

A density functional theory-based chemical potential equalisation approach to molecular polarizability

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Abstract. The electron density changes in molecular systems in the presence of external electric fields are modeled for simplicity in terms of the induced charges and dipole moments at the individual atomic sites. A chemical potential equalisation scheme is proposed for the calculation of these quantities and hence the dipole polarizability within the framework of density functional theory based linear response theory. The resulting polarizability is expressed in terms of the contributions from individual atoms in the molecule. A few illustrative numerical calculations are shown to predict the molecular polarizabilities in good agreement with available results. The usefulness of the approach to the calculation of intermolecular interaction needed for computer simulation is highlighted.

Keywords. Chemical potential equalisation; molecular polarisability; density functional theory.

1. Introduction

The knowledge about the response of an atomic or molecular system to an external electric field is important for an understanding of their interaction with radiation, intermolecular interaction and various other physicochemical phenomena of interest. The linear and nonlinear responses are characterised respectively by the polarizability and hyperpolarizability quantities both of which can be calculated through the evaluation of expectation values of single particle operators and hence density functional theory (DFT)^{1,2} which employs the single particle electron density³ as the basic variable is most suitable for this purpose from the point of view of conceptual simplicity as well as computational economy. DFT has also provided foundation^{2,4} to a number of chemical concepts used widely for the understanding of chemical binding, reactivity and interaction. Thus, the chemical potential of the electron cloud has been identified⁵ as the electronegativity⁶ parameter of chemistry, the charge capacity has been linked⁷ with the concepts of chemical hardness^{8,9} and softness and the frontier orbital theory¹⁰ has been rationalised¹¹ in terms of the density derivatives within the framework of DFT. The calculation of polarizability of many electron

systems using DFT has followed mainly two routes, the first one dealing¹² directly with the density perturbation in an external field using variational or numerical method, while the second one makes use of a hybrid prescription^{13–15} exploiting the interconnection of the response functions¹⁶ with some of the conceptual developments as mentioned above.

The major features of the electron density changes during intermolecular interaction, molecule formation or interaction with external fields can, however, be often captured in terms of much simplified representation of the properties of atoms in molecules rather than using the full density function in 3-D space of the molecule. Recent years have seen an upsurge of interest in the development and extension of the conceptual framework in this direction. Thus, a perturbation theory of chemical binding has been developed^{17–20} where the concept of chemical potential equalisation^{4,5} (CPE) has been generalised to include the concept of bond chemical potential,^{17,18} spin-polarised electronegativity^{19,20} etc., thereby incorporating the effect of charge delocalisation and spin pairing during molecule formation particularly for covalent binding. There have also been developments of other descriptions²¹ where the atomic dipoles arising due to distortion of the charge distribution from spherical symmetry due to bonding have been taken into account. Most widely used application of CPE pro-

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cedure however is to the calculation of partial atomic charges^{22–24} in molecules with the ambitious goal of development of dynamic charge models^{25–28} for predicting the intermolecular forces for computer simulation studies.

The purpose of the present work is to study the applicability of simple chemical potential equalisation approaches within a DFT framework to the study of response properties of molecules in external fields. For simplicity, we have restricted ourselves to the study of electric dipole polarizability only although extension to multipolar polarizability is straightforward.

There have been many attempts²⁹ in the past to obtain molecular polarizability by adding together the contributions from the constituent atoms. The effect of the bonded environment of an atom had been accounted for in some of these additive models in an average manner by invoking the concept of atomic hybridisation dependent parameters. Attempt has also been made³⁰ to obtain the molecular polarizability in terms of the effective atomic polarizabilities dependent on the net atomic charges on molecule formation. In an elegant approach, Applequist³¹ has proposed an electrostatic interaction model where the atomic response that leads to an effective atomic polarizability is not only due to the externally applied electric field but also due to an effective field arising from the induced dipole moments of all the atoms in the molecule. A major drawback of the electrostatic point dipole model has been corrected by Thole³² by modifying the dipole tensor through the use of a shape function at shorter distances. The interacting dipole model of Applequist³¹ however treated the molecule as a collection of polarizable points and only the induced interacting atomic dipoles contributed to the induced dipole moment and hence the polarizability. The model was subsequently extended to incorporate the interatomic charge transfer effects by Olson and Sundberg³³ and was further generalised by Applequist³⁴ himself in a series of papers as well as by others.^{35,36}

The present work is close in spirit to these electrostatic models^{31–34} developed by several authors during the last two decades where the concept of effective atomic polarizabilities has been invoked to reproduce the molecular polarizability. The major new features of the present approach involve the consideration of the density changes in terms of its first two moments, viz. the atomic charge and dipole within the framework of a chemical potential equalisation procedure in contrast to a purely electrostatic

model. It basically provides a simple linear response theoretic approach within DFT for the study of redistribution of the electron density due to an external field and is in the spirit of a semiempirical model for polarisation and charge transfer. Although the final equations possess classical-like appearance, the underlying physics is based on a rigorous quantum mechanical framework of DFT.

Chemical potential equalisation schemes have been attempted^{37–39} recently for the induced atomic charges in a molecule due to an applied field and thereby calculation of the polarizability. However, the main limitation of these works is that they are based on the charges alone and hence the polarizability in the perpendicular direction in a planar molecule is predicted to be zero. Although attempts have been made³⁷ to use the Drude oscillator model to mimic this, a more satisfactory approach seems to lie in the consideration of the atom centered dipoles used earlier in electrostatic models. This will also unify the proposed chemical potential equalisation approach with the well developed interaction model of Applequist^{31–34} resulting into an integrated approach. A close connection with the distributed polarizability approaches^{40–42} will also be apparent.

In what follows, we first discuss the theoretical framework for density functional investigation of chemical potential equalisation of atomic constituents in molecular systems in §2 and the choice of various atomic and other (interatomic) parameters appearing in this theory is considered in §3. The linear response version of the equations corresponding to the chemical potential equalisation for molecular polarizability is discussed in §4. The results of numerical calculations for various molecular systems have been presented in §5 which is followed by a few concluding remarks in §6.

