Computational Materials Science 134 (2017) 206–213

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Self-consistent charge and dipole density functional tight binding method and application to carbon-based systems

Ying Wu *, Adelina Ilie, Simon Crampin

Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom
Centre for Graphene Science, University of Bath, Bath BA2 7AY, United Kingdom

A R T I C L E I N F O

Article history:
Received 23 November 2016
Received in revised form 17 February 2017
Accepted 22 March 2017
Available online 14 April 2017

Keywords:
Dipole
DFTB
DFT
Tight-binding

A B S T R A C T

The density functional tight binding (DFTB) method is a fast, semi-empirical, total energy electronic structure method based upon and parameterized to density functional theory (DFT). The standard self-consistent charge (SCC) DFTB approximates the charge fluctuations in a system using a multipole expansion truncated to the monopole term. For systems with asymmetric charge distributions, such as might be induced by an applied external field, higher terms in the multipole expansion are likely to be important. We have extended the formalism to include dipoles (SCCD), have implemented the method computationally, and test it by calculating the response of various carbon nanotubes and fullerenes to an applied electric field. A comparison of polarizabilities with experimental data or more sophisticated DFT calculations indicates a substantial improvement over standard SCC-DFTB. We also discuss the issues surrounding parameterization of the new SCCD-DFTB scheme.

1. Introduction

To accurately calculate the electronic structure of solid state materials, the density functional theory (DFT) has proven to be a trustworthy method if used appropriately. However, for large systems DFT is increasingly expensive. For these systems, a much faster semi-empirical method based upon the DFT framework, density functional tight binding (DFTB) method [1,2], can provide insight into the physical properties with a balance of accuracy and efficiency. First generation DFTB [1] approximates the total energy as a sum of the eigenvalues of all occupied states (also known as band structure energy) and a two-body repulsive energy, which is fitted to full DFT results. With careful parametrization, this method yields insightful structural and band structure results of various systems [1] possessing relatively small charge redistribution. Elstner et al. [2] extended the method to accommodate systems with considerable charge redistribution by introducing a charge fluctuation determined self-consistently to minimize the total energy. This method, self-consistent-charge-DFTB (SCC-DFTB), fundamentally enables the treatment of charge redistribution, and exhibits better results and transferability [2,3]. Further extension of the DFTB framework are possible, e.g. as described in Ref. [4].

Standard SCC-DFTB truncates the charge fluctuation around each atom to the monopole term. For systems with significantly asymmetrical charge distributions it is natural to consider achieving greater accuracy by extending the monopole approximation to higher terms. Bodrog and Aradi [4] have proposed using tabulated multipole interaction matrices and discussed formally some of the consequences for computation of the Hamiltonian and total energy. The specific method yielding the multipole interaction matrix and the parameterization have not been presented, nor implemented or applied. Motivated by a need to model with low cost large-scale graphene/graphitic films under the influence of external fields acting on the nanoscale, we develop the extension of the standard second-order DFTB framework to dipole terms proposed in Ref. [4]. We describe and implement a method to construct and tabulate the multipole interaction matrix, discuss parameterization issues, and validate and assess the dipole extension for carbon-based systems.

2. Self-consistent charge DFTB

First, we briefly summarize the theoretical background of SCC-DFTB. From DFT theory and the Kohn-Sham ansatz [5], the charge density $n(\mathbf{r})$ in the SCC-DFTB scheme [2] is expressed as a superposition of a reference density $n_0(\mathbf{r})$ and small charge fluctuation $\delta n(\mathbf{r})$. The total energy is

---

* Corresponding author at: Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom.

E-mail address: y.wu@bath.ac.uk (Y. Wu).

http://dx.doi.org/10.1016/j.commatsci.2017.03.032

$$E[n] = \sum_k f_k \langle \Psi_k | \left(-\frac{\nabla^2}{2} + \widehat{V}_{\text{ext}} + \int d\mathbf{r}' \frac{n_0(\mathbf{r}') + \delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{xc}}[n_0 + \delta n] \right) | \Psi_k \rangle$$
$$- E_{\text{H}}[n_0 + \delta n] + E_{\text{xc}}[n_0 + \delta n] - \int d\mathbf{r} V_{\text{xc}}[n_0 + \delta n](n_0(\mathbf{r})$$
$$+ \delta n(\mathbf{r})) + E_{\text{II}}, \tag{1}$$

