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A simplified charge transfer model: calculations using an explicit kinetic energy functional

H. Odaka[a,*], S. Ohnishi[b], S. Iwata[c]

[a]*Computer and Analysis Technology Center, Asahi Glass Co., Ltd. 1150 Hazawa-cho, Kanagawa-ku, Yokohama, 221, Japan*
[b]*NEC Fundamental Research Labs., Miyukigaoka 34 Tsukuba, Ibaraki, 305, Japan*
[c]*RACE, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 156, Japan*

Abstract

A charge transfer calculation which uses an explicit kinetic energy functional is reported. By combining the implicit Poisson equation (Andrew E. DePristo, Phy. Rev. A, 54, 3863 (1996)) with the Thomas–Fermi kinetic energy functional, we developed a new scheme to calculate charge transfer in a crystal system. The applicability of this scheme is investigated for S_nO_2 crystals, where the variation of total charge in a muffin-tin sphere is analyzed as a function of lattice constant and the results of these analyses are compared with the exact result calculated by using the full potential augmented wave method. Our new scheme is found to predict correct direction of charge transfer.

Keywords: Implicit Poisson equation; Thomas–Fermi kinetic energy functional; Charge transfer

1. Introduction

First-principle (FP) calculations provide an accurate means to calculate the electronic structures and binding energies for many material systems. As a result, FP calculations have been one of the most important tools in materials design. However, since many FP calculations depend on the Kohn–Sham (KS) one-electron-orbital framework [1], and this requires a large calculation to solve a highly non-linear complex optimization problem, prediction of material properties is a very difficult problem. While efficient methods are under development to solve this complicated optimization problem by self-consistent procedures, non-self-consistent approaches are also being investigated, especially as a simplified method to estimate material properties.

Harris proposed one of these approaches [2], where, using summed atomic densities as a starting point in the KS one-electron-orbital framework, one can calculate the total energy of materials efficiently. This method utilizes summed atomic densities to provide the external potential, and then solves the one-electron Schrodinger equation for the one-electron KS orbitals and energies in this potential. Recently, Andrew developed a new formalism [3] where the charge density distribution of the grand canonical sate can be calculated by solving an implicit Poisson equation (IPE). Since this method dose not use the KS one-electron-orbital framework to describe the kinetic energy of electrons but adopts the explicit kinetic energy functional, one can expect a more efficient calculation than the Harris functional. The feasibility of this method was tested numerically only for the atom-in-jellium system. In this study we investigate the applicability of the IPE approach in a real system by evaluating charge transfer in a crystal.

2. Method

2.1. Implicit Poisson equation

Based on the density functional theory, the total energy of a materials system can be described as a function of the electron density of $\rho(r)$

$$E(\rho(r)) = G(\rho(r)) + \frac{1}{2}\iint \frac{\rho(r)\rho(r')}{|r-r'|}\,\mathrm{d}r\,\mathrm{d}r' + \int \frac{Z_R\rho(r)}{|r-R|}\,\mathrm{d}r + \sum_{RR'} \frac{Z_R Z_R}{|R-R'|} \tag{1}$$

$$G(\rho(r)) = E_{\mathrm{KI}}(\rho(r)) + E_{\mathrm{XC}}(\rho(r))$$

Here $E_{\mathrm{KI}}(\rho(r))$ and $E_{\mathrm{XC}}(\rho(r))$ represent the kinetic and

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*Corresponding author.

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exchange-correlation energy of electrons, respectively. The variational principle, $\delta E(\rho(r))/\delta\rho(r)=0$, yields the Hohenberg–Kohn equation, subject to the constraint of a constant number of electrons,

$$V_{\mathrm{KXC}}(\rho(r)) + \int \frac{\rho(r')}{|r-r'|}\mathrm{d}r' - \sum_R \frac{Z_R}{|r-R|} = \mu \tag{2}$$

where the kinetic-exchange-correlation potential is defined as

$$V_{\mathrm{KXC}}(\rho(r)) = \frac{\delta G(\rho(r))}{\delta\rho(r)} \tag{3}$$

and the normalization condition on $\rho(r)$ is enforced by suitable choice of chemical potential μ. For an isolated atom, Eq. (3) can be written as

$$V_{\mathrm{KXC}}(\rho_R(r)) + \int \frac{\rho(r')}{|r-r'|}\mathrm{d}r' - \sum_R \frac{Z_R}{|r-R|} = \mu_R \tag{4}$$

where $\rho_R(r)$ is an atomic charge density. The redistribution of charge density caused by the condensation of atoms can be defined as the deviation from atomic density.

$$\Delta\rho(r) = \rho(r) - \sum_R \rho_R(r) \tag{5}$$

Combining Eq. (2), (4) and (5) leads to an exact implicit Poisson equation [3] (IPE).

$$\Delta\rho(r) = \frac{1}{4\pi}{}^{T^2}\left(V_{\mathrm{KXC}}\left(\sum_R \rho_R(r) + \Delta\rho(r)\right) - \sum_R V_{\mathrm{KXC}}(\rho_R(r))\right) \tag{6}$$

Assuming a Taylor series expansion of $V_{\mathrm{KXC}}(\rho(r))$ by $\rho(r)$ exists, one obtains the first order solution, $\Delta\rho^{(1)}(r)$, of Eq. (6).

$$\Delta\rho^{(1)}(r) = \frac{1}{4\pi}{}^{T^2}\left[V_{\mathrm{KXC}}\left(\sum_R \rho_R(r)\right) - \sum_R V_{\mathrm{KXC}}(\rho_R(r))\right] \tag{7}$$

This implies that the redistribution of charge density is large when the difference between the kinetic-exchange-correlation potentials is large.