2. Density functional theory and effective chemical potential equalisation of atoms in molecules

In DFT, the ground state electronic energy of a many-electron system characterised by the external potential $v(\mathbf{r})$ arising due to the nuclei and/or any other external source of electric field, can be expressed as a unique functional $E_v[\mathbf{r}(\mathbf{r})]$ of its electron density $\mathbf{r}(\mathbf{r})$ and is given by,

$$E_v[\mathbf{r}(\mathbf{r})] = \int d\mathbf{r} \mathbf{r}(\mathbf{r}) v(\mathbf{r}) + F[\mathbf{r}(\mathbf{r})], \quad (1)$$

where $F[\mathbf{r}(\mathbf{r})]$ is a universal functional of the density consisting of kinetic, Coulomb and exchange-correlation energy components. The equilibrium density $\mathbf{r}_0(\mathbf{r})$ is the solution of the Euler equation corresponding to the energy minimisation, viz.

$$\mathbf{m} = \frac{dE_v[\mathbf{r}(\mathbf{r})]}{d\mathbf{r}(\mathbf{r})} = v(\mathbf{r}) + \frac{dF[\mathbf{r}(\mathbf{r})]}{d\mathbf{r}(\mathbf{r})}, \quad (2)$$

where \mathbf{m} is the Lagrange multiplier associated with the density normalisation [$\int d\mathbf{r}\mathbf{r}(\mathbf{r}) = N_{el}$] and signifies the chemical potential of the electron cloud and hence the electronegativity \mathbf{c} (with a negative sign) as demonstrated by Parr *et al*⁵, viz.

$$\mathbf{c} = -\left(\frac{\partial E}{\partial N_{el}}\right)_v = -\int d\mathbf{r}\left(\frac{dE_v[\mathbf{r}(\mathbf{r})]}{d\mathbf{r}(\mathbf{r})}\right)\left(\frac{\partial \mathbf{r}(\mathbf{r})}{\partial N_{el}}\right)_v = -\mathbf{m} \quad (3)$$

with N_{el} denoting the number of electrons in the system. The second derivative has also been defined⁷ to represent the hardness parameter \mathbf{h} as

$$\mathbf{h} = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N_{el}^2}\right) \quad (4)$$

which has further been expressed⁴³ in terms of the density as

$$\begin{aligned} \mathbf{h} &= \int d\mathbf{r}f(\mathbf{r})\mathbf{h}(\mathbf{r}) \\ &= \int d\mathbf{r}f(\mathbf{r})\int d\mathbf{r}'\mathbf{r}'\mathbf{h}(\mathbf{r}, \mathbf{r}') \end{aligned} \quad (5)$$

where $\mathbf{h}(\mathbf{r})$ denotes the local hardness⁴³ and the energy functional derivative $\mathbf{h}(\mathbf{r}, \mathbf{r}')$ given by

$$\mathbf{h}(\mathbf{r}, \mathbf{r}') = \left(\frac{d^2 F[\mathbf{r}(\mathbf{r})]}{d\mathbf{r}(\mathbf{r})d\mathbf{r}(\mathbf{r}')}\right) \quad (6)$$

represents the hardness kernel.¹⁶ The function $f(\mathbf{r})$ used here is the Fukui function¹¹ which has been known to play an important role in the theory of chemical reactivity and is defined as $f(\mathbf{r}) = (\partial \mathbf{r}(\mathbf{r})/\partial N_{el})_{v(\mathbf{r})}$ although one can also use $(\mathbf{r}(\mathbf{r})/N_{el})$ or any other function integrating to unity in place of this function for evaluating the hardness⁴⁴ through (5).

If the system is perturbed by a perturbing potential $d\mathbf{v}(\mathbf{r})$ so that the new potential is $v(\mathbf{r}) + d\mathbf{v}(\mathbf{r})$ and the corresponding density change is $d\mathbf{r}(\mathbf{r})$, the energy

change can be expressed²⁷ in terms of the various functional derivatives using (1) and retaining terms up to second order as

$$\begin{aligned} \Delta E &= E[\mathbf{r}(\mathbf{r}) + d\mathbf{r}(\mathbf{r}), v(\mathbf{r}) + d\mathbf{v}(\mathbf{r})] - E[\mathbf{r}(\mathbf{r}), v(\mathbf{r})] \\ &= \int d\mathbf{r}\left(\frac{dE[\mathbf{r}(\mathbf{r})]}{d\mathbf{r}(\mathbf{r})}\right)_{v(\mathbf{r})} d\mathbf{r}(\mathbf{r}) + \int d\mathbf{r}\left(\frac{dE[\mathbf{r}(\mathbf{r})]}{dv(\mathbf{r})}\right)_{\mathbf{r}(\mathbf{r})} d\mathbf{v}(\mathbf{r}) \\ &\quad + \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}'\left(\frac{d^2 E[\mathbf{r}(\mathbf{r})]}{d\mathbf{r}(\mathbf{r})d\mathbf{r}(\mathbf{r}')}\right)_{v(\mathbf{r})} d\mathbf{r}(\mathbf{r})d\mathbf{r}' \\ &\quad + \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}'\left(\frac{d^2 E[\mathbf{r}(\mathbf{r})]}{dv(\mathbf{r})dv(\mathbf{r}')}\right)_{\mathbf{r}(\mathbf{r})} d\mathbf{v}(\mathbf{r})d\mathbf{v}' \\ &\quad + \iint d\mathbf{r}d\mathbf{r}'\left(\frac{d^2 E[\mathbf{r}(\mathbf{r})]}{d\mathbf{r}(\mathbf{r})dv(\mathbf{r}')}\right) d\mathbf{r}(\mathbf{r})d\mathbf{v}(\mathbf{r}'). \end{aligned} \quad (7)$$

Analogously the change in chemical potential $\mathbf{m} = \mathbf{m}_0 + \Delta\mathbf{m}$ is given up to first order change in $d\mathbf{r}(\mathbf{r})$ by,

$$\begin{aligned} \Delta\mathbf{m} &= \mathbf{m} - \mathbf{m}_0 \\ &= d\mathbf{v}(\mathbf{r}) + \int d\mathbf{r}'\mathbf{h}(\mathbf{r}, \mathbf{r}')d\mathbf{r}'(\mathbf{r}'), \end{aligned} \quad (8)$$

as obtained by using (2) and (6) as well as the relation⁴⁵ $(d^2 E/d\mathbf{r}(\mathbf{r})d\mathbf{v}(\mathbf{r}')) = d(\mathbf{r} - \mathbf{r}')$. The density change $d\mathbf{r}(\mathbf{r})$ can also be written as a sum of contributions due to the change in the number of electrons dN_{el} and the potential, viz.

$$d\mathbf{r}(\mathbf{r}) = f(\mathbf{r})dN_{el} + \int d\mathbf{r}'\mathbf{c}_0(\mathbf{r}, \mathbf{r}')d\mathbf{v}(\mathbf{r}'), \quad (9)$$

involving the Fukui function $f(\mathbf{r})$ and the response function $\mathbf{c}_0(\mathbf{r}, \mathbf{r}')$ given by $\mathbf{c}_0(\mathbf{r}, \mathbf{r}') = (d\mathbf{r}(\mathbf{r})/d\mathbf{v}(\mathbf{r}'))_{N_{el}}$.

