Issues about Self-consistent TB Charge Iteration

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1 Notation

I define dimensionless *charge* at an atomic site, q_i, as

$$q_i = \sum_{n=1}^{4M} \sum_{\alpha=1}^{4} |\langle i\alpha|\psi_n\rangle|^2 \tag{1}$$

where $|i\alpha\rangle$ is the αth atomic wave-function of atom i and $|\psi_n\rangle$ is the nth occupied wave-function. At present I take $|i\alpha\rangle$'s to be mutually orthogonal. There are M atoms with 4 valence orbital each (in the case of Si and C) in a primitive cell and we in general do not expect them to be equivalent (related by space group operations).

Apparently, q_i is related to the real charge Q_i in electromagnetic sense by

$$Q_i = -eq_i, \quad e = 1.60217733 \times 10^{-19} C. \tag{2}$$

It is very confusing to talk about Q_i and q_i at the same time, so I decide to stick to q_i always. In TB fitting we use A as length unit and eV as energy unit, so the SI formula

$$E = \frac{Q_i Q_j}{4\pi\epsilon_0 r}, \quad \epsilon_0 = 8.854187817 \times 10^{-12} F/m(\text{vacuum permittivity}) \tag{3}$$

becomes

$$E = \lambda_0 \frac{q_i q_j}{r}, \quad \lambda_0 = 14.3996517269, \tag{4}$$

where it is understood that E is in eV, r is in A.

2 Charge Quadratic Form

Following a review by Elstner *et al*[1], one can show that conventional (non self-consistent) TB scheme is first-order approximation to DFT, while self-consistent TB is second-order; and this expansion is likely to stop here because the next orders come exclusively from E_{xc} which is localized.

Given the DFT total energy functional

$$E[\rho] = \sum_n \langle\psi_n| - \frac{\nabla^2}{2}|\psi_n\rangle + V_{ext}\cdot\rho + \frac{1}{r}:\rho\rho/2 + E_{xc}[\rho] + \sum_{i\neq j}\frac{Z_iZ_j}{R_{ij}}/2, \quad \int \rho d\mathbf{r} = \sum_i Z_i, \quad (5)$$

where I use the shorthand

$$V_{ext}\cdot\rho = \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \quad \frac{1}{r}:\rho\rho = \int\int' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \quad (6)$$

A true minimization of E with respect to ρ (equal in magnitude to a density distribution of fictitious Kohn-Sham non-interacting electrons) yields the exact solution, ρ_{exact}, but it is sometimes a daunting task. So one can instead come up with a guess density ρ_0 directly based on $\{\mathbf{R}\}$ – the ion positions, close to ρ_{exact} as much as possible, and the resultant energy $E[\rho_0] \equiv V(\{\mathbf{R}\})$ can be understood as a "classical" empirical potential. ρ_0, however, is not ρ_{exact}, and one can do *much* better by expanding $E[\rho]$ around ρ_0 and seek minima from there. Define

$$\delta\rho = \rho - \rho_0, \quad (7)$$

then there is

$$E[\rho] = E[\rho_0] + \left.\frac{\delta E}{\delta\rho}\right|_0 \cdot\delta\rho + \left.\frac{\delta^2 E}{\delta\rho^2}\right|_0 : \delta\rho\delta\rho/2 + \ldots \quad (8)$$

If one approximates the landscape around ρ_0 to be linear and relaxes *once*, he obtains non self-consistent TB solution ρ_1; if one takes into account of the curvature and relaxes several times iteratively, he obtains the self-consistent TB solution[2] ρ_2. The procedure is in fact a multi-dimensional variant of Newton's method of root finding.

