A coarse-grained density functional theory, chemical potential equalization and electric response in molecular systems

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ABSTRACT

A simple coarse grained description of the electron density changes in molecular systems due to change in external potential, which may include the effect of external electric fields in addition to the potential due to the nuclei, has been proposed in terms of the induced atom–atom charges and atomic dipoles. The density functional perturbation theory has been used for deriving the expressions for the interaction energy and the effective chemical potentials in terms of these coarse grained variables. A route to the calculation of these quantities and hence the dipole polarizability of the molecular system is provided. The proposed approach would also be useful for obtaining polarizable charge based force field for intermolecular interaction in computer simulation.

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1. Introduction

Density functional theory (DFT) [1] has proved itself to be a valuable tool for the quantum mechanical description of electronic structure and properties of atoms, molecules, clusters and solids. The central theme of DFT is the use of the single-particle electron density [2] as the basic variable to express the energy of a many-electron system as a unique functional of the density. Starting with the pioneering work of Hohenberg and Kohn [3], DFT has been elevated from its status of being a ground state theory to include excited states [4] and time-dependent phenomena [5]. Besides providing conceptual simplicity and computational economy, DFT has given birth to a number of important chemical concepts [1,6] and has also provided rigorous foundation to many of the existing concepts, important examples being the concepts of electronegativity [7], chemical hardness [8], Fukui function [9] and several other chemical reactivity indices [10,11].

DFT in its usual form uses the full electron density [1,2,12] function in 3D space to describe the system which itself is a tremendous simplification. However, for describing molecule formation, intermolecular interaction or interaction with external fields, further simplification is possible through a coarse graining of the electron density, viz in terms of its monopole or dipole representation, such as charges and dipoles at atomic sites. Partial atomic charges in molecules [13] have been used for describing ionic binding which was later extended to covalent binding [14] as well. Analogously the use of atomic dipoles has been proposed [15] for describing electric response of molecular systems and hence to predict the molecular polarizability. Application of these coarse grained variables has also been extended [16] to solids for describing the phonons and the response properties. Recently, both the charge and dipole variables have been jointly used [17] to describe molecular response properties. Most of these approaches, however, employ these course grained variables directly for expansion of the relevant energy quantities. There have, however, been attempts to provide a microscopic quantum mechanical picture in terms of the physically appealing electron density variable, followed by subsequent coarse graining to derive expressions for the energy and other quantities in terms of atomic charge and dipole variables [18].

The basic approach starts with a functional Taylor expansion of the energy of the system in terms of the electron density and the potential, which is then followed by suitable approximations to express the energy in terms of the coarse grained variables such as atomic charges and dipoles, which has been discussed in details recently by Wadehra and Ghosh [18]. However, the use of atomic charges as the variables has met with difficulties [19] due to super-linear dependence of the polarizability on the size of long chain and large molecular systems. The so called split charge formalism [20] in terms of charge transfer between adjacent bonded atoms has been introduced by Chelli et al. and others [21,22] as a rescue. This has recently been supplemented [23] by combining the atomic dipole variables along with the split charge variables. The approach, however, is based on expansion directly in terms of the coarse grained variables and not on a microscopic theory. Hence it is the purpose of the present work to provide a rigorous foundation of the joint split charge and dipole approach based on a functional Taylor expansion within the framework of microscopic density functional theory. The present work can thus be also con-

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sidered as an extension of our earlier work [18]. In what follows, we first discuss the theoretical formalism for molecule formation, electric response and various parametrization, and then present a few concluding remarks.

2. Theory

The central theme of DFT lies in expressing the ground state electronic energy of a many-electron system characterized by the external potential $v(\mathbf{r})$ as a unique functional $E_v[\rho(\mathbf{r})]$ of its electron density $\rho(\mathbf{r})$ as given by

$$E_v[\rho(\mathbf{r})] = \int d\mathbf{r}\rho(\mathbf{r})v(\mathbf{r}) + F[\rho(\mathbf{r})]. \tag{1}$$

Here, the external potential $v(\mathbf{r})$ usually consists of the potential due to the nuclei in the case of atoms and molecules but can include the effect of any other external source of electric field as well. The quantity $F[\rho(\mathbf{r})]$ is a universal functional of electron density and consists of kinetic, Coulomb and exchange-correlation energy components. For a fixed external potential $v(\mathbf{r})$, the energy functional $E_v[\rho(\mathbf{r})]$ assumes the minimum value at the equilibrium density, given by the solution of the Euler equation

$$\mu = \delta E_v[\rho]/\delta\rho(\mathbf{r}) = v(\mathbf{r}) + \delta F[\rho]/\delta\rho(\mathbf{r}). \tag{2}$$

The chemical potential μ, arising as a Lagrange multiplier associated with the density normalization, has been identified [7] as the electronegativity χ (with negative sign) and has played a leading role in the conceptual theory of chemical binding and reactivity [1]. While χ represents the first derivative of the energy with respect to the number of electrons N_{el}, the chemical hardness η has been identified with the corresponding second derivative and has also been expressed in terms of functional derivative with respect to the density through the concept of local hardness [24,25], viz.

$$\eta = \int d\mathbf{r} f(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') \eta(\mathbf{r}, \mathbf{r}'), \tag{3}$$

where $f(\mathbf{r})(= (\partial\rho(\mathbf{r})/\partial N_{el}))$ denotes the Fukui function [1,9] which has played an important role in the theory of chemical reactivity and $\eta(\mathbf{r}, \mathbf{r}')$ denotes the hardness kernel [24,25] defined as

$$\eta(\mathbf{r}, \mathbf{r}') = \delta^2 F[\rho]/\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}'). \tag{4}$$