While these equations are general and applicable to any many-electron system, we here specialise to a molecular species consisting of N atoms with their nuclei located at the fixed positions $\{\mathbf{R}_a\}$ corresponding to the equilibrium geometry of the molecule. Let the density change $d\mathbf{r}(\mathbf{r})$ on molecule formation and due to the applied electric field \mathbf{E} be partitioned in some way and be expressed as a sum of the atomic components, viz.

$$d\mathbf{r}(\mathbf{r}) = \sum_a d\mathbf{r}_a(\mathbf{r}) = \sum_a d\mathbf{r}_a(\mathbf{r}_a), \quad (10)$$

where $\mathbf{r}_a = \mathbf{r} - \mathbf{R}_a$ denotes the atom-centered coordinate with the origin located at the a -th atom. In

this partitioning of a molecular system into atomic subsystems, the regions may be overlapping but one can assume without any loss of generality that the density components $\mathbf{dr}_a(\mathbf{r})$ vanish outside the \mathbf{a} -th atomic region.

We now consider the \mathbf{a} -th atom and the region \mathbf{r}_a surrounding this atomic site \mathbf{R}_a for which the chemical potential $\mathbf{m} \equiv \mathbf{m}_a(\mathbf{r}_a)$ as given by (8) can be written as

$$\begin{aligned} \mathbf{m}_a &= \mathbf{m}_a^0 + d\mathbf{v}(\mathbf{r}_a) + \int d\mathbf{r}' \mathbf{h}(\mathbf{r}_a, \mathbf{r}') d\mathbf{r}' \\ &= \mathbf{m}_a^0 + d\mathbf{v}(\mathbf{r}_a) + \sum_b \int d\mathbf{r}'_b \mathbf{h}(\mathbf{r}_a, \mathbf{r}'_b) d\mathbf{r}'_b, \end{aligned} \quad (11)$$

with the symbol $\mathbf{m}_a^0 (\equiv \mathbf{m}_a(0))$ denoting the chemical potential of the \mathbf{a} -th atom. In writing (11), the assumption that $\mathbf{dr}_b(\mathbf{r}')$ is nonzero only within the region of the \mathbf{b} -th atom has been used. Consider now the Taylor series expansions of the potential and the hardness kernel as

$$d\mathbf{v}(\mathbf{r}_a) = d\mathbf{v}(\mathbf{a}) + \mathbf{r}_a \cdot \nabla_a d\mathbf{v}(\mathbf{a}) + \frac{1}{2} \mathbf{r}_a^2 \nabla_a^2 d\mathbf{v}(\mathbf{a}) + \mathbf{K} \quad (12)$$

and

$$\begin{aligned} \mathbf{h}(\mathbf{r}_a, \mathbf{r}'_b) &= \mathbf{h}(\mathbf{a}, \mathbf{b}) + \mathbf{r}_a \cdot \nabla_a \mathbf{h}(\mathbf{a}, \mathbf{b}) + \mathbf{r}'_b \cdot \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b}) \\ &+ \frac{1}{2} \mathbf{r}_a^2 \nabla_a^2 \mathbf{h}(\mathbf{a}, \mathbf{b}) + \frac{1}{2} \mathbf{r}'_b{}^2 \nabla_b^2 \mathbf{h}(\mathbf{a}, \mathbf{b}) \\ &+ \mathbf{r}_a \mathbf{r}'_b \cdot \nabla_a \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b}) + \dots, \end{aligned} \quad (13)$$

where the arguments (\mathbf{a}) and (\mathbf{a}, \mathbf{b}) as in $d\mathbf{v}(\mathbf{a})$, $\mathbf{h}(\mathbf{a}, \mathbf{b})$ etc. indicate that the quantities are evaluated at the atomic site $\mathbf{a}(\mathbf{r}_a = 0)$ and sites $\mathbf{a}, \mathbf{b}(\mathbf{r}_a = \mathbf{r}_b = 0)$ respectively. Also the notations $\nabla_a f(\mathbf{a})$ and $\nabla_a f(\mathbf{a}, \mathbf{b})$ indicate derivatives of $f(\mathbf{r}_a)$ and $f(\mathbf{r}_a, \mathbf{r}_b)$ with respect to \mathbf{r}_a , evaluated at $\mathbf{r}_a = 0$ and also $\mathbf{r}_b = 0$ for the latter. Substituting these expressions (12) and (13) into (11), one obtains

$$\begin{aligned} \mathbf{m}_a &= \mathbf{m}_a^0 + d\mathbf{v}(\mathbf{a}) + \mathbf{r}_a \cdot \nabla_a d\mathbf{v}(\mathbf{a}) + \frac{1}{2} \mathbf{r}_a^2 \nabla_a^2 d\mathbf{v}(\mathbf{a}) \\ &+ \sum_b \mathbf{h}(\mathbf{a}, \mathbf{b}) \int d\mathbf{r}'_b d\mathbf{r}'_b(\mathbf{r}'_b) \\ &+ \mathbf{r}_a \cdot \sum_b \nabla_a \mathbf{h}(\mathbf{a}, \mathbf{b}) \int d\mathbf{r}'_b d\mathbf{r}'_b(\mathbf{r}'_b) \\ &+ \sum_b \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b}) \cdot \int d\mathbf{r}'_b \mathbf{r}'_b d\mathbf{r}'_b(\mathbf{r}'_b) \\ &+ \frac{1}{2} \mathbf{r}_a^2 \sum_b \nabla_a^2 \mathbf{h}(\mathbf{a}, \mathbf{b}) \int d\mathbf{r}'_b d\mathbf{r}'_b(\mathbf{r}'_b) \end{aligned}$$