To first order,

$$E \approx E_1[\rho] \equiv E[\rho_0] + \left.\frac{\delta E}{\delta\rho}\right|_0 \cdot(\rho-\rho_0) = \left(E[\rho_0] - \left.\frac{\delta E}{\delta\rho}\right|_0\cdot\rho_0\right) + \left.\frac{\delta E}{\delta\rho}\right|_0\cdot\rho, \quad (9)$$

the minima of which is obtained by solving

$$\left.\frac{\delta E}{\delta\rho}\right|_0 |\psi_n\rangle = \left(-\frac{\nabla^2}{2} + V_{ext} + \frac{1}{r}:\rho_0 + \left.\frac{\delta E_{xc}}{\delta\rho}\right|_0\right)|\psi_n\rangle = \epsilon_n|\psi_n\rangle, \quad (10)$$

[1] Elstner M, Porezag D, Jungnickel G, Elsner J, Haugk M, Frauenheim T, Suhai S, Seifert G, *Physical Review* B **58** 7260-7268 (1998).

[2] Called "tight-binding" because in guessing ρ_0, one makes up the picture of each ion owning an electron cloud and ρ_0 is *some*, perhaps nonlinear, combination of these clouds.

which in local basis is a set of linear equations, and $\langle i\alpha| \left.\frac{\delta E}{\delta\rho}\right|_0 |j\beta\rangle$ are in fact just the matrix elements that are to be parameterized, consciously following the above route of thinking or not. The point is, after (10) are solved, the linear correction to (9) is entirely included in

$$E_{TB} \equiv \sum_n \epsilon_n = \sum_n \langle\psi_n|\epsilon_n|\psi_n\rangle = b\left.\frac{\delta E}{\delta\rho}\right|_0 \cdot \rho. \tag{11}$$

The leftovers,

$$E_{rep} = E[\rho_0] - \left.\frac{\delta E_{xc}}{\delta\rho}\right|_0 \cdot \rho_0 = \left(\sum_{i\neq j}\frac{Z_iZ_j}{R_{ij}} - \frac{1}{r} : \rho_0\rho_0\right)/2 + \left(E_{xc}[\rho_0] - \left.\frac{\delta E_0}{\delta\rho}\right|_0 \cdot \rho_0\right) \tag{12}$$

can be divided into two parts, E_{rep}^P (the first bracket), and E_{rep}^E (the second). Assuming ρ_0 is some simple combination of atomic orbital charge densities with *no* charge transfer, E_{rep}^P is then pair-additive and should follow the Buckingham functional form $\sum_{\alpha,\beta} e^{-\beta}/r^{\alpha}$, since the orbital densities decays so with r; and E_{rep}^E is of the embedded-atom form proposed by Daw and Baskes because it is in line with their "projected charge density" idea.

In the next order, two additional terms will be included,

$$E \approx E_2 \equiv E_1[\rho] + \Delta E = E_1[\rho] + \left.\frac{\delta^2 E_{xc}}{\delta\rho^2}\right|_0 : \delta\rho\delta\rho/2 + \frac{1}{r} : \delta\rho\delta\rho/2. \tag{13}$$

Imagine that we have a cluster of 10^3 Si and C atoms – the guess charge density ρ_0 prior to relaxation has electron density attached to each ion with 4 electrons in each, but during relaxation because E_s, E_p of C is lower than that of Si, there is a systematic trend in the cluster of electrons flowing from Si to C. If we plot $\delta\rho(\mathbf{r})$, it will be largely positive around C atoms and negative around Si atoms, so it would be helpful to decompose it as

$$\delta\rho(\mathbf{r}) = \sum_i \delta\rho_i(\mathbf{r}). \tag{14}$$

In (13), when ions $\mathbf{R}_i$ and $\mathbf{R}_j$ are far apart, the first term ceases to contribute since E_{xc} is local, while the second term, a double integral

$$\int\int' \frac{\delta\rho_i(\mathbf{r})\delta\rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \approx \frac{(\int \delta\rho_i(\mathbf{r})d\mathbf{r})(\int' \delta\rho_j(\mathbf{r}')d\mathbf{r}')}{|\mathbf{R}_i - \mathbf{R}_j|} \tag{15}$$