Now consider a system with N_{el} electrons to be perturbed by a perturbing potential $\delta v(\mathbf{r})$ leading to the corresponding density change $\delta\rho(\mathbf{r})$. The corresponding energy change ΔE can be expressed in terms of the functional Taylor expansion

$$\begin{aligned}
\Delta E &= E_{v(\mathbf{r})+\delta v(\mathbf{r})}[\rho(\mathbf{r}) + \delta\rho(\mathbf{r})] - E_{v(\mathbf{r})}[\rho(\mathbf{r})] \\
&= \int d\mathbf{r}[\rho(\mathbf{r}) + \delta\rho(\mathbf{r})][v(\mathbf{r}) + \delta v(\mathbf{r})] + F[\rho(\mathbf{r}) + \delta\rho(\mathbf{r})] \\
&\quad - \int d\mathbf{r}\rho(\mathbf{r})v(\mathbf{r}) - F[\rho(\mathbf{r})] \\
&= \int d\mathbf{r}\delta\rho(\mathbf{r})[v(\mathbf{r}) + \delta F[\rho]/\delta\rho(\mathbf{r})] + \int d\mathbf{r}\delta v(\mathbf{r})\rho(\mathbf{r}) \\
&\quad + \int d\mathbf{r}\delta\rho(\mathbf{r})\delta v(\mathbf{r}) + (1/2)\int\int d\mathbf{r}d\mathbf{r}'\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}') \\
&\quad \times [\delta^2 F[\rho]/\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')],
\end{aligned} \tag{5}$$

which can also be rewritten as

$$\begin{aligned}
\Delta E &= \int d\mathbf{r}\delta\rho(\mathbf{r})\mu + \int d\mathbf{r}\delta v(\mathbf{r})\rho(\mathbf{r}) + \int d\mathbf{r}\delta\rho(\mathbf{r})\delta v(\mathbf{r}) \\
&\quad + (1/2)\int\int d\mathbf{r}d\mathbf{r}'\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')\eta(\mathbf{r}, \mathbf{r}').
\end{aligned} \tag{6}$$

The density change can be written as a sum of contributions due to the change in the number of electrons dN_{el} and the potential $\delta v(\mathbf{r})$,

involving the Fukui function $f(\mathbf{r})$ and the response function $\chi_o(\mathbf{r}, \mathbf{r}')$ $(= \delta\rho(\mathbf{r})/\delta v(\mathbf{r}'))$, viz.

$$\delta\rho(\mathbf{r}) = f(\mathbf{r})dNel + \int d\mathbf{r}'\delta v(\mathbf{r}')\chi_o(\mathbf{r}, \mathbf{r}'). \tag{7}$$

The corresponding chemical potential change $\Delta\mu(= \mu - \mu_o)$ can be expressed as

$$\Delta\mu = \mu - \mu_0 = \delta v(\mathbf{r}) + \int d\mathbf{r}'\delta\rho(\mathbf{r}')\eta(\mathbf{r}, \mathbf{r}'). \tag{8}$$

We now apply these general equations to the case of a N-atom molecular system at its equilibrium geometry determined by the fixed atomic positions $\{\mathbf{R}_\alpha\}$, where the subscript $\alpha = 1, \ldots N$ denotes the atoms. We first consider the formation of the molecule from the N atoms placed at the above positions and then consider the molecule to be subjected to a uniform electric field. We assume the overall density change $\delta\rho(\mathbf{r})$ of the molecule to be partitioned as a sum of atomic components $\delta\rho(\mathbf{r}) = \sum_\alpha \delta\rho_\alpha(\mathbf{r}_\alpha)$, with $\mathbf{r}_\alpha(=\mathbf{r} - \mathbf{R}_\alpha)$ denoting the atom-centered coordinate with the origin located at the αth atom. We also assume that each atomic density change $\delta\rho_\alpha(\mathbf{r}_\alpha)$ is contributed by the sum of density changes associated with other atoms bonded to this atom. Thus, we express the αth atomic density change as $\delta\rho_\alpha(\mathbf{r}_\alpha) = \sum_\beta n_{\alpha\beta}\delta\rho_{\alpha\beta}(\mathbf{r}_\alpha)$ where $\delta\rho_{\alpha\beta}(\mathbf{r}_\alpha)$ denotes the density change at the atom α (located at $\mathbf{R}_\alpha$) due to charge flow and/or density distortion through its bonding with the atom β (located at $\mathbf{R}_\beta$). The quantity $n_{\alpha\beta}$ denotes the bond occupation number (in analogy to bond order) and has the value unity ($n_{\alpha\beta} = 1$) if the atoms α and β are bonded and is zero otherwise. Here, one has $n_{\alpha\alpha} = 0$ and the summation over β defining $\delta\rho_\alpha(\mathbf{r}_\alpha)$ actually runs for $\beta \neq \alpha$. The quantity $\delta\rho_{\alpha\alpha}(\mathbf{r}_\alpha)$ is also zero which makes its integral $q_{\alpha\alpha}$ (as defined later) also zero. We have implicitly assumed, for simplicity but without loss of generality, that the density quantities $\delta\rho_\alpha(\mathbf{r}_\alpha)$ and $\delta\rho_{\alpha\beta}(\mathbf{r}_\alpha)$ vanish outside the αth atomic region although regions of different atomic subsystems can be overlapping. It may be noted that this partitioning is not unique and has been used here only to obtain coarse-grained results (after integration) in terms of the charges and dipoles at atomic sites, which are to be directly determined by solving the final equations that will be derived here.

