe the processes of molecular formation in terms of atomic characteristics.

The values of the net charges that minimize the energy (eq 7) under the condition (eq 11) are

$$Q_a = -Q_b = \frac{\mu_b^* - \mu_a^*}{\tilde{\eta}_a + \tilde{\eta}_b - 2J_{ab}\,(R_{ab})} \tag{12}$$

It is easy to prove that only the difference between μ_b^* and μ_a^* defines the direction of the charge transfer. The sufficient conditions for the extremum to be a minimum yield

$$\tilde{\eta}_a > 0, \quad \tilde{\eta}_b > 0, \quad \tilde{\eta}_a\tilde{\eta}_b - J_{ab}^2(R_{ab}) > 0 \tag{13}$$

We then have

$$\tilde{\eta}_a + \tilde{\eta}_b - 2J_{ab}(R_{ab}) > \tilde{\eta}_a + \tilde{\eta}_b - 2\sqrt{\tilde{\eta}_a\tilde{\eta}_b} > 0 \tag{14}$$

because $(x + y)/2 > \sqrt{xy}$ for any positive x and y. Thus, we proved that the denominator must always be positive and the sign in eq 12 is defined by the numerator.

We performed calculations based in eq 12 using the squares of Slater orbitals (the idea was first suggested in ref 17) for the functions $f(\vec{r})$. For many cases reasonable results for the net charges were obtained (see ref 15). Below we propose another approximation for the density perturbations $\rho_a'(\vec{r})$ which allows us to improve on the previously predicted results for charge transfer in heteronuclear diatomic molecules and quantitatively describe the bonding in homonuclear diatomics.

Consider now density perturbations to have the form

$$\rho_a'(\vec{r}) = q_a f_a(\vec{r} - \vec{r}_a - \vec{x}_a) + Q_a f_a(\vec{r} - \vec{r}_a + \vec{x}_a) \tag{15}$$

and

$$\rho_b'(\vec{r}) = q_b f_b(\vec{r} - \vec{r}_b + \vec{x}_b) + Q_b f_b(\vec{r} - \vec{r}_b - \vec{x}_b) \tag{16}$$

where $f_a(\vec{r})$ and $f_b(\vec{r})$ are again some known nonnegative functions normalized to unity. Now there are two charge distributions on each atom separated by the distances $2x_a$ and $2x_b$, respectively. Symmetry considerations imply that both vectors $\vec{x}_a$ and $\vec{x}_b$ are positioned along the internuclear axis.

With density perturbations described by eqs 15 and 16, the energy in eq 4 becomes a quadratic function of four charges q_a, Q_a, q_b, and Q_b. We will make a change to more meaningful variables by the following linear transformation:

$$\begin{aligned} q_a + Q_a &= S_a \qquad & q_b + Q_b &= S_b \\ q_a - Q_a &= D_a \qquad & q_b - Q_b &= D_b \end{aligned} \tag{17}$$

Variables S_a and S_b signify the total amount of charge that has been transferred from one atom to the other, while D_a and D_b show how this charge is distributed within an atom. With an additional assumption that x_a, $x_b \ll R_{ab}$ we obtain for the energy

$$\begin{aligned} E(S_a, S_b, D_a, D_b) = E_0 + \mu_a^* S_a + z_a\Delta\mu_a D_a + \mu_b^* S_b + \\ z_b\Delta\mu_b D_b + {}^1/_2\left(\tilde{\eta}_a - \frac{\Delta\tilde{\eta}_a}{2}\right)S_a^2 + {}^1/_4\Delta\tilde{\eta}_a D_a^2 + {}^1/_2\left(\tilde{\eta}_b - \right. \\ \left. \frac{\Delta\tilde{\eta}_b}{2}\right)S_b^2 + {}^1/_4\Delta\tilde{\eta}_b {D_b}^2 + J_{ab}S_aS_b + z_aJ_{ab}D_aS_b + z_bJ_{ab}S_aD_b + \\ (z_a^2 + z_b^2)J_{ab}S_aS_b + 2z_az_bJ_{ab}D_aD_b \end{aligned} \tag{18}$$