In real system calculations, one can start from the $\rho_R(r)$ calculated by solving the KS equation. The Janak theorem [4] gives,

$$V_{\mathrm{KXC}}(\rho_R(r)) = \varepsilon_{\max} - \int \frac{\rho_R(r)}{|r-r'|}\,\mathrm{d}r' - \frac{Z_R}{|r-R|} \tag{8}$$

where $\varepsilon_{\max}$ is the eigenvalue of the highest occupied state.

Combining Eq. (7) with (8). we get another expression for charge redistribution.

$$\Delta\rho^{(1)}(r) = \frac{1}{4\pi}{}^{T^2}\mu(\rho(r))$$

$$\mu(\rho(r)) = V_{\mathrm{KXC}}(\rho(r)) + \int \frac{\rho(r)}{|r-r'|}\mathrm{d}r' - \sum_R \frac{Z_R}{|r-R|}$$

$$\rho(r) = \sum_R \rho_R(r-R) \tag{9}$$

This equation implies that the redistribution of the charge density is determined from the second derivative of the chemical potential function, $\mu(\rho(r))$, and grand state can be gotten on ${}^{T^2}\mu(\rho(r))=0$. The amount of charge transfer, QQ, in a close region can be calculated in terms of Gauss theorem.

$$QQ = \frac{1}{4\pi}\int \mathrm{d}S\ grad\cdot\mu(\rho(r)) \tag{10}$$

2.2. Coulomb potential analysis method

In the evaluation of Eq. (9) and (10), the most complicated problem is how to calculate non-local Coulomb energy for the sum of numerical atomic charge density. We overcame it by using a pseudo charge technique similar to Laasonen et al. [5]. In order to construct pseudo charge density, we substitute the real charge density for a pseudo charge distribution constructed using polynomials of r inside a muffin-tin sphere,

$$\rho^{\mathrm{ps}}(r) = \sum_{n=0}^{nf_{\max}} C^{2n}\left(\frac{r}{r_{\mathrm{c}}}\right)^{2n} \tag{11}$$

with the number of terms ensuring sufficient smoothness of polynomial. We want $\rho_{\mathrm{ps}}(r)$ as smooth as possible. Therefore, following lines similar to Rappe et al., we insist that the Fourier coefficients above a certain cut off wave vector G_{c} should be as small as possible. Thus, we minimize

$$I = \int_{G\mathrm{c}}^{\infty} G^4\rho^{\mathrm{ps}}(G)^2\,\mathrm{d}G \tag{12}$$

for C^{2n} where

$$\rho^{\mathrm{ps}}(G) = \int_0^{\infty} r^2\ \rho_{\mathrm{ps}}(r)J_0(r)\,\mathrm{d}r \tag{13}$$

and $J_0(r)$ is the spherical Bessel function of order 0. The minimization should be performed subject to the following continuity and multipole-moment-conservation requirements:

$$\rho^{(n)}(r_{\mathrm{c}}) = \rho^{\mathrm{ps}^{(n)}}(r_{\mathrm{c}})$$

$$\int_0^{r_{\mathrm{c}}} \rho(r)r^2\,\mathrm{d}r = \int_0^{r_{\mathrm{c}}} \rho^{\mathrm{ps}}(r)r^2\,\mathrm{d}r \tag{14}$$

$$(n = 0, 1, 2, \ldots nc_{\max})$$

where (n) indicates nth radial derivatives.

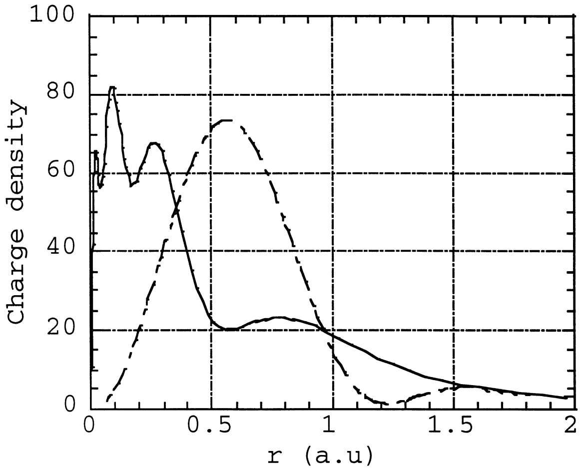

Fig. 1. Comparison of charge density in real space. The solid curve represents the original charge and the dashed curve pseudo charge.