With this partitioning of density, the energy change as given by Eq. (6) can be rewritten as

$$\begin{aligned}
\Delta E &= \sum_\alpha \sum_\beta \int d\mathbf{r}_\alpha n_{\alpha\beta}\delta\rho_{\alpha\beta}(\mathbf{r}_\alpha)\mu_\alpha^\beta + \sum_\alpha \sum_\beta \int d\mathbf{r}_\alpha\delta v_\alpha(\mathbf{r}_\alpha)\rho_\alpha(\mathbf{r}_\alpha) \\
&\quad + \sum_\alpha \sum_\beta \int d\mathbf{r}_\alpha n_{\alpha\beta}\delta\rho_{\alpha\beta}(\mathbf{r}_\alpha)\delta v_\alpha(\mathbf{r}_\alpha) \\
&\quad + (1/2)\sum_\alpha \sum_\beta \int d\mathbf{r}_\alpha n_{\alpha\beta}\delta\rho_{\alpha\beta}(\mathbf{r}_\alpha) \\
&\quad \times \sum_{\alpha'} \sum_{\beta'} \int d\mathbf{r}'_{\alpha'} n_{\alpha'\beta'}\delta\rho_{\alpha'\beta'}(\mathbf{r}'_{\alpha'})\eta(\mathbf{r}_\alpha, \mathbf{r}'_{\alpha'}),
\end{aligned} \tag{9}$$

where the chemical potential μ_α^β dictates the density change at atom α through its bonding with atom β.

The chemical potential as given by Eq. (8) can analogously be written, for the region of the αth atom, as

$$\mu_\alpha(\mathbf{r}_\alpha) = \mu_\alpha^0 + \delta v_\alpha(\mathbf{r}_\alpha) + \sum_{\alpha'} \sum_{\beta'} \int d\mathbf{r}'_{\alpha'} n_{\alpha'\beta'}\delta\rho_{\alpha'\beta'}(\mathbf{r}'_{\alpha'})\eta(\mathbf{r}_\alpha, \mathbf{r}'_{\alpha'}), \tag{10}$$

where the quantity μ_α^0 denotes the chemical potential at the atomic site α ($\mathbf{r}_\alpha = 0$).

We now consider the expansion of the density change $\delta\rho_{\alpha\beta}(\mathbf{r}_\alpha)$ in terms of spherical harmonics as given by

$$\delta\rho_{\alpha\beta}(\mathbf{r}_\alpha) = \sum_{l,m} \delta\rho_{\alpha\beta}^{l,m}(r_\alpha)Y_{l,m}(\Omega_\alpha). \tag{11}$$

The overall dipole moment of the molecule $\mathbf{p}_{mol}$ is given by the integral

$$\mathbf{p}_{mol} = \int d\mathbf{r}\, \mathbf{r}\, \delta\rho(\mathbf{r}) = \sum_\alpha \int d\mathbf{r}_\alpha\, \mathbf{r}\, \delta\rho_\alpha(\mathbf{r}_\alpha)$$

$$= \sum_\alpha \sum_\beta \int d\mathbf{r}_\alpha (\mathbf{R}_\alpha + \mathbf{r}_\alpha)\delta\rho_{\alpha\beta}(\mathbf{r}_\alpha) = \sum_\alpha \sum_\beta [\mathbf{R}_\alpha q_{\alpha\beta} + \mathbf{p}_{\alpha\beta}], \quad (12)$$

where we have used the relation $\mathbf{r}_\alpha (= \mathbf{r} - \mathbf{R}_\alpha)$ and the definitions of the charge transfer $q_{\alpha\beta}\left(= \int d\mathbf{r}_\alpha \delta\rho_{\alpha\beta}(\mathbf{r}_\alpha)\right)$ between the atoms α and β (from α to β to be more specific) and the atomic dipole $\mathbf{p}_{\alpha\beta}\left(= \int d\mathbf{r}_\alpha \mathbf{r}_\alpha \delta\rho_{\alpha\beta}(\mathbf{r}_\alpha)\right)$ centered at the αth atom, contributed by the electron density distortion resulting from bonding with atom β. Clearly the functions $\delta\rho_{\alpha\beta}^{l,m}(r_\alpha)$ will contribute to the charge for $l = m = 0$, to the z-component of the atomic dipole for $l = 1$, $m = 0$ and to the x,y-components of the atomic dipole for $l = 1$, and combinations of $m = 1$ and -1.

This prompts us to restrict to the simple expansion of the density change as a superposition of only the spherical and aspherical dipolar terms, in the spirit of the work of Chelli and Procacci [26], as

$$\delta\rho_{\alpha\beta}(\mathbf{r}_\alpha) = q_{\alpha\beta}\phi_{\alpha\beta}^s(\mathbf{r}_\alpha) + \mathbf{p}_{\alpha\beta} \cdot \boldsymbol{\phi}_{\alpha\beta}^p(\mathbf{r}_\alpha), \quad (13)$$

where the first spherical part has been written as a product of the charge transfer $q_{\alpha\beta}$ and the shape function (s-type) $\phi_{\alpha\beta}^s(\mathbf{r}_\alpha)$ normalized to unity (but with vanishing first moment), while the (p-type) vector function $\boldsymbol{\phi}_{\alpha\beta}^p(\mathbf{r}_\alpha)$ normalizes to zero but its product with each Cartesian component of $\mathbf{r}_\alpha$ (i.e. x_α, y_α or z_α) normalizes to unity. This normalization is consistent with the integrals of the density change $\delta\rho_{\alpha\beta}(\mathbf{r}_\alpha)$ and its first moment to yield respectively the charge transfer $q_{\alpha\beta}\left(= \int d\mathbf{r}_\alpha \delta\rho_{\alpha\beta}(\mathbf{r}_\alpha)\right)$ between the atoms α and β (from α to β) and the atomic dipole $\mathbf{p}_{\alpha\beta}\left(= \int d\mathbf{r}_\alpha \mathbf{r}_\alpha \delta\rho_{\alpha\beta}(\mathbf{r}_\alpha)\right)$ centered at the αth atom, contributed by the electron density distortion resulting from bonding with atom β as mentioned earlier. Typical examples for these two functions involve simple Gaussian and Gaussian multiplied by the coordinate [26]. It may be noted that a more general expansion in terms of a basis set has been considered earlier by York and Yang [27]. The overall atomic charge and dipole at the atom α is obtained by summing over the contributions from the bonded atoms $\{\beta\}$ as given by