often can be well-approximated by "point-charge" interaction[3]. On the other hand, when $\mathbf{R}_i$ and $\mathbf{R}_j$ are nearest or second nearest neighbors, clearly (15) is not a valid approximation any more since $\delta\rho_i(\mathbf{r})$ and $\delta\rho_j(\mathbf{r}')$ overlaps – the net effect is a softening of the interaction, since, in the numerical limit of $\mathbf{R}_i \to \mathbf{R}_j$ while "freezing" $\delta\rho_i(\mathbf{r})$ and $\delta\rho_j(\mathbf{r}')$, the integral does not blowing up as $1/r$ but approaches a finite value. That is, the introduction of finite orbital size, a_i, increases the average distance between two electrons sitting on different orbitals.

[3]So long as $\int \delta\rho_i(\mathbf{r})d\mathbf{r} \neq 0$, RHS of (15) is the leading-order contribution. The next order is the "atomic polarizability" part where although there is no net transfer of charge from atom i to other atoms, its electron cloud is polarized in the direction of the electric field (one sp^3 hybridized orbital is more favored than others).

A special case of (13) and (14) is $i = j$. The effect of E_{xc} is strongest here; and the interaction, though in a slightly different flavor ("self" as opposed to $i \neq j$ interaction), numerically must be on the same smooth branch as $i \neq j$ if i and j are of the same type.

Let us define

$$\Delta q_i \equiv \int \delta\rho_i(\mathbf{r}) d\mathbf{r} = q_i - 4, \tag{16}$$

where we relate to another definition, (1). This association is not mathematically rigorous, as follows. Suppose $\psi = a_1\phi_1 + a_2\phi_2$ where ϕ_1, ϕ_2 are orthogonal. The charge density is $\rho = \psi^*\psi = a_1^*a_1\phi_1^*\phi_1 + a_2^*a_2\phi_2^*\phi_2 + (a_1^*a_2\phi_1^*\phi_2 + c.c.)$. In order to derive (16) from (14), we in fact approximate ρ as $a_1^*a_1\phi_1^*\phi_1 + a_2^*a_2\phi_2^*\phi_2$, neglecting the interference term. That is, even when the local orbitals are mutually orthogonal, a Mulliken analysis does not provide complete information about the system charge distribution – the magnitude of the interference charge density, say in the bonding direction, is *not* a simple decomposition of atomic orbital densities. However, the situation is not too bad since the interference terms are spatially fluctuating, while $a_1^*a_1\phi_1^*\phi_1$ terms are positive definite and is concentrated around the hosting atom.

We can now write down the general quadratic form of the second-order correction to the (tight-binding) total energy functional using Mulliken charges,

$$\Delta E = \sum_i \gamma_{ii}\Delta q_i^2/2 + \sum_{i\neq j} \gamma_{ij}\Delta q_i \Delta q_j/2, \quad \Delta q_i = q_i - 4, \tag{17}$$

under the following approximations:

- Local orbitals are mutually orthogonal.
- Leading order effect is charge transfer *between* atoms; charge transfer between orbitals of the *same* atom (which gives rises to atomic polarizability) is not as important.
- Interaction strength is proportional to simple products of Mulliken charges; charge density interference effects can be safely neglected.

γ_{ij} should have the following properties:

- $$\lim_{R_{ij}\to\infty} \gamma_{ij} = \frac{\lambda_0}{R_{ij}}, \tag{18}$$

  for γ_{ij} in eV and R_{ij} in A.
- If atoms i and j are of the same type, when $R_{ij} \to 0$, γ_{ij} should smoothly, perhaps monotonically, approaches the constant value of γ_{ii}.

3 U-terms

The first term (single summation) in (17) is what we call the Hubbard, or u-term. As a shorthand one writes

$$U = \sum_i u_i \Delta q_i^2/2, \quad u_i \equiv \gamma_{ii}. \tag{19}$$

For carbon u_i is on the order of $3 - 4$ eV. Because U is positive definite, it is a negative-feedback or stabilizing mechanism which is always against charge transfer.