where

$$z_a = \frac{x_a}{R_{ab}}, \quad z_b = \frac{x_b}{R_{ab}} \tag{19}$$

$$\Delta\mu_a = \mu_a^* - \mu_a = \int \left[v_b(\vec{r}_1 - \vec{r}_b) + \int \frac{\rho_b(\vec{r}_2 - \vec{r}_b)}{|r_1 - r_2|} \mathrm{d}\vec{r}_2 \right] f_a(\vec{r}_1 - \vec{r}_a)\mathrm{d}\vec{r}_1$$

$$\Delta\mu_b = \mu_b^* - \mu_b = \int \left[v_a(\vec{r}_1 - \vec{r}_a) + \int \frac{\rho_a(\vec{r}_2 - \vec{r}_a)}{|r_1 - r_2|} \mathrm{d}\vec{r}_2 \right] f_b(\vec{r}_1 - \vec{r}_b)\mathrm{d}\vec{r}_1 \tag{20}$$

$$\Delta\tilde{\eta}_a = \tilde{\eta}_a - \int\int \eta_a(\vec{r}_1, \vec{r}_2) f_a(\vec{r}_1 - \vec{x}_a) f_a(\vec{r}_2 + \vec{x}_a)\mathrm{d}\vec{r}_1\,\mathrm{d}\vec{r}_2 \tag{21}$$

$$\Delta\tilde{\eta}_b = \tilde{\eta}_b - \int\int \eta_b(\vec{r}_1, \vec{r}_2) f_b(\vec{r}_1 - \vec{x}_b) f_b(\vec{r}_2 + \vec{x}_b)\mathrm{d}\vec{r}_1\,\mathrm{d}\vec{r}_2$$

and μ_a^*, μ_b^*, $\tilde{\eta}_a$, $\tilde{\eta}_b$, and J_{ab} are defined by formulas 8−10.

Constraint 5 will now read

$$S_a + S_b = 0 \tag{22}$$

III. Results

A. Heteronuclear Diatomics. Minimization of eq 18 under the condition 22 with respect to four charge variables yields the following result for the total charge transfer:

$$S_a = -S_b = \frac{\mu_b^* - \mu_a^*}{\tilde{\eta}_a + \tilde{\eta}_b - 2J_{ab}}\left(1 + \frac{\Delta\tilde{\eta}_a + \Delta\tilde{\eta}_b}{2(\tilde{\eta}_a + \tilde{\eta}_b - 2J_{ab})} + O(z_{a,b}^2)\right) \tag{23}$$

Thus, we obtain our previous result (formula 12) and a correction to it (second term in the brackets). This result is correct up to the second order with respect to small parameters z_a and z_b. From the analysis of the sufficient conditions we can conclude that the denominator must have a positive sign and again the direction of the charge transfer is defined by the difference between μ_a^* and μ_b^*. Sufficient conditions imply that $\Delta\tilde{\eta}_a > 0$ and $\Delta\tilde{\eta}_b > 0$ which means that the correction tends to increase the values of the net charges obtained from eq 23 compared to the ones from eq 12.

Let us show that the use of formula 23 can indeed improve the results of calculations for the net charges in diatomic molecules. We use the squares of spherically symmetric Slater orbitals for functions $f_a(\vec{r})$ and $f_b(\vec{r})$:

$$\begin{aligned} f_a(\vec{r}) &= \phi_a^2(\vec{r}) \\ f_b(\vec{r}) &= \phi_b^2(\vec{r}) \end{aligned} \tag{24}$$

where

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

$$\phi_b(r) = A_n r^{n_b - 1} e^{-\zeta_b r} \qquad (25)$$

In eq 25, n_a and n_b are the principal quantum numbers of the valent orbitals of atoms A and B and A_n is a normalization constant.

Parameters ζ_a and ζ_b are fixed by the conditions (for discussion see refs 15 and 17):

$$\zeta_a = \frac{2n_a + 1}{2R_a} \quad \zeta_b = \frac{2n_b + 1}{2R_b} \qquad (26)$$

where R_a and R_b are the appropriate covalent radii of atoms A and B. The values for μ_a and μ_b in eq 8 are taken as $-(I_{a,b} + A_{a,b})/2$, where $I_{a,b}$ is an ionization potential and $A_{a,b}$ is an electron affinity of atom A or B. The atomic densities entering the second term in eq 8 were calculated through the atomic DFT program. We use the Coulomb part of the hardness kernel to calculate the values of $\tilde{\eta}_a$ and $\tilde{\eta}_b$.