$$q_\alpha = \sum_\beta n_{\alpha\beta} q_{\alpha\beta}; \quad \mathbf{p}_\alpha = \sum_\beta n_{\alpha\beta} \mathbf{p}_{\alpha\beta}, \quad (14)$$

and the charge conservation at the level of each bond is maintained through the relation $q_{\alpha\beta} = -q_{\beta\alpha}$.

We also consider the Taylor series expansions of the perturbing potential $\delta v_\alpha(\mathbf{r}_\alpha)$ and the hardness kernel $\eta(\mathbf{r}_\alpha, \mathbf{r}_\beta)$ around the atomic sites as given by

$$\delta v_\alpha(\mathbf{r}_\alpha) = \delta v_\alpha(\alpha) + \mathbf{r}_\alpha \cdot \nabla_\alpha \delta v_\alpha(\alpha) + (1/2)r_\alpha^2 \nabla_\alpha^2 \delta v_\alpha(\alpha) + \dots, \quad (15)$$

and

$$\eta(\mathbf{r}_\alpha, \mathbf{r}_\beta) = \eta(\alpha, \beta) + \mathbf{r}_\alpha \cdot \nabla_\alpha \eta(\alpha, \beta) + \mathbf{r}_\beta \cdot \nabla_\beta \eta(\alpha, \beta)$$
$$+ (1/2)r_\alpha^2 \nabla_\alpha^2 \eta(\alpha, \beta) + (1/2)r_\beta^2 \nabla_\beta^2 \eta(\alpha, \beta)$$
$$+ \mathbf{r}_\alpha \mathbf{r}_\beta \cdot \nabla_\alpha \nabla_\beta \eta(\alpha, \beta) + \dots, \quad (16)$$

where the arguments (α) and (α, β) indicate that the dependent quantities correspond to evaluation at the atomic sites $\alpha(\mathbf{r}_\alpha = 0)$ and sites α and $\beta(\mathbf{r}_\alpha = \mathbf{r}_\beta = 0)$.

Substituting these expressions for the density change (Eq. (13)), potential (Eq. (15)) and the hardness kernel (Eq. (16)), the expressions for the energy change (Eq. (9)) and the chemical potential (Eq. (10)) can be rewritten as

$$\Delta E = \sum_\alpha \sum_\beta \int d\mathbf{r}_\alpha n_{\alpha\beta}\left[q_{\alpha\beta}\phi_{\alpha\beta}^s(\mathbf{r}_\alpha) + \mathbf{p}_{\alpha\beta}.\phi_{\alpha\beta}^p(\mathbf{r}_\alpha)\right]\mu_\alpha^\beta$$

$$+ \sum_\alpha \sum_\beta \int d\mathbf{r}_\alpha \left[\delta v_\alpha(\alpha) + \mathbf{r}_\alpha \cdot \nabla_\alpha \delta v_\alpha(\alpha) + (1/2)r_\alpha^2 \nabla_\alpha^2 \delta v_\alpha(\alpha)\right]\rho_\alpha(\mathbf{r}_\alpha)$$

$$+ \sum_\alpha \sum_\beta \int d\mathbf{r}_\alpha n_{\alpha\beta}\left[q_{\alpha\beta}\phi_{\alpha\beta}^s(\mathbf{r}_\alpha) + \mathbf{p}_{\alpha\beta}.\phi_{\alpha\beta}^p(\mathbf{r}_\alpha)\right]$$

$$\times \left[\delta v_\alpha(\alpha) + \mathbf{r}_\alpha.\nabla_\alpha \delta v_\alpha(\alpha) + (1/2)r_\alpha^2 \nabla_\alpha^2 \delta v_\alpha(\alpha)\right]$$

$$+ (1/2)\sum_\alpha \sum_\beta \int d\mathbf{r}_\alpha n_{\alpha\beta}\left[q_{\alpha\beta}\phi_{\alpha\beta}^s(\mathbf{r}_\alpha) + \mathbf{p}_{\alpha\beta}.\phi_{\alpha\beta}^p(\mathbf{r}_\alpha)\right]$$

$$\times \sum_{\alpha'} \sum_{\beta'} \int d\mathbf{r}'_{\alpha'} n_{\alpha'\beta'}\left[q_{\alpha'\beta'}\phi_{\alpha'\beta'}^s(\mathbf{r}_{\alpha'}) + \mathbf{p}_{\alpha'\beta'}.\phi_{\alpha'\beta'}^p(\mathbf{r}_{\alpha'})\right]$$

$$\times \left[\eta(\alpha, \alpha') + \mathbf{r}_\alpha.\nabla_\alpha \eta(\alpha, \alpha') + \mathbf{r}_{\alpha'}.\nabla_{\alpha'} \eta(\alpha, \alpha') + (1/2)r_\alpha^2 \nabla_\alpha^2 \eta(\alpha, \alpha')\right.$$

$$\left. + (1/2)r_{\alpha'}^2 \nabla_{\alpha'}^2 \eta(\alpha, \alpha') + \mathbf{r}_\alpha \mathbf{r}_{\alpha'}.\nabla_\alpha \nabla_{\alpha'} \eta(\alpha, \alpha')\right], \quad (17)$$