Because it happens in LDA calculation and several other cases, it is often taken for granted that there exists a so-called *double counting* property for this problem. I shall show below that it happens *only* if u_i is the same among all atoms (and the number of valence electrons must be identical too; GaAs, for instance, will not have this property).

This issue arises because the quadratic contribution in the total energy functional is not fully included in the $E_{TB} \equiv \sum_n \epsilon_n$ summation, unlike the linear contribution, and would have to be explicitly compensated for in E_{rep}. With functional variation $\partial/(\partial\langle\psi_n|)$, one can show that the effect of (17) on band structure is merely to modify the diagonal matrix elements, as,

$$\langle i\alpha|\mathcal{H}_0|i\alpha\rangle \to \langle i\alpha|\mathcal{H}_0|i\alpha\rangle + \frac{\partial \Delta E}{\partial q_i} = \langle i\alpha|\mathcal{H}_0|i\alpha\rangle + \sum_j \gamma_{ij}\Delta q_j. \tag{20}$$

When the self-consistent charge iteration has converged and one arrive at a stable set of $\{\Delta q_i\}$, the E_{TB} summation would have increased by

$$\sum_n \epsilon_n \to \sum_n \epsilon_n + \sum_{i,j} (\gamma_{ij}\Delta q_j) q_i. \tag{21}$$

And so in order to recover the original total energy value (13), or (17), one would have to add a term in E_{rep},

$$E_{rep} \to E_{rep} + \left(\sum_{i,j} \gamma_{ij}\Delta q_i \Delta q_j/2 - \sum_{i,j} (\gamma_{ij}\Delta q_j) q_i \right). \tag{22}$$

Let us look specifically at the u-term; the compensation due to that term alone is

$$C_U \equiv \sum_i u_i \left(\Delta q_i^2/2 - \Delta q_i q_i \right) = \sum_i u_i \left((q_i - 4)^2/2 - (q_i - 4) q_i \right). \tag{23}$$

If $u_i \equiv u$ for all i, then clearly,

$$C_U = -u \sum_i (q_i - 4)^2/2 - 4u \sum_i (q_i - 4) = -U, \tag{24}$$

as $\sum_i (q_i - 4) = 0$. But otherwise $C_U = -U$ could not be arrived. The reason that this "universal" feature of LDA calculation is sometimes absent here is because instead of dealing with only the q_i's ($\rho(\mathbf{r})$ of LDA), we are dealing with hybrid of q_i and $q_i - q_i^0$'s ($q_i^0 = 4$ in this case).

4 Off-diagonal, Bare Coulomb contributions

Let us define the bare Coulomb energy contribution, C, as

$$C \equiv \sum_{i \neq j} \gamma_{ij}^C \Delta q_i \Delta q_j / 2, \quad \gamma_{ij}^C \equiv \frac{\lambda_0}{R_{ij}}. \tag{25}$$

Although $\gamma_{ij}^C \neq \gamma_{ij}$, it is useful to define C because it can be easily summed in a crystal by the Ewald summation techniques[4]. We will talk about the softening corrections $\gamma_{ij} - \gamma_{ij}^C$ for $i \neq j$ in the next section.

In a crystal, an atom in the primitive cell are replicated by the Bravais translations infinite times; so does its Δq_i. One finds it necessary to re-sum (25), where, instead of i running though the entire crystal, only runs though atoms in the primitive cell; and C will be re-defined as the bare Coulomb energy per cell. The new sum takes the form

$$C = \sum_{i,j}^{\text{primitive}} P_{ij} \Delta q_i \Delta q_j / 2L, \tag{26}$$

where L is some convenient *characteristic length* of the crystal such as lattice constant, and P_{ij} would be a constant matrix that only depends on the crystal structure (not its size). Notice that unlike (25), $i = j$ is not excluded from the (26) summation, because an atom can have Coulomb interaction with its images (not literally itself). Furthermore, the matrix $\underline{\underline{P}}$ is not unique, one can re-define $\underline{\underline{P}}$ by adding arbitrary rows or columns of $(1, 1, .., 1)$ to it without changing any real results. The reason is because, in a primitive cell,

$$\sum_i^{\text{primitive}} \Delta q_i = \sum_i^{\text{primitive}} (q_i - 4) = 0. \tag{27}$$