3. Results and discussion

The applicability of IPE with the Thomas–Fermi kinetic energy functional is studied by calculating the charge transfer in a muffin-tin sphere as a function of lattice constant. This numerical test is performed in S_nO_2 crystal: the space group symmetry is $P4_2/mnm$ and the stable length of the *a* and *b* axis, 8.954 a.u. and that of the *c*-axis, 6.024 a.u. Both of the muffin-tin radii of Sn and O are set to be 1.81 a.u which is slightly smaller than the touching sphere of Sn and O of S_nO_2 whose *c*-axis is deformed to be 4.0 a.u.

In the calculation of pseudo charge density, we use $G_c = 0.0$ (see Eq. (12)), $nf_{\max} = 7$ (see Eq. (11)), and $nc_{\max}$ (see Eq. (14)) for both Sn and O. The real space representation of the pseudo charge density of Sn is compared with that of real charge density in Fig. 1. Fig. 2 shows how the Fourier coefficients of the pseudo charge density behave as a function of G^2 when optimally generated according to the above method. It is clear that the reciprocal-space representation is suitable for plane wave expansion of charge density. In the charge transfer calculation, the cutoff energy for charge density expansion is 200 Ry.

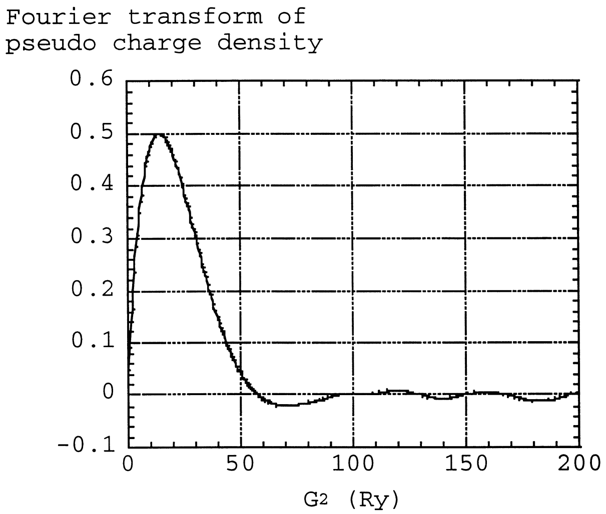

Fig. 2. Fourier transforms of pseudo charge density: *y* axis is $G^2\rho^R(G)$.

Table 1
Total charge in muffin-tin sphere

	FLAPW		IPE	
c-axis (a.u.)	Sn	O	Sn	O
4.0	46.26	8.51	46.44	8.37
4.5	46.07	8.27	46.13	7.92
5.0	45.94	8.08	45.95	7.76
5.5	45.86	7.94	45.90	7.72
6.0	45.80	7.83	45.79	7.60
6.5	45.77	7.74	45.73	7.54
7.0	45.76	7.65	45.71	7.52

In Table 1, the variation of total charge in each muffin-tin sphere is given as a function of the *c*-axis length. Full Potential Linear Augmented Plane Wave (FLAPW) method (WIEN package) [6] is used to calculate the results. The total charge of Sn and O are found to decrease with increasing *c*-axis length, respectively, i.e., the charge is shifted to the interstitial region. We can see a similar tendency of charge transfer in the calculation results of IPE with the TF kinetic energy functional. In Table 2 the components of charge transfer are shown. The charge transfer is classified into two components. The first is the tail effects of the atomic charge density excluding the self atom, i.e., $QT = \Sigma_{R \neq 0}\, \rho(r - R)$ which is tabulated in the second and fourth column in Table 2. The second is the quantum effects, defined in Eq. (10) and given in the third and fifth column in Table 2. The total charge transfer from an isolated atom in the muffin-tin sphere can, therefore, be obtained by summing *QT* and *QQ*. In the analysis of charge transfer, the overestimate of charge transfer of *QT* is corrected by *QQ* in Sn and the underestimate is

Table 2
Components of charge transfer by IPE

	Sn		O	
c-axis (a.u.)	*QT*	*QQ*	*QT*	*QQ*
4.0	0.778	−0.192	1.008	0.442
4.5	0.528	−0.249	0.776	0.225
5.0	0.367	−0.267	0.609	0.228
5.5	0.263	−0.216	0.492	0.310
6.0	0.193	−0.256	0.403	0.278
6.5	0.147	−0.273	0.338	0.282
7.0	0.118	−0.260	0.290	0.307

QT: tail effect.
QQ: quantum effect.

corrected in O. Thus, the solution of first order IPE with TF functional can predict a correct direction of charge transfer in a real crystal system.

4. Conclusions

Based on the IPE with TF kinetic energy functional, we have investigated the charge transfer in the crystal as a function of lattice constant. The total charge in the muffin-tin spheres decrease with increasing lattice constant: this tendency is in agreement with the results calculated by the full FLAPW method. The first order solution of IPE with a TF kinetic energy functional corrected the overestimate (underestimate) of charge transfer for Sn(O).

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