$$\begin{aligned} &- \sum_b \mathbf{h}(\mathbf{a}, \mathbf{b}) \int d\mathbf{r}'_b \mathbf{r}'_b{}^2 d\mathbf{r}'_b(\mathbf{r}'_b) \\ &+ \mathbf{r}_a \cdot \sum_b \nabla_a \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b}) \int d\mathbf{r}'_b \mathbf{r}'_b d\mathbf{r}'_b(\mathbf{r}'_b), \end{aligned} \quad (14)$$

which can be rewritten, on using the definitions of the atomic charges q_b and dipoles \mathbf{p}_b at the atomic site \mathbf{b} (with N_b^{el} denoting the corresponding number of electrons) given by

$$q_b = -\Delta N_b^{el} = -\int d\mathbf{r}'_b d\mathbf{r}'_b(\mathbf{r}'_b) \quad (15)$$

and

$$\mathbf{p}_b = \int d\mathbf{r}'_b \mathbf{r}'_b d\mathbf{r}'_b(\mathbf{r}'_b) \quad (16)$$

in the simple form

$$\begin{aligned} \mathbf{m}_a &= \mathbf{m}_a^0 + d\mathbf{v}(\mathbf{a}) - \mathbf{r}_a \cdot \mathbf{E}_a - \frac{1}{2} \mathbf{r}_a^2 \nabla_a \cdot \mathbf{E}_a \\ &- \sum_b \mathbf{h}(\mathbf{a}, \mathbf{b}) q_b - \mathbf{r}_a \cdot \sum_b \nabla \mathbf{h}(\mathbf{a}, \mathbf{b}) q_b \\ &+ \frac{1}{2} \sum_b \nabla_a^2 \mathbf{h}(\mathbf{a}, \mathbf{b}) q_b \\ &+ \sum_b \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b}) \cdot \mathbf{p}_b + \mathbf{r}_a \cdot \sum_b \nabla_a \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b}) \mathbf{p}_b, \end{aligned} \quad (17)$$

where terms involving quadrupole moments have been neglected. Here $\mathbf{E}_a (= -\nabla_a d\mathbf{v}(\mathbf{a}))$ represents the electric field at the atomic site \mathbf{a} . This equation essentially expresses the chemical potential of an atom in a molecular species simplified under the assumption of superposed atomic site densities and approximated in terms of its first two moments, viz. the atomic charges and the dipole moments denoted respectively by q_a and \mathbf{p}_a for the \mathbf{a} -th atomic site. Thus, in this model a molecule is a collection of atom centers containing point charges and dipoles, the magnitudes of which are determined through the chemical potential equalisation of DFT by equating \mathbf{m}_a as embodied in the above equation for all the atoms.

Now, since this equation is valid for any value of \mathbf{r}_a and the left side is a constant, one can generate two sets of equations by equating on both sides the constant terms and the terms linear in \mathbf{r}_a respectively, viz.

$$\mathbf{m}_a = \mathbf{m}_a^0 + d\mathbf{v}(\mathbf{a}) - \sum_b \mathbf{h}(\mathbf{a}, \mathbf{b}) q_b + \sum_b \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b}) \cdot \mathbf{p}_b \quad (18)$$

and

$$0 = \mathbf{E}_a + \sum_b \nabla_a \mathbf{h}(\mathbf{a}, \mathbf{b}) q_b - \sum_b \nabla_a \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b}) \mathbf{p}_b \quad (19)$$

which can be rewritten by separating out the $\mathbf{b} = \mathbf{a}$ terms as

$$\mathbf{m}_a = \mathbf{m}_a^0 + \mathbf{d}_v(\mathbf{a}) - \mathbf{h}(\mathbf{a}, \mathbf{a}) q_a - \sum_{b \neq a} \mathbf{h}(\mathbf{a}, \mathbf{b}) q_b + \sum_{b \neq a} [\nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b})] \mathbf{p}_b, \quad (20)$$

and

$$0 = \mathbf{E}_a + \sum_{b \neq a} [\nabla_a \mathbf{h}(\mathbf{a}, \mathbf{b})] q_b - [\nabla_a \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b})]_{|a=b} \mathbf{p}_a - \sum_{b \neq a} [\nabla_a \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b})] \mathbf{p}_b, \quad (21)$$

for $\mathbf{a} = 1, \dots, N$. Here the diagonal ($\mathbf{a} = \mathbf{b}$) contributions from the quantities $\nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b})$ and $\nabla_a \mathbf{h}(\mathbf{a}, \mathbf{b})$ vanish as the charges and dipoles at the same sites do not interact with each other in this point charge dipole approximation and hence the potential and the field generated at site \mathbf{a} due to the dipole \mathbf{p}_a and the charge q_a respectively are omitted.

Since at equilibrium the chemical potentials of all the atoms are equalised, one can obtain a set of $N - 1$ equations by equating $\mathbf{m}_a = \mu_b$ given by (20) for all the atoms. The N -th equation is provided by the charge conservation (neutrality for a neutral molecule) $\sum q_a = 0$. This set of N scalar equations together with N vector equations corresponding to (21) determine the N scalar atomic charges $\{q_a\}$ and N vector atomic dipoles $\{\mathbf{p}_a\}$.

3. Choice of the atomic and interatomic parameters

While the parameters appearing in (20) and (21) can be obtained in principle from a suitable form of the hardness kernel $\mathbf{h}(\mathbf{r}, \mathbf{r}')$ used in (13) for approximation, it is often more appealing to identify them from physical considerations by comparing the equations with those of the so called atoms-in-molecules approach or the atom-charge-dipole interaction model for binding and polarizability respectively. Thus, one can identify the parameters as follows. The scalar hardness kernel $\mathbf{h}(\mathbf{a}, \mathbf{b})$ used here resembles the atom-in-molecule hardness matrix $\{\mathbf{h}_{ab}\}$ introduced and

widely investigated by Nalewajski⁴⁶ and can be modeled along similar lines.⁴⁷ The other vector and tensor quantities introduced here, however, have no such precedence and are modeled through electrostatic analogy. For this purpose, we have used a slightly different and simplified notation for the hardness kernels, viz. the scalar $\mathbf{h}(\mathbf{a}, \mathbf{b}) = \mathbf{h}_{ab}^{0,0}$, the vectors $\nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b}) = \mathbf{h}_{ab}^{0,1}$, $\nabla_a \mathbf{h}(\mathbf{a}, \mathbf{b}) = \mathbf{h}_{ab}^{1,0}$ and the tensor $\nabla_a \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b}) = \mathbf{h}_{ab}^{1,1}$, where the first or second superscripts as unity denotes the derivative with respect to the first or second argument respectively, while the superscript zero indicates no derivative.