Using Ewald techniques, one can quickly convert (25) to (26), calculating $\underline{\underline{P}}$ for a given crystal structure. This has been implemented in my program[5], *Ewald/simple_ewald.c*. A typical P_{ij}/L [eV/A] look like

```
| -12.84698661332600 -0.2926096942631040 |
| -0.2926096942631040 -12.84698661332600 |
```

which is for 3C-SiC (ZnS) structure at $L = 4.338948$ A. Thus, given that there is positive unit Δq on C and negative unit δq on Si, the bare Coulomb energy per cell should be

[4] Toukmaji AY, Board JA, Ewald summation techniques in perspective: a survey, *Computer Physics Communications* **95** 73-92 (1996).

[5] *simple_ewald.c* does not contain the λ_0 factor, which is implemented in the main program *fitall.F*.

```
                | -12.84698661332600 -0.2926096942631040 |    ( 1 )
0.5 * (1,-1) * | -0.2926096942631040 -12.84698661332600 |    (-1 ) = -12.5543769
```

or -6.277188 eV per atom. This agrees well with the published result of Madelung constant[6] for ZnS structure, $\alpha = 1.6381$, where since the nearest neighbor distance is $r_n = 4.338948 \times \sqrt{3}/4$ A, predicts the bare Coulomb energy per cell to be

$$C = -\frac{\lambda_0 \alpha}{r_n} = 12.5547282 \ \text{eV}.$$

5 Off-diagonal, Softening contribution

We expect there is significant softening of γ_{ij} from λ_0/R_{ij} behavior at small and medium R_{ij}, such that it can smoothly turn over to a constant value at $R_{ij} = 0$, which should just be $u_i = \gamma_{ii}$ if i and j are of the same type. Since u_i for carbon is about $3-4$ eV, and $\lambda_0 \approx 14$, this turn-around should happen before $R_{ij} = 3.5 - 4.5$ A, which for diamond at equilibrium would be 4-7th nearest neighbors away. We see that the softening effect is indeed important!

The requirement for the softening term

$$S \equiv \sum_{i \neq j} (\gamma_{ij} - \gamma_{ij}^C) \Delta q_i \Delta q_j / 2 \equiv \sum_{i \neq j} S_{ij} \Delta q_i \Delta q_j / 2 \tag{28}$$

is that it must be amenable to real-space summation and cutoff schemes, which essentially means that S_{ij} must decay exponentially at large R_{ij}. A basic template for achieving such goal is to assume

$$\gamma_{ij} = \frac{\lambda_0}{R + a_0 e^{-kR}}, \quad i \neq j \tag{29}$$

with

$$u_i \equiv \frac{\lambda_0}{a_0} \tag{30}$$

if i and j are of the same species. This way,

$$S_{ij} = \frac{\lambda_0}{R + a_0 e^{-kR}} - \frac{\lambda_0}{R} = \frac{-\lambda_0 a_0 e^{-kR}}{R(R + a_0 e^{-kR})}, \tag{31}$$

which is fast decaying at large R, just like any classical pair potential.

[6]pp. 228, *Theory of Lattice Dynamics in the Harmonic Approximation*, second edition, ed. by A. A. Maradudin, E. W. Montroll, G. H. Weiss and I. P. Ipatova, (Academic Press, NY, 1971).