The molecular dipole moment is now given as

$$d_{ab} = S_a R_{ab} + D_a x_a + D_b x_b \qquad (27)$$

Our estimations show that the last two terms are very small compared to the first term in eq 27 and they can be safely neglected. Thus, the molecular dipole moment is still defined by the total charge transfer from one atom to the other.

In Table 1 we present the results of our calculations for sixteen alkali-metal halide molecules. The values of Q^{exp} were taken from ref 17 where they were calculated by dividing the experimental dipole moments by the experimental bond distance. Q^{cpe} are the results obtained from formula 12, and S^{cpe} are the new results calculated from formula 23 when $\Delta\tilde{\eta}_a$ and $\Delta\tilde{\eta}_b$ are taken as free parameters to get the best fit to the experimental data.

The values of $\Delta\tilde{\eta}$ for each element are given in Table 2. We can see that all the values of $\Delta\tilde{\eta}$ are small compared to the appropriate $\tilde{\eta}$, as expected. With such a choice the maximum error is 22.2% and the average error is only 5.4%. This is much better than reported in ref 14 and ref 17 for the similar set of molecules. The error is due to the omission of the terms proportional to $z_{a,b}^2$ in eq 23 and, of course, to initial approximations 15 and 16.

B. Homonuclear Diatomics. Another important feature of approximations 15 and 16 is that now we can describe the bonding in homonuclear diatomic molecules. In this case $\mu_a^* = \mu_b^*$, and thus from formula 23 it follows that $S_a = S_b = 0$, but the energy expression (18) can be minimized with respect to D_a and D_b. We then obtain

$$D_a = D_b = -\frac{2z\Delta\mu}{\Delta\tilde{\eta} + 4z^2 J_{ab}} \qquad (28)$$

where $z = z_a = z_b$, $\Delta\mu = \Delta\mu_a = \Delta\mu_b$, and $\Delta\tilde{\eta} = \Delta\tilde{\eta}_a = \Delta\tilde{\eta}_b$.

For the energy we get

$$E = E_0 - \frac{2z^2\Delta\mu^2}{\Delta\tilde{\eta} + 4z^2 J_{ab}} \qquad (29)$$

This means that even though there is no charge transfer in the homogeneous diatomic molecule, there are physical dipoles “sitting” on top of each atom. Their repulsion increases the energy, but the interaction of these dipoles with the neighboring atom decreases the energy more and, thus, is the basis for the chemical bond in the molecule.

TABLE 1: Charges on Halides

	Q^{exp}	Q^{cpe}	S^{cpe}
LiF	0.837	0.731	0.824
LiCl	0.731	0.619	0.687
LiBr	0.694	0.549	0.610
LiI	0.647	0.441	0.503
NaF	0.879	0.697	0.761
NaCl	0.792	0.697	0.748
NaBr	0.757	0.684	0.734
NaI	0.708	0.634	0.700
KF	0.821	0.706	0.749
KCl	0.800	0.742	0.766
KBr	0.783	0.752	0.771
KI	0.740	0.734	0.770
RbF	0.781	0.728	0.776
RbCl	0.784	0.760	0.774
RbBr	0.768	0.766	0.763
RbI	0.753	0.749	0.760

TABLE 2: Values of $\tilde{\eta}$ (Coulomb Part) and $\Delta\tilde{\eta}$ (in eV)

	$\tilde{\eta}$	$\Delta\tilde{\eta}$
Li	8.24	1.43
Na	6.13	0.84
K	4.95	0.19
Rb	4.63	0.01
F	18.20	1.34
Cl	12.86	0.33
Br	11.21	0.17
I	9.62	0.40

TABLE 3: Atomic Dipoles on Homonuclear Diatomic Molecules (debyes)

	d^{scf}	d^{mp2}	d^{cpe}
H_2	0.28	0.27	0.33
N_2	0.54	0.73	0.48
O_2	0.21	0.27	0.36
F_2	0.17	0.25	0.23
Cl_2	0.54	0.56	0.27