Thus, the diagonal element $\mathbf{h}(\mathbf{a}, \mathbf{a}) (= \mathbf{h}_{aa}^{0,0})$ of the scalar kernel $\mathbf{h}(\mathbf{a}, \mathbf{b})$ is clearly the hardness \mathbf{h}_a^0 of the \mathbf{a} -th atomic species while the off-diagonal element $\mathbf{h}_{ab}^{0,0}$ corresponds to the charge-charge interaction and hence can be represented by the Coulomb potential between the sites \mathbf{a} and \mathbf{b} in terms of their internuclear distance $R_{ab} = |\mathbf{R}_{ab}|$ with $\mathbf{R}_{ab} = \mathbf{R}_a - \mathbf{R}_b$ or in a better way by the Mataga–Nishimoto–Ohno formula^{47,48} of semiempirical quantum chemistry. Thus, one has

$$\mathbf{h}(\mathbf{a}, \mathbf{a}) = \mathbf{h}_{aa}^{0,0} = \mathbf{h}_a^0 \quad (22)$$

$$\mathbf{h}(\mathbf{a}, \mathbf{b}) = \mathbf{h}_{ab}^{0,0} = 1/eR_{ab} \quad (\text{Coulomb approximation}) \quad (23)$$

$$\mathbf{h}(\mathbf{a}, \mathbf{b}) = \mathbf{h}_{ab}^{0,0} = 1/(R_{ab} + a_{ab}); a_{ab} = 2/(\mathbf{h}_a^0 + \mathbf{h}_b^0) \quad (\text{Mataga–Nishimoto–Ohno formula}) \quad (24)$$

where e represents a measure of the dielectric constant of the electron cloud medium for the Coulomb interaction approximation. One can also rewrite (24) in the form of (23) by defining an effective dielectric constant \mathbf{e}_{ab} specific to the bonded atom pair \mathbf{a} and \mathbf{b} as

$$\mathbf{h}_{ab}^{0,0} = 1/\mathbf{e}_{ab}R_{ab}; \quad \mathbf{e}_{ab} = (1 + a_{ab}/R_{ab}). \quad (25)$$

The vector quantities $\nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b}) = \mathbf{h}_{ab}^{0,1}$ and $\nabla_a \mathbf{h}(\mathbf{a}, \mathbf{b}) = \mathbf{h}_{ab}^{1,0}$ correspond to charge–dipole interaction representing essentially the potential at the \mathbf{a} -th atom due to a unit point dipole at the \mathbf{b} -th atom and the field at the \mathbf{a} -th atom due to a unit point charge at the \mathbf{b} -th atom respectively. One can thus write

$$\nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b}) = \mathbf{h}_{ab}^{0,1} = \mathbf{R}_{ab}/eR_{ab}^3 \quad (26)$$

and

$$\nabla_a \mathbf{h}(\mathbf{a}, \mathbf{b}) = \mathbf{h}_{ab}^{1,0} = -\mathbf{R}_{ab}/eR_{ab}^3 \quad (27)$$

for $\mathbf{a} \neq \mathbf{b}$ and zero otherwise as already indicated. Clearly, one has the result $\nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b}) = -\nabla_a \mathbf{h}(\mathbf{a}, \mathbf{b})$, i.e., $\mathbf{h}_{ab}^{0,1} = -\mathbf{h}_{ba}^{1,0}$ and $\mathbf{h}_{aa}^{0,1} = \mathbf{h}_{aa}^{1,0} = 0$.

Analogously, the tensor quantity $\nabla_a \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b})$ corresponds to the dipole-dipole interaction representing essentially the field at the \mathbf{a} -th atom due to a unit point dipole at the \mathbf{b} -th atom and hence can be expressed by the dipole-dipole tensor of electrostatics as

$$\nabla_a \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b}) = \mathbf{h}_{ab}^{\mathbf{t}} = -\frac{1}{eR_{ab}^3} \left[\mathbf{t} - \frac{3}{R_{ab}^2} \mathbf{R}_{ab} \mathbf{R}_{ab} \right]. \quad (28)$$

The corresponding diagonal term $\nabla_a \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b})|_{\mathbf{a}=\mathbf{b}}$ can be easily interpreted as the inverse polarizability as is evident by considering (19) or (21) for a single atom, where the off-diagonal terms are absent and hence one has $0 = \mathbf{E}_a - \nabla_a \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b})|_{\mathbf{a}=\mathbf{b}} \mathbf{p}_a$. One can thus write,

$$\nabla_a \nabla_b \mathbf{h}(\mathbf{a}, \mathbf{b})|_{\mathbf{a}=\mathbf{b}} = \hat{\mathbf{h}}_{aa}^{1,1} = \hat{\mathbf{a}}_a^{-1}, \quad (29)$$

where $\hat{\mathbf{a}}_a$ represents the polarizability tensor of the \mathbf{a} -th atom. This quantity can be interpreted as the hardness parameter for the induction of atomic dipole just as \mathbf{h} is the hardness for charge transfer.

It may be noted that here the parameters $\mathbf{h}_{ab}^{0,0}$, $\mathbf{h}_{ab}^{0,1} = -\mathbf{h}_{ab}^{1,0}$ and $\mathbf{h}_{ab}^{1,1}$ denoting respectively the scalar, vector and tensor quantities, with the superscripts 0 and 1 referring to charge and dipole respectively, are given by the simple expressions of electrostatics as indicated above. As has already been pointed out, the expression given by (25) for $\mathbf{h}_{ab}^{0,0}$ in the case of bonded atoms is also of the same form but with an effective dielectric constant specific to an atom pair.