and

$$\mu_\alpha(\mathbf{r}_\alpha) = \mu_\alpha^0 + \delta v_\alpha(\alpha) + \mathbf{r}_\alpha.\nabla_\alpha \delta v_\alpha(\alpha) + (1/2)r_\alpha^2 \nabla_\alpha^2 \delta v_\alpha(\alpha)$$

$$+ \sum_{\alpha'} \sum_{\beta'} \int d\mathbf{r}'_{\alpha'} n_{\alpha'\beta'}\left[q_{\alpha'\beta'}\phi_{\alpha'\beta'}^s(\mathbf{r}_{\alpha'}) + \mathbf{p}_{\alpha'\beta'}.\phi_{\alpha'\beta'}^p(\mathbf{r}_{\alpha'})\right]$$

$$\times [\eta(\alpha, \alpha') + \mathbf{r}_\alpha \nabla_\alpha \eta(\alpha, \alpha') + \mathbf{r}_{\alpha'}.\nabla_{\alpha'} \eta(\alpha, \alpha')$$

$$+ (1/2)r_\alpha^2 \nabla_\alpha^2 \eta(\alpha, \alpha') + (1/2)r_{\alpha'}^2 \nabla_{\alpha'}^2 \eta(\alpha, \alpha')$$

$$+ \mathbf{r}_\alpha \mathbf{r}_{\alpha'}.\nabla_\alpha \nabla_{\alpha'} \eta(\alpha, \alpha')]. \quad (18)$$

These expressions can be further simplified, in terms of the coarse grained variables $q_{\alpha\beta}$ and $\mathbf{p}_{\alpha\beta}$, by using the integrals of the functions involved, to obtain the results

$$\Delta E = \sum_\alpha \sum_\beta n_{\alpha\beta} q_{\alpha\beta} \mu_\alpha^\beta + \sum_\alpha \sum_\beta n_{\alpha\beta} q_{\alpha\beta} \delta v_\alpha(\alpha)$$

$$+ \sum_\alpha \sum_\beta n_{\alpha\beta} \mathbf{p}_{\alpha\beta} \cdot \nabla_\alpha \delta v_\alpha(\alpha) + (1/2)\sum_\alpha \sum_\beta \langle r_\alpha^2 \rangle n_{\alpha\beta} q_{\alpha\beta} \nabla_\alpha^2 \delta v_\alpha(\alpha)$$

$$+ (1/2)\sum_\alpha \sum_\beta n_{\alpha\beta} q_{\alpha\beta} \sum_{\alpha'} \sum_{\beta'} n_{\alpha'\beta'} q_{\alpha'\beta'} \eta(\alpha, \alpha')$$

$$+ (1/2)\sum_\alpha \sum_\beta n_{\alpha\beta} q_{\alpha\beta} \sum_{\alpha'} \sum_{\beta'} n_{\alpha'\beta'} \mathbf{p}_{\alpha'\beta'} \cdot \nabla_{\alpha'} \eta(\alpha, \alpha')$$

$$+ (1/2)\sum_\alpha \sum_\beta n_{\alpha\beta} \mathbf{p}_{\alpha\beta} \cdot \sum_{\alpha'} \sum_{\beta'} n_{\alpha'\beta'} q_{\alpha'\beta'} \nabla_\alpha \eta(\alpha, \alpha')$$

$$+ (1/4)\sum_\alpha \sum_\beta n_{\alpha\beta} q_{\alpha\beta} \sum_{\alpha'} \sum_{\beta'} n_{\alpha'\beta'} q_{\alpha'\beta'} \langle r_\alpha^2 \rangle \nabla_\alpha^2 \eta(\alpha, \alpha')$$

$$+ (1/4)\sum_\alpha \sum_\beta n_{\alpha\beta} q_{\alpha\beta} \sum_{\alpha'} \sum_{\beta'} n_{\alpha'\beta'} q_{\alpha'\beta'} \langle r_{\alpha'}^2 \rangle\ \nabla_{\alpha'}^2 \eta(\alpha, \alpha')$$

$$+ (1/2)\sum_\alpha \sum_\beta n_{\alpha\beta} \mathbf{p}_{\alpha\beta} \cdot \sum_{\alpha'} \sum_{\beta'} n_{\alpha'\beta'} \mathbf{p}_{\alpha'\beta'} \cdot \nabla_\alpha \nabla_{\alpha'} \eta(\alpha, \alpha'), \quad (19)$$

and

$$\mu_\alpha(\mathbf{r}_\alpha) = \mu_\alpha^0 + \delta v_\alpha(\alpha) + \mathbf{r}_\alpha \cdot \nabla_\alpha \delta v_\alpha(\alpha) + (1/2)r_\alpha^2 \nabla_\alpha^2 \delta v_\alpha(\alpha)$$

$$+ \sum_{\alpha'} \sum_{\beta'} [n_{\alpha'\beta'} q_{\alpha'\beta'} \eta(\alpha, \alpha') + n_{\alpha'\beta'} q_{\alpha'\beta'} \mathbf{r}_\alpha \cdot \nabla_\alpha \eta(\alpha, \alpha')$$

$$+ n_{\alpha'\beta'} \mathbf{p}_{\alpha'\beta'} \cdot \nabla_{\alpha'} \eta(\alpha, \alpha') + (1/2)r_\alpha^2 n_{\alpha'\beta'} q_{\alpha'\beta'} \nabla_\alpha^2 \eta(\alpha, \alpha')$$

$$+ (1/2)\langle r_{\alpha'}^2 \rangle n_{\alpha'\beta'} q_{\alpha'\beta'} \nabla_{\alpha'}^2 \eta(\alpha, \alpha')$$

$$+ n_{\alpha'\beta'} \mathbf{r}_\alpha \mathbf{p}_{\alpha'\beta'} \cdot \nabla_\alpha \nabla_{\alpha'} \eta(\alpha, \alpha')]. \quad (20)$$