Taking the limit $x \rightarrow 0$ in eq 28, we can find the values of “mathematical dipoles” located on both atoms (we use the facts that $z = x/R_{ab}$ and $\Delta\tilde{\eta}|_{x\rightarrow 0} = 0$)

$$d = Dx = \frac{\Delta\mu R_{ab}}{2J_{ab}} \qquad (30)$$

Equation 30 can be used for calculations of such atomic dipoles for homonuclear diatomic molecules and they are represented in Table 3 as d^{cpe}. Equations 20 and 10 were used to find $\Delta\mu$ and J_{ab} with the shape function $f_a(\bar{r})$ again defined by eqs 24 and 25. Table 3 also shows the results for atomic dipoles d^{scf} and d^{mp2}. These were obtained by placing point dipoles at each atomic center and finding the values of such dipoles through the fit of the electrostatic potential produced by these dipoles to the calculated electrostatic potential due to the charge distribution of the molecule. This was done for self-consistent field and Moller-Plasset perturbation theory densities using the ‘AtomDipole’ option of ‘Population’ keyword in Gaussian-94 package.[18] All the values are in Debyes.

It is interesting that without the help of any free parameters we can get reasonable results for the values of the atomic dipoles using a simple quadratic model given by eq 18.

IV. Conclusions

Let us now summarize the completed work. Formula 4 is an approximation to the molecular energy in terms of perturbations on the atomic densities. Depending on what molecular properties we want to study, we can use different representations of these density perturbations. In case of heteronuclear diatomic molecules if we represent the density perturbation on each atom in the form of spherically distributed charge centered on the nucleus (eq 6), we obtain a familiar quadratic model for molecular energy (see eq 7). The amount of charge transfer that enters eq 7 can be determined from the minimization of this expression under the constraint given by eq 11. The sufficient conditions for the energy minimum (eq 13 and 14) tell us that the direction of the charge transfer is given by the sign of the difference of the chemical potentials. It is important to realize that the chemical potential that enters eq 7 is not an absolute chemical potential, but a modified chemical potential that depends on the atomic partner in the diatomic molecule (see eq 8).

When we assign a charge distribution to every atom in a diatomic in the form described by eqs 15 and 16, we are able to improve quite significantly the results for the total charge transfer in heteronuclear diatomics (Table 1). Moreover, we are also able to explain the bonding in homonuclear diatomic molecules. This shows that our approach allows to treat homonuclear diatomics in the same way as heteronuclear. In the limit of a point dipole approximation to the charge distribution on an atom in homonuclear diatomics (see eq 30), we obtain results which are in a reasonable agreement with the results from ab initio calculations.

Although in this work we deal with diatomic molecules, it is clear that a spirit of this approach can be used to study polyatomic molecules. This will be very useful for molecular dynamics simulations, especially of large systems, due to the low computational cost of solving linear equations that emerge from the quadratic nature of the basic energy expression in the model.

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References and Notes

(1) Allen M. P.; Tildesley, D. *Computer Simulations of Liquids*; Oxford University Press: New York, 1987.

(2) Car R.; Parrinello M. *Phys. Rev. Lett.* **1985**, *55*, 2471.

(3) Stone, A. J. *The Theory of Intermolecular Forces*; Oxford University Press: New York, 1996.

(4) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, *91*, 6269.

(5) Alejandre, J.; Tildesley, D. J.; Chapela, G. *J. Chem. Phys.* **1995**, *102*, 4574.

(6) (a) Perera, L.; Berkowitz, M. L. *J. Chem. Phys.* **1991**, *95*, 1954. (b) Perera, L.; Berkowitz, M. L. *J. Chem. Phys.* **1993**, *99*, 4236.

(7) Stuart, S. J.; Berne, B. J. *J. Chem. Phys.* **1996**, *100*, 11934.

(8) Yeh, I. C.; Perera, L.; Berkowitz, M. L. *Chem. Phys. Lett.* **1997**, *264*, 31.

(9) For recent example, see: Tobias, D. J.; Tu, K.; Klein, M. L. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 15.

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

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

(12) (a) Parr, R. G.; Donnely, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *69*, 4431. (b) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

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

(14) Winkler, R.; Pantelidis, S. T. J. *Chem. Phys.* **1997**, *106*, 7714.

(15) Itskowitz, P.; Berkowitz, M. L. *J. Phys. Chem.* **1997**, *101*, 5687.

(16) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1993**, *115*, 1084.

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

(18) Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C., Pople, J. A., *Gaussian 94*, Revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.