4. Chemical potential equalisation, linear response and molecular polarizability

It is well known that a molecule formation is associated with equalisation of chemical potential of the constituent atoms mediated through electron density redistribution. When an external electric field is applied to the molecule, a further reorganisation of the electron density takes place and modified charges and dipoles are induced at each site. The chemical potential equalisation equations in the presence of the field provides equations for evaluation of these quantities. For this purpose, we first rewrite (20) representing

the effective chemical potential (of the \mathbf{a} -th atom) in the already discussed notation as

$$\mathbf{m}_a = \mathbf{m}_a^0 - \mathbf{h}_a^0 q_a + \left(\mathbf{f}_a^0 - \sum_{b=1}^N \mathbf{h}_{ab}^{0,0} q_b + \sum_{b=1}^N \hat{\mathbf{h}}_{ab}^{0,1} \cdot \mathbf{p}_b \right), \quad (30)$$

$\mathbf{a} = 1, 2, \dots, N$

where the notation \sum' indicates omission of $\mathbf{b} = \mathbf{a}$ term in the summation, $\mathbf{f}_a^0 = d\mathbf{v}(\mathbf{a})$ is the potential at the \mathbf{a} -th atomic site due to an external field \mathbf{E}^0 which is considered to be uniform for the purpose of polarizability calculation here, but can be in general a position dependent field. Also \mathbf{m}_a^0 and \mathbf{h}_a^0 represent the chemical potential and hardness parameters of the \mathbf{a} -th atom in a suitable neutral atom reference state (prior to charge transfer) for the molecule.

Equating the effective chemical potential as given by (20) or (30) for all the sites, one obtains $(N-1)$ equations which are linear in the charges $\{q_a\}$ and the dipole moments $\{\mathbf{p}_a\}$ of the atomic sites. Another equation is provided by the charge neutrality of the molecule, viz.

$$\sum_{a=1}^N q_a = 0 \quad (31)$$

where the right hand side which is zero here for a neutral molecule, is to be replaced by the net charge of the molecule for an ionic species. It may be noted that these atomic charges and dipoles for the molecule in presence of the field, include contributions from interatomic charge transfer during molecule formation (from the reference state) in addition to the field-induced contributions. Writing these equations for the unperturbed molecule (using $\mathbf{f}_a^0 = 0$ and $\mathbf{E}_a = \mathbf{E}^0 = 0$), one obtains equations for the charges and dipoles due to molecule formation from the reference state. Subtraction of the corresponding equations in the two sets leads to N equations involving the induced charges and dipoles $\{dq_a\}$ and $\{d\mathbf{p}_a\}$ respectively. The final equations can be written in matrix form as

$$\sum_{b=1}^N b_{ab}^{0,0} dq_b + \sum_{b=1}^N \hat{c}_{ab}^{0,1} \cdot d\mathbf{p}_b = d_a, \quad \mathbf{a} = 1, 2, \dots, N, \quad (32)$$

where the coefficients $b_{ab}^{0,0}$, $\hat{c}_{ab}^{0,1}$ and d_a are given by

$$b_{ab}^{0,0} = (\mathbf{h}_{ab}^{0,0} - \mathbf{h}_{ba}^{0,0}) + d_{a1}, \quad (33)$$

$$\vec{c}_{ab}^{0,1} = (\mathbf{h}_{ab}^{0,1} - \mathbf{h}_{1b}^{0,1}), \quad (34)$$

$$d_a = (\mathbf{f}_1^0 - \mathbf{f}_a^0), \quad (35)$$

with $\mathbf{h}_{ab}^{0,0} = \mathbf{h}_a^0$ and $\mathbf{h}_{aa}^{0,1} = 0$ as implied. The results $b_{ab}^{0,0} = 1$, $\vec{c}_{ab}^{0,1} = 0$ and $d_a = 0$ for $\mathbf{a} = 1$ follow directly from the general results.

Analogously, (21) can be written for the induced dipoles as

$$\mathbf{dp}_a = \vec{a}_a \cdot \left(\mathbf{E}^0 - \sum_{b=1}^N \mathbf{h}_{ab}^{1,1} dq_b - \sum_{b=1}^N \mathbf{h}_{ab}^{1,1} \mathbf{dp}_b \right),$$

$$\mathbf{a} = 1, 2, \dots, N, \quad (36)$$

which can be rewritten in the general matrix form as

$$\sum_{b=1}^N \mathbf{h}_{ab}^{1,0} dq_b + \sum_{b=1}^N \mathbf{k}_{ab}^{1,1} \cdot \mathbf{dp}_b = \vec{s}_a, \quad \mathbf{a} = 1, 2, \mathbf{K}, N, \quad (37)$$

with the coefficients $\vec{h}_{ab}^{1,0}$, $\vec{k}_{ab}^{1,1}$ and \vec{s}_a given by

$$\mathbf{h}_{ab}^{1,0} = \vec{a}_a \cdot \mathbf{h}_{ab}^{1,0}, \quad (38)$$

$$\vec{k}_{ab}^{1,1} = \vec{a}_a \cdot \mathbf{h}_{ab}^{1,1}, \quad (39)$$

$$\vec{s}_a = \vec{a}_a \cdot \mathbf{E}^0. \quad (40)$$

where use has been made of the fact that $\mathbf{h}_{aa}^{1,0} = 0$ and $\mathbf{h}_{aa}^{1,1} = \vec{a}_a^{-1}$. The results $\vec{h}_{aa}^{1,0} = 0$ and $\vec{k}_{aa}^{1,1} = \vec{1}$ follow automatically for the case of $\mathbf{a} = \mathbf{b}$ from the general expressions in (38) and (39) respectively.