where f_k is the Fermi-Dirac occupation function of the state k, and Ψ_k is the corresponding single-particle wave function. $\widehat{V}_{\text{ext}}$ describes the nuclear potential acting on the electrons, $\widehat{V}_{\text{H}}[n]$ is the Hartree potential and $\widehat{V}_{\text{xc}}[n]$ is the exchange-correlation potential. $E_{\text{H}}[n]$ is the Hartree energy, E_{II} the nuclear-nuclear Coulomb energy and $E_{\text{xc}}[n]$ the exchange-correlation energy. Writing the Kohn-Sham Hamiltonian as $\widehat{H} = \widehat{H}_0 + \left(\widehat{H} - \widehat{H}_0\right)$, where $\widehat{H}_0$ refers to the system of reference charge density n_0, and expanding $E_{\text{xc}}[n_0 + \delta n]$ as a Taylor series gives the energy to second order in $\delta n(\mathbf{r})$

$$E[n] \approx \sum_k f_k \langle \Psi_k | \widehat{H}_0 | \Psi_k \rangle$$
$$+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \left. \frac{\delta^2 E_{\text{xc}}[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \right|_{n_0(\mathbf{r}), n_0(\mathbf{r}')} \right) \delta n(\mathbf{r}') \delta n(\mathbf{r})$$
$$- \int d\mathbf{r} V_{\text{xc}}[n_0] n_0(\mathbf{r}) - \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n_0(\mathbf{r}) n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n_0] + E_{\text{II}}. \tag{2}$$

The total energy comprises band structure energy E_{BS} (first term), second order energy E_{2nd} (second term) and the repulsive energy E_{rep} (remainder). The repulsive energy E_{rep} is approximately expressed as a sum of pair potentials that are a function of the distance between atoms i and j, $V_{\text{rep}}^{i,j}(R)$, the form of which is obtained by fitting to full DFT calculations [1,2,6]

$$E_{\text{rep}} = \sum_{i,j>i} V_{\text{rep}}^{i,j}(R) = \sum_{i,j>i} \left(E_{\text{DFT}}^{i,j}(R) - E_{\text{el}}^{i,j}(R) \right) \tag{3}$$

where E_{el} is the DFTB total energy without repulsive term. The band structure energy contains no contribution from charge fluctuations, with the Hamiltonian $\widehat{H}_0$ determined by the reference charge density $n_0(\mathbf{r})$, which in the DFTB scheme is constructed as a sum of atomic charge densities. Correspondingly, single-particle wave functions are expanded as linear combinations of atomic orbitals $\varphi_\mu(\mathbf{r})$,

$$\Psi_k(\mathbf{r}) = \sum_\mu c_\mu^k \varphi_\mu(\mathbf{r}). \tag{4}$$

where $\varphi_\mu(\mathbf{r}) = \varphi_\alpha(\mathbf{r} - \mathbf{R}_i)$ and composite index $\mu = (\alpha, i)$ distinguishes orbital α on atom i at $\mathbf{R}_i$. The band structure energy is

$$E_{\text{BS}} = \sum_k f_k \langle \Psi_k | \widehat{H}_0 | \Psi_k \rangle = \sum_k f_k \sum_\mu \sum_\nu c_\mu^{k*} c_\nu^k H_{\mu\nu}^0. \tag{5}$$

Composite indices $\mu = (\alpha, i)$, $\nu = (\beta, j)$ are used throughout the text below.

The atomic orbitals $\varphi_\mu(\mathbf{r})$ are determined by self-consistently solving modified Kohn-Sham equations for an isolated confined atom using DFT [5]:

$$\left[\widehat{T}_s + V_i^{\text{eff}}[n](\mathbf{r}) \right] \varphi_\mu(\mathbf{r}) = \epsilon_\mu^{\text{eff}} \varphi_\mu(\mathbf{r}), \quad \forall \mu \tag{6}$$

where the effective potential $V_i^{\text{eff}}[n](\mathbf{r})$

$$V_i^{\text{eff}}[n](\mathbf{r}) = V_{\text{ext},i}(\mathbf{r}) + V_{\text{H}}[n](\mathbf{r}) + V_{\text{xc}}^{LDA}[n](\mathbf{r}) + \left(\frac{r_i}{r_0} \right)^N, \tag{7}$$

additionally contains a confining potential introduced to improve performance [7]. $V_{\text{ext},i}(\mathbf{r})$ is the electrostatic potential from the ion i, and $r_i = |\mathbf{r}_i| = |\mathbf{r} - \mathbf{R}_i|$.

Following Ref. [1], the Hamiltonian matrix elements $H_{\mu\nu}^0$ are evaluated using the two-center approximation

$$H_{\mu\nu}^0 = \begin{cases} \epsilon_\mu^{\text{atom}} & \mu = \nu \\ \langle \varphi_\mu | \widehat{T}_s + V_i + V_j | \varphi_\nu \rangle & i \neq j \\ 0 & i = j, \mu \neq \nu. \end{cases} \tag{8}$$

V_i is the effective free atom potential of atom i given by the expression in Eq. (7) but without the confining potential. The diagonal term $\epsilon_\mu^{\text{atom}}$ is the energy eigenvalue obtained by solving Eq. (6) again omitting the confining potential.