The expressions for the energy change and chemical potential have thus been obtained in terms of the coarse grained density $\{q_{\alpha\beta}\}$ and dipole $\{\mathbf{p}_{\alpha\beta}\}$ variables, which however so far appear as independent quantities. We now make use of the condition of charge conservation at each bond level as given by the result

$q_{\alpha\beta} = -q_{\beta\alpha}$, for which we first consider symmetrization of the expressions [23] by an interchange of the summation index to write

$$\sum_\alpha \sum_\beta n_{\alpha\beta} q_{\alpha\beta} f_\alpha = \sum_\beta \sum_\alpha n_{\beta\alpha} q_{\beta\alpha} f_\beta = -\sum_\beta \sum_\alpha n_{\beta\alpha} q_{\alpha\beta} f_\beta, \qquad (21)$$

for a quantity f_α corresponding to the atom α, and hence obtain the result

$$\sum_\alpha \sum_\beta n_{\alpha\beta} q_{\alpha\beta} f_\alpha = (1/2)\left[\sum_\alpha \sum_\beta n_{\alpha\beta} q_{\alpha\beta} f_\alpha + \sum_\beta \sum_\alpha n_{\beta\alpha} q_{\beta\alpha} f_\beta\right]$$
$$= (1/2)\sum_\alpha \sum_\beta n_{\alpha\beta} q_{\alpha\beta} f_{\alpha\beta}, \qquad (22)$$

by making use of the charge conservation condition in the last step. Here the quantity $f_{\alpha\beta}$ is defined as $f_{\alpha\beta} = f_\alpha - f_\beta$. Also, since the variables $q_{\alpha\beta}$ and $q_{\beta\alpha}$ are negative of each other, these two variables are not independent and hence one can introduce further simplification by considering the index β to be always either greater than or less than α. This enables us to rewrite Eq. (22) as

$$\sum_\alpha \sum_\beta n_{\alpha\beta} q_{\alpha\beta} f_\alpha = \sum_\alpha \sum_{\beta > \alpha} n_{\alpha\beta} q_{\alpha\beta} f_{\alpha\beta}, \qquad (23)$$

where the condition $\beta > \alpha$ has been imposed on the right hand side of Eq. (22). Analogously, we can re-express the following type of quantity as

$$\sum_\alpha \sum_\beta n_{\alpha\beta} q_{\alpha\beta} \sum_{\alpha'} \sum_{\beta'} n_{\alpha'\beta'} q_{\alpha'\beta'} f(\alpha,\alpha')$$
$$= (1/2)\sum_\alpha \sum_\beta n_{\alpha\beta} q_{\alpha\beta} \sum_{\alpha'} \sum_{\beta'} n_{\alpha'\beta'} q_{\alpha'\beta'} f(\alpha,\alpha';\beta')$$
$$= (1/4)\sum_\alpha \sum_\beta n_{\alpha\beta} q_{\alpha\beta} \sum_{\alpha'} \sum_{\beta'} n_{\alpha'\beta'} q_{\alpha'\beta'} f(\alpha;\beta,\alpha';\beta'), \qquad (24a)$$
$$= \sum_\alpha \sum_{\beta > \alpha} n_{\alpha\beta} q_{\alpha\beta} \sum_{\alpha'} \sum_{\beta' > \alpha'} n_{\alpha'\beta'} q_{\alpha'\beta'} f(\alpha;\beta,\alpha';\beta'), \qquad (24b)$$

where the quantities $f(\alpha,\alpha';\beta')$ and $f(\alpha;\beta,\alpha';\beta')$ are defined as $f(\alpha,\alpha';\beta') = f(\alpha,\alpha') - f(\alpha,\beta')$ and $f(\alpha;\beta,\alpha';\beta') = f(\alpha,\alpha';\beta') - f(\beta,\alpha';\beta') = [f(\alpha,\alpha') - f(\alpha,\beta')] - [f(\beta,\alpha') - f(\beta,\beta')]$.

Using these expressions, the energy expression given by Eq. (19) can now be rewritten as

$$\Delta E = \sum_\alpha \sum_{\beta > \alpha} n_{\alpha\beta} q_{\alpha\beta} \mu_{\alpha\beta} + \sum_\alpha \sum_{\beta > \alpha} n_{\alpha\beta} q_{\alpha\beta} \delta v_{\alpha\beta}$$
$$+ \sum_\alpha \sum_\beta n_{\alpha\beta} \mathbf{p}_{\alpha\beta} \cdot \nabla_\alpha \delta v_\alpha(\alpha)$$
$$+ (1/2)\sum_\alpha \sum_{\beta > \alpha} n_{\alpha\beta} q_{\alpha\beta}[\langle r_\alpha^2\rangle \nabla_\alpha^2 \delta v_\alpha(\alpha) - \langle r_\beta^2\rangle \nabla_\beta^2 \delta v_\beta(\beta)]$$
$$+ (1/2)\sum_\alpha \sum_{\beta > \alpha} n_{\alpha\beta} q_{\alpha\beta} \sum_{\alpha'} \sum_{\beta' > \alpha'} n_{\alpha'\beta'} q_{\alpha'\beta'}[\eta(\alpha;\beta,\alpha';\beta') + \eta_{ex}(\alpha,\alpha',\beta,\beta')]$$
$$+ (1/2)\sum_\alpha \sum_{\beta > \alpha} n_{\alpha\beta} q_{\alpha\beta} \sum_{\alpha'} \sum_{\beta'} n_{\alpha'\beta'} \mathbf{p}_{\alpha'\beta'} \cdot [\nabla_{\alpha'}\eta(\alpha,\alpha') - \nabla_{\alpha'}\eta(\beta,\alpha')]$$
$$+ (1/2)\sum_\alpha \sum_\beta n_{\alpha\beta} \mathbf{p}_{\alpha\beta} \cdot \sum_{\alpha'} \sum_{\beta' > \alpha'} n_{\alpha'\beta'} q_{\alpha'\beta'}[\nabla_\alpha \eta(\alpha,\alpha') - \nabla_\alpha \eta(\alpha,\beta')]$$
$$+ (1/2)\sum_\alpha \sum_\beta n_{\alpha\beta} \mathbf{p}_{\alpha\beta} \sum_{\alpha'} \sum_{\beta'} n_{\alpha'\beta'} \mathbf{p}_{\alpha'\beta'} \cdot \nabla_\alpha \nabla_{\alpha'} \eta(\alpha,\alpha'). \qquad (25)$$