Thus, (32) and (37) with the coefficients defined by (33)–(35) and (38)–(40), constitute a set of $4N$ linear equations for $4N$ unknowns (charge and three components of the dipole vector for each of the N atomic sites) which can be solved to calculate the induced charges dq_a and dipoles \mathbf{dp}_a at each (\mathbf{a} -th) atomic site in the molecule. The net induced dipole moment is then calculated by evaluating the expression,

$$\mathbf{dp}_{mol} = \sum_{a=1}^N (\mathbf{R}_a dq_a + \mathbf{dp}_a), \quad (41)$$

and hence the molecular polarizability components can be calculated as

$$\mathbf{a}_{xx} = (\vec{\mathbf{p}}_{mol})_x / E_x^0, \quad \mathbf{a}_{yy} = (\mathbf{dp}_{mol})_y / E_y^0;$$

$$\mathbf{a}_{zz} = (\mathbf{dp}_{mol})_z / E_z^0 \quad (42)$$

5. Results and discussion

Thus, with all the parameters defined, we now have one scalar equation (32) and one vector equation (37) corresponding to each of the N atoms for determining the induced charges $\{dq_a\}$ and dipoles $\{\mathbf{dp}_a\}$ at these atomic sites in the molecule. The atomic parameters entering in these equations consist of the polarizability and hardness quantities of the atoms of the molecule. Although one can use available experimental or even calculated values of the atomic polarizability, when the field is applied to the molecule, it is the bonded atom which gets polarised and hence the polarizability should be effectively that of the bonded atoms which is less than that of the free atoms. We, therefore, propose to employ a multiplicative correction factor which we presently determine empirically. Analogously, the hardness parameters defined in (4) and calculated as $(I - A)/2$, within the finite difference approximation, from the experimental ionisation potential (I) and the electron affinity (A) values for the free atoms are corrected to partially account for the bonded atoms with increased hardness. For simplicity, we assume this factor to be inverse of that used for the polarizability in view of the inverse proportionality observed⁴⁹ between these two quantities. The factors for polarizability, however, are assumed to be unity in the perpendicular direction for a planar molecule and for the two perpendicular directions for a linear molecule.

Illustrative numerical calculations of the mean polarizability of several diatomic as well as polyatomic molecules have been carried out using the experimental values of the atomic polarizability and hardness parameters. However, as already indicated the polarizabilities have been scaled by a constant factor to account for the reduction in polarizability in bond formation with a parallel increase in hardness implemented through inverse of this scale factor, thus introducing only one scale parameter. The site-site charge-charge hardness $\mathbf{h}_{ab}^{0,0}$ given by (24) (or (25) in the form of an effective dielectric constant \mathbf{e}_{ab}) which corresponds to the Mataga–Nishimoto–Ohno formula has been assumed only for the bonded atom pairs. For non-bonded pairs, this hardness quantity has been given by the Coulomb approximation (23), with an empirically assumed value of the dielectric constant. Thus essentially one employs the Coulomb approximation in both cases but the dielectric constant for nonbonded atom pair is an empirical parameter while the same is an effective dielectric constant for the bonded atom pair for bonded atoms.

The other hardness quantities $\mathbf{h}_{ab}^{0,1}$, $\mathbf{h}_{ab}^{1,0}$ and $\mathbf{h}_{ab}^{1,1}$ are calculated using the expressions given by (26)–(29). These quantities determine the coefficients appearing in the linear equations (32) and (37) which are solved numerically by using the standard matrix inversion techniques to determine the induced atomic charges $\{\mathbf{dq}_a\}$ and dipole moments $\{\mathbf{dp}_a\}$ as a function of the field strength. The mean polarizability is then calculated using these calculated charges and dipoles.

The polarizability and hardness parameters as well as the correction factor \mathbf{a}_{fac} for each atom as used in the calculation has been given in table 1. These values of \mathbf{a}_{fac} are chosen so as to reproduce the experimental polarizabilities of the corresponding homonuclear diatomic molecules. Two sets of calculations have been carried out corresponding to two choices of the dielectric constant. Thus, the first corresponds to the use of an effective ϵ as given by (25), while

Table 1. Atomic parameters (in a.u.) used in the calculation.

Atom	Polarizability \mathbf{a}	Hardness \mathbf{h}	\mathbf{a}_{fac}
H	4.5	0.235	0.45
C	11.9	0.184	0.3
O	5.41	0.223	0.3
Cl	14.7	0.172	0.5

Table 2. Polarizability \mathbf{a} (in a.u.) of simple molecular systems.

Molecule	Calculated \mathbf{a}	Experimental \mathbf{a}
HCl	17.11 ^(a)	17.76
	17.12 ^(b)	
CO	12.92	13.17
	13.21	
H ₂ O	9.72	9.79
	8.54	
CO ₂	16.65	19.66
	17.42	
C ₂ H ₂	21.99	22.49
	22.25	
HCHO	15.02	18.92
	15.20	
CH ₄	20.70	17.52
	20.82	
CCl ₄	79.03	70.93
	79.29	
CH ₃ Cl	34.38	31.2
	34.51	
CHCl ₃	63.56	64.17
	63.77	

^(a)Corresponds to using an effective ϵ as defined in (25) of the text; ^(b)Obtained by using the same $\epsilon = 2.0$ for all the molecules

the second one uses the same value of $\epsilon = 2.0$ for all the molecules considered here. The calculated mean polarizabilities for a number of diatomic and polyatomic molecules are shown in table 2 alongwith the experimental results and it is clear that the agreement is quite good. It is also apparent from the two sets of the results that the calculated polarizabilities are not very sensitive to the value of the dielectric constant used. At present one empirical parameter has been used for each atom but we hope to rationalise this in terms of the different properties and charges on the atoms and also possibly the anisotropy of the bonded atom.

6. Concluding remarks

The present work reports a DFT-based chemical potential equalisation approach for the calculation of response properties of molecules in an external field. The chemical potential equalisation is done in two stages, viz. the first one during the molecule formation from isolated atoms and the second one after the external field is applied. The induced charges and dipoles at the atomic sites are calculated from a set of linear equations derived here. A unified picture, supported by a sound theoretical framework, that has thus emerged encompasses all the earlier empirical approaches for the evaluation of molecular polarizability from the atomic ones.

The calculated polarizabilities obtained here from the chosen atomic parameters are found to be in good agreement with the available experimental values. The importance of the work lies in the ease with which one can calculate the response properties which can ultimately be used for the calculation of intermolecular interactions or forces using this method. This simplicity can be immensely time saving in molecular simulation studies. Further work in this direction is in progress.