Regarding the second order energy in Eq. (2), if the local density approximation (LDA) is used for exchange-correlation contributions, then these vanish when $\mathbf{r} \neq \mathbf{r}'$. Ignoring the on-site term of the exchange-correlation contributions, then only the electrostatic interaction from charge fluctuations remain. The fluctuation $\delta n(\mathbf{r})$ can be partitioned into atom-centered contributions $\delta n(\mathbf{r}) = \sum_i \delta n_i(\mathbf{r}_i)$, each expressed as a superposition of multipole densities $\delta n_i(\mathbf{r}) = \sum_\ell \rho_i(\mathbf{r})[\Delta Q_\ell]$, where ℓ is the number denoting the rank of the Cartesian multipole.[1] The multipole densities themselves $\rho_i(\mathbf{r})[\Delta Q_\ell]$ can be expressed in terms of a standard normalized isotropic density $\rho_i^{\text{iso}}(r)$ scaled by the multipole moment ΔQ_ℓ. For example, dipole densities can be constructed from $\rho_i^{\text{iso}}(r)$ in an analogous manner to how a standard dipole can be constructed from opposing point charges.

Standard SCC-DFTB uses the monopole approximation, in which the expansion of the density fluctuation only includes the charge difference

$$\delta n_i(\mathbf{r}) \approx \rho_i(\mathbf{r})[\Delta q_i] = \Delta q_i \rho_i^{\text{iso}}(r). \tag{9}$$

Then E_{2nd} becomes

$$E_{\text{2nd}} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \int \int \frac{\delta n_i(\mathbf{r}_i) \delta n_j(\mathbf{r}_j')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \Delta q_i \hat{\Gamma}_{ij}^{00} \Delta q_j \tag{10}$$

where

$$\hat{\Gamma}_{ij}^{00} = \int \int \frac{\rho_i^{\text{iso}}(r_i) \rho_j^{\text{iso}}(r_j')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \tag{11}$$

Analytical forms such as those based upon normalized Gaussian or exponential-decay distributions $\rho_{i,\text{GAU}}^{\text{iso}}(r) = (\sigma_i/\pi)^{3/2} e^{-\sigma_i r^2}$ and $\rho_{i,\text{EXP}}^{\text{iso}}(r) = (\tau_i^3/8\pi) e^{-\tau_i r}$ respectively, are adopted for $\rho^{\text{iso}}(r)$ to evaluate $\hat{\Gamma}_{ij}^{00}$, introducing a parameter (σ_i or τ_i) for each atom. Then

$$\hat{\Gamma}_{ij,\text{GAU}}^{00} = \begin{cases} \frac{1}{R_{ij}} \operatorname{erf}\left(\sqrt{\frac{\sigma_i \sigma_j}{\sigma_i + \sigma_j}} R_{ij} \right) & i \neq j \\ \sqrt{\frac{2\sigma_i}{\pi}} & i = j, \end{cases}$$
$$\hat{\Gamma}_{ij,\text{EXP}}^{00} = \begin{cases} \frac{1}{R_{ij}} - e^{-\tau_i R_{ij}} \left(\frac{\tau_j^4 \tau_i}{2(\tau_i^2 - \tau_j^2)^2} - \frac{\tau_j^6 - 3\tau_j^4 \tau_i^2}{(\tau_i^2 - \tau_j^2)^3 R_{ij}} \right) & \\ -e^{-\tau_j R_{ij}} \left(\frac{\tau_i^4 \tau_j}{2(\tau_j^2 - \tau_i^2)^2} - \frac{\tau_i^6 - 3\tau_i^4 \tau_j^2}{(\tau_j^2 - \tau_i^2)^3 R_{ij}} \right) & i \neq j, \tau_i \neq \tau_j \\ \frac{1}{R_{ij}} - e^{-\tau_i R_{ij}} \left(\frac{1}{R_{ij}} + \frac{11}{16} \tau_i + \frac{3}{16} \tau_i^2 R_{ij} + \frac{1}{48} \tau_i^3 R_{ij}^2 \right) & i \neq j, \tau_i = \tau_j \\ \frac{5}{16} \tau_i & i = j, \end{cases} \tag{12}$$

where $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$. The on-site value $\hat{\Gamma}_{ii}^{00}$ is directly related to σ_i (τ_i), meaning the parameter can be obtained from $\hat{\Gamma}_{ii}^{00}$ which can be approximated by the difference of ionization energy I_i and electron affinity A_i of the atom, or the Hubbard U [3]: $\hat{\Gamma}_{ii}^{00} = U_i \approx I_i - A_i$.

---

[1] For example, Q_1 denotes the dipole moment made from p_x, p_y and p_z components.