where the bond chemical potential $\mu_{\alpha\beta}$ is defined as $\mu_{\alpha\beta} = \mu_\alpha^\beta - \mu_\beta^\alpha$ and the term $\eta_{ex}(\alpha,\alpha',\beta,\beta')$ represents the expression

$$\eta_{ex}(\alpha,\alpha',\beta,\beta') = (1/2)\{\langle r_\alpha^2\rangle \nabla_\alpha^2[\eta(\alpha,\alpha') - \eta(\alpha,\beta')]$$
$$- \langle r_\beta^2\rangle \nabla_\beta^2[\eta(\beta,\alpha') - \eta(\beta,\beta')]$$
$$+ [\langle r_{\alpha'}^2\rangle \nabla_{\alpha'}^2 \eta(\alpha,\alpha') - \langle r_{\beta'}^2\rangle \nabla_{\beta'}^2 \eta(\alpha,\beta')]$$
$$- [\langle r_{\alpha'}^2\rangle \nabla_{\alpha'}^2 \eta(\alpha,\alpha') - \langle r_{\alpha'}^2\rangle \nabla_{\alpha'}^2 \eta(\beta,\alpha')]\}. \qquad (26)$$

This equation can be further simplified to

$$\Delta E = \sum_\alpha \sum_{\beta > \alpha} n_{\alpha\beta} q_{\alpha\beta}[\mu_{\alpha\beta} + \delta v_{\alpha\beta}] + \sum_\alpha \mathbf{p}_\alpha \cdot \nabla_\alpha \delta v_\alpha(\alpha)$$
$$+ (1/2)\sum_\alpha \sum_{\beta > \alpha} n_{\alpha\beta} q_{\alpha\beta} \sum_{\alpha'} \sum_{\beta' > \alpha'} n_{\alpha'\beta'} q_{\alpha'\beta'}[\eta(\alpha;\beta,\alpha';\beta')$$
$$+ \eta_{ex}(\alpha,\alpha',\beta,\beta')] + (1/2)\sum_\alpha \sum_{\beta > \alpha} n_{\alpha\beta} q_{\alpha\beta} \sum_{\alpha'} \mathbf{p}_{\alpha'}$$
$$\cdot [\nabla_{\alpha'}\eta(\alpha,\alpha') - \nabla_{\alpha'}\eta(\beta,\alpha')] + (1/2)\sum_\alpha \mathbf{p}_\alpha$$
$$\cdot \sum_{\alpha'} \sum_{\beta' > \alpha'} n_{\alpha'\beta'} q_{\alpha'\beta'}[\nabla_\alpha \eta(\alpha,\alpha') - \nabla_\alpha \eta(\alpha,\beta')]$$
$$+ (1/2)\sum_\alpha \mathbf{p}_\alpha \sum_{\alpha'} \mathbf{p}_{\alpha'} \cdot \nabla_\alpha \nabla_{\alpha'} \eta(\alpha,\alpha'). \qquad (27)$$

The chemical potential expression of Eq. (20) can analogously be simplified as

$$\mu_\alpha(\mathbf{r}_\alpha) = \mu_\alpha^0 + \delta v_\alpha(\alpha) + \mathbf{r}_\alpha \cdot \nabla_\alpha \delta v_\alpha(\alpha) + (1/2)r_\alpha^2 \nabla_\alpha^2 \delta v_\alpha(\alpha)$$
$$+ \sum_{\alpha'} \sum_{\beta' > \alpha'} n_{\alpha'\beta'} q_{\alpha'\beta'} \eta(\alpha,\alpha';\beta') + \mathbf{r}_\alpha \cdot \sum_{\alpha'}$$
$$\times \sum_{\beta' > \alpha'} n_{\alpha'\beta'} q_{\alpha'\beta'}[\nabla_\alpha \eta(\alpha,\alpha') - \nabla_\alpha \eta(\alpha,\beta')]$$
$$+ \sum_{\alpha'} \mathbf{p}_{\alpha'} \cdot \nabla_{\alpha'}\eta(\alpha,\alpha') + (1/2)r_\alpha^2 \sum_{\alpha'} \sum_{\beta' > \alpha'} n_{\alpha'\beta'} q_{\alpha'\beta'} \nabla_\alpha^2 \eta(\alpha,\alpha';\beta')$$
$$+ (1/2)\sum_{\alpha'} \sum_{\beta' > \alpha'} n_{\alpha'\beta'} q_{\alpha'\beta'}\{\langle r_{\alpha'}^2\rangle \nabla_{\alpha'}^2 \eta(\alpha,\alpha')$$
$$- \langle r_{\beta'}^2\rangle \nabla_{\beta'}^2 \eta(\alpha,\beta')\} + \mathbf{r}_\alpha \sum_{\alpha'} \mathbf{p}_{\alpha'} \cdot \nabla_\alpha \nabla_{\alpha'} \eta(\alpha,\alpha'). \qquad (28)$$