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References

1. Hohenberg P and Kohn W 1964 *Phys. Rev.* **B136** 864; Kohn W and Sham L J 1965 *Phys. Rev.* **A140** 1133
2. Parr R G and Yang W 1989 *Density functional theory of atoms and molecules* (New York: Oxford University Press)
3. March N H and Deb B M (eds) 1987 *Single particle density in physics and chemistry* (New York: Academic Press)
4. Parr R G and Yang W 1995 *Annu. Rev. Phys. Chem.* **46** 701
5. Parr R G, Donnelly R A, Levy M and Palke W E 1978 *J. Chem. Phys.* **68** 3801
6. Sen K D and Jorgensen C K (eds) 1987 *Electronegativity: Structure and bonding*, vol 66 (Berlin: Springer-Verlag)
7. Parr R G and Pearson R G 1983 *J. Am. Chem. Soc.* **105** 7512
8. Pearson R G 1973 *Hard and soft acids and bases* (Stroudsville, PA: Dowden, Hutchinson and Ross)
9. Sen K D (ed.) 1982 *Chemical hardness, structure and bonding*, vol 80 (Berlin: Springer-Verlag)
10. Fukui K 1982 *Science* **218** 747
11. Parr R G and Yang W 1984 *J. Am. Chem. Soc.* **106** 4049
12. Ghosh S K and Deb B M 1982 *Chem. Phys.* **71** 295
13. Ghanty T K and Ghosh S K 1994 *J. Am. Chem. Soc.* **116** 8801
14. Ghanty T K and Ghosh S K 1994 *J. Phys. Chem.* **98** 9197
15. Vela A and Gazquez J L 1990 *J. Am. Chem. Soc.* **112** 1490
16. Berkowitz M and Parr R G 1988 *J. Chem. Phys.* **88** 2554
17. Ghosh S K and Parr R G 1987 *Theor. Chem. Acta* **72** 379
18. Ghanty T K and Ghosh S K 1991 *J. Phys. Chem.* **95** 6512; 1992 *Inorg. Chem.* **31** 1951
19. Ghosh S K 1994 *Int. J. Quant. Chem.* **49** 239
20. Ghanty T K and Ghosh S K 1994 *J. Am. Chem. Soc.* **116** 3943
21. Ghanty T K and Ghosh S K 1994 *J. Phys. Chem.* **98** 1840
22. Mortier W, Ghosh S K and Shankar S 1986 *J. Am. Chem. Soc.* **108** 4315
23. Ghanty T K and Ghosh S K 1992 *J. Mol. Struct. Theochem.* **276** 83
24. Itskowitz P and Berkowitz M 1998 *J. Phys. Chem.* **A101** 5687; 1998 *J. Phys. Chem.* **A102** 4808
25. Rappe A K and Goddard III W A 1991 *J. Phys. Chem.* **95** 3358
26. Rick S W, Stuart S J and Berne B J 1994 *J. Chem. Phys.* **101** 6141
27. York D M and Yang W 1996 *J. Chem. Phys.* **104** 159
28. Stern H A, Kaminski G A, Banks J L, Zhou R, Berne B J and Freisner R A 1999 *J. Phys. Chem.* **B103** 4730; Banks J L, Kaminski G A, Zhou R, Mainz D T, Berne B J and Freisner R A 1999 *J. Chem. Phys.* **110** 741; Stern H A, Rittner F, Berne B J and Freisner R A 2001 *J. Chem. Phys.* **115** 2237
29. Miller K J 1990 *J. Am. Chem. Soc.* **112** 8533, 8543; Miller K J and Savchik J A 1979 *J. Am. Chem. Soc.* **101** 7206
30. No K T, Cho K H, John M S and Scheraga H A 1993 *J. Am. Chem. Soc.* **115** 2005
31. Applequist J 1977 *Acc. Chem. Res.* **10** 79; Applequist J, Carl J R and Fung K K 1972 *J. Am. Chem. Soc.* **94** 2952
32. Thole B T 1981 *Chem. Phys.* **59** 341; van Duijnen P T and Swart M 1998 *J. Phys. Chem.* **102** 2399
33. Olson M L and Sundberg K R 1978 *J. Chem. Phys.* **69** 5400
34. Applequist J 1985 *J. Chem. Phys.* **83** 809; Applequist J 1993 *J. Phys. Chem.* **97** 6016; Shanker B and Applequist J 1996 *J. Phys. Chem.* **A100** 10834; Bode K A and Applequist J 1996 *J. Phys. Chem.* **100** 17820; Applequist J 1998 *J. Phys. Chem.* **A102** 7723
35. Jensen L, Astrand P O, Sylvester-Hvid K O and Mikkelsen K V 2000 *J. Phys. Chem.* **A104**, 1563; Jensen L, Schmidt O H, Mikkelsen K V and Astrand P O 2000 *J. Phys. Chem.* **B104** 10462
36. Jensen L, Astrand P O and Mikkelsen K V 2001 *Int. J. Quantum Chem.* **84** 513
37. Dinur U 1990 *J. Phys. Chem.* **97** 7894; 1994 *J. Mol. Struct. Theochem.* **303** 227
38. Itskowitz P and Berkowitz M 1998 *J. Chem. Phys.* **109** 10142
39. Chelli R, Procacci P, Righini R and Califano S 1999 *J. Chem. Phys.* **111** 8569
40. Stone A J 1985 *Mol. Phys.* **56** 1065
41. Stone A J 1996 *The theory of intermolecular forces* (Oxford: Clarendon)
42. in het Panhuis M, Popelier P L A, Munn R W and Angyan J G 2001 *J. Chem. Phys.* **114** 7951
43. Berkowitz M, Ghosh S K and Parr R G 1985 *J. Am. Chem. Soc.* **107** 6811; Ghosh S K 1990 *Chem. Phys. Lett.* **172** 77
44. Harbola M K, Chattaraj P K and Parr R G 1991 *Israel J. Chem.* **31** 395
45. Gazquez J L and Vela A 1988 *Int. J. Quantum Chem.* **S22** 71
46. Nalewajski R F, Korchowiec J and Michalak A 1996 *Top. Curr. Chem.* **183** 25
47. Nalewajski R F, Korchowiec J and Zhou Z 1988 *Int. J. Quantum. Chem. Symp.* **22** 349
48. Mataga N and Nishimoto K 1957 *Z. Phys. Chem.* **13** 140; Ohno K 1968 *Theor. Chim. Acta* **10** 111
49. Ghanty T K and Ghosh S K 1993 *J. Phys. Chem.* **97** 4951