Since this expression for chemical potential is valid for any point $\mathbf{r}_\alpha$ in the region of αth atom, one can easily write the two equations

$$\mu_\alpha = \mu_\alpha^0 + \delta v_\alpha(\alpha) + \sum_{\alpha'} \sum_{\beta' > \alpha'} n_{\alpha'\beta'} q_{\alpha'\beta'} \eta(\alpha,\alpha';\beta')$$
$$+ \sum_{\alpha'} \mathbf{p}_{\alpha'} \cdot \nabla_{\alpha'}\eta(\alpha,\alpha') + (1/2)\sum_{\alpha'} \sum_{\beta' > \alpha'} n_{\alpha'\beta'} q_{\alpha'\beta'}\{\langle r_{\alpha'}^2\rangle \nabla_{\alpha'}^2 \eta(\alpha,\alpha')$$
$$- \langle r_{\beta'}^2\rangle \nabla_{\beta'}^2 \eta(\alpha,\beta')\}, \qquad (29a)$$

and

$$0 = \nabla_\alpha \delta v_\alpha(\alpha) + \sum_{\alpha'} \sum_{\beta' > \alpha'} n_{\alpha'\beta'} q_{\alpha'\beta'}[\nabla_\alpha \eta(\alpha,\alpha') - \nabla_\alpha \eta(\alpha,\beta')]$$
$$+ \sum_{\alpha'} \mathbf{p}_{\alpha'} \cdot \nabla_\alpha \nabla_{\alpha'} \eta(\alpha,\alpha'), \qquad (29b)$$

where higher derivatives of $\delta v_\alpha(\alpha)$ have been neglected. The equations can also be recast by separating out the diagonal term ($\alpha = \alpha'$) from the sums to indicate the contributions from the αth atom and other atoms.

One can also obtain the set of equations for the atom–atom charges and atomic dipoles by minimizing the energy expression given by Eq. (27) with respect to the variables $q_{\alpha\beta}$ and $\mathbf{p}_\alpha$.

Eqs. (29) provide a set of linear equations which can be solved to obtain the atom–atom charges and atomic dipoles from which the atomic charges can be obtained by first obtaining the charges $q_{\beta\alpha}$ from $-q_{\alpha\beta}$ and then carrying out the summation as given in Eq. (14). For non-neutral systems, the charge conservation constraint, $\sum_\alpha q_\alpha$ = total charge of the system, is to be imposed. The calculated charges and dipoles can be substituted in Eq. (27) to obtain the interaction energy. The quantity μ_α is the same for all the atoms and is to be determined during the solution process, μ_α^0 is an atomic parameter, $\eta(\alpha,\alpha)$ is the atomic self hardness term, $\eta(\alpha,\alpha')$ is the mutual atom–atom hardness which can be approximated using the explicit form of the functional $F[\rho]$. Within the electrostatic approximation (i.e. assuming the kinetic and exchange correlation contribution to cancel out or be neglected), the terms $\eta(\alpha,\alpha')$,

$\nabla_\alpha \eta(\alpha, \alpha')$ etc. can be given by the standard electrostatic results. For example, the term $\nabla_{\alpha'} \eta(\alpha, \alpha')$ represents the field, $\nabla_\alpha \nabla_{\alpha'} \eta(\alpha, \alpha')$ is the standard dipole–dipole tensor of electrostatics, with the corresponding diagonal term denoting the inverse polarizability of the atom concerned.

One may use these equations to calculate the charge and dipole quantities in two stages, initially during the formation of the molecule from isolated atoms and then under the action of a homogeneous electric field to obtain the modified charges and dipoles. Alternatively one can directly consider the modified atoms in the molecule with parameters corresponding to the atoms in the molecule with partial charges and dipoles in them, and investigate the effect of the external field. In either case, one has to solve a set of linear equations in the variables $q_{\alpha\beta}$ and $\mathbf{p}_\alpha$. Finally the overall induced dipole moment can be calculated using Eq. (12) and hence the polarizability components can be obtained as the induced dipole moment per unit field.

3. Concluding remarks

The present work has been concerned with a microscopic density functional theory based derivation of equations dealing with the induced atom–atom charge transfer and atomic dipole variables in molecular systems subjected to external fields. The approach is based on density functional perturbation theory followed by suitable coarse graining of the density based quantities and the expressions derived correspond to the interaction energy and the effective chemical potentials in terms of these coarse grained variables. The proposed approach would be useful for obtaining polarizable charge based force field for intermolecular interaction in computer simulation. The simplicity and ease of calculation based on the atom–atom charge transfer and atomic dipole variables which have already been pointed out in several earlier works can in fact be immensely time saving in calculating intermolecular polarization [28] based interaction used in molecular simulation studies. In this context, it may be worthwhile to discuss a few points about the transferability of force-field parameters which is an important issue in simulation. In the proposed approach, although transferability is not assumed for any of the quantities such as charge, dipole etc., in terms of which the interaction potential at each geometrical configuration is to be calculated, the atomic parameters such as atomic chemical potential, hardness, polarizability etc. are expected to be transferable within limits except for minor scaling required for different class of molecules. The environmental effects appear mainly through the atom–atom or bond parameters. The present work can thus augment the conventional ab-initio calculation of intermolecular potential [29] as well as simple additive models of molecular polarizability [30]. While a microscopic derivation of atomistic description of quantum systems has been presented here, work on its detailed numerical implementation and application is in progress and will be reported in future.

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