6 Stability Support

We see that the energy involved in the Coulomb term potentially can be quite big: for example if one puts unit charges on Si and C atoms in a typical 3C-SiC crystal, the bare Coulomb energy per atom is 6 eV. Although the problem is alleviated by the fact that the actual interaction must *not* be bare, and usually there is not as much as unit charges on atoms, it still can become a big *stability* issue in the parameter fitting stage, i.e., for some injudicious choice of parameters all charges flow to carbon during self-consistent iteration, and the program outputs crazy results.

As mentioned, the u-term is always stabilizing because it is positive definite. But first-neighbor interactions in 3C-SiC are destabilizing, since if there is charge transfer between Si and C, the total energy is reduced by that term; and second-neighbor interactions in 3C-SiC are stabilizing again, and so on. Because the intrinsic energy scale involved is so big, a delicate balance must be established between the neighboring shells, and for *all* crystal structures, be it 3C-SiC or NiAs-SiC. A slight softening of the interaction strength at one shell without corresponding measures at other shells may lead to distaster.

There may be a fundamental way out of this problem, which overthrows some of our previous assumptions. That is to add large screening to the bare Coulomb interactions at large R_{ij},

$$\frac{\gamma_{ij}}{R} \to \frac{\gamma_{ij}}{\epsilon_A R}. \tag{32}$$

This screening effect must physically come from the "atomic polarizability" part[7] which is missing in the "Mulliken approach" of (17), where the "atomic" dielectric constant, ϵ_A, is related to the susceptibility of single, isolated *atom* in vacuum. A detailed calculation is needed to estimate the possible order of magintude of this ϵ_A.

As a side remark, in analyzing the possible outcome of a softening scheme, it might be helpful to first look at the structural analysis results in *GR/*, outputs of *fitall.F*, which not only orders the interactions by separations, but also distinguishes between different screening, thus effectively dividing the neighbors of an atom into equivalent symmetry classes (see Appendix A). Another piece of related code is the revamped *Kpts/Bin/group.f*, which enumerates the space-group operations of a given crystal structure and then automatically generates the IBZ k-point mesh for E_{TB} and Mulliken charge summation. Also, before the fitting begins, *fitall.F* divides the atoms in the cell into equivalent classes by comparing their Si and C coordination numbers, so "Mulliken charges" generated by IBZ summation can be

[7] Imagine putting a pair of point test-charges in the crystal. The screened interaction energy is $1/\epsilon r$, but ϵ comes from two effects: one is accounted for in (17), where electrons flows from bulk to atoms surrounding the test charges, effectively annulling part of its q. The other effect is that the electron clouds of atoms sitting in between the two test-charges are polarized, as one hybrid orbital is more favored than other three, and that although nothing flows *out* of the atom, it nevertheless generates a dipole, just like what happens when we place an *isolated atom* in an external electric field.

symmetrized, without which are erroneous if there are non-symmorphic operations in the space-group. For details see Appendix B.

A practical measure to guarantee that unphysical charge transfer "runaways" do not happen in the fitting stage is to add a fictitious "stability support" term, T, which looks like the u-term,

$$T \equiv \sum_i \frac{\Delta q_i^{2\alpha}}{2\alpha}, \tag{33}$$

to (13), where α is some constant much greater than 1, that for small charge transfers ($\Delta q_i < 1$) its effect is almost negligible, but prohibiting large charge transfers. When we have located a good set of parameters, we can then remove the T term.

7 Conclusion

The second-order correction to the DFT total energy, starting from a certain guess charge density ρ_0, may be well-approximated by

$$\Delta E\left(\{\Delta q_i\}\right) = U + C + S + (T), \quad \Delta q_i \equiv q_i - 4, \tag{34}$$

where U is the conventional Hubbard u-term, $u_i = \gamma_{ii}$; C is the bare Coulomb energy that can be re-summed by the Ewald technique; S is the softening correction which should decay exponentially when $R \to \infty$ so it can be summed in real-space; and T is the fictitious stability support in parameter fitting stage to prevent charge iteration runaways. In general, the "double counting" property occurring in LDA is non-existent here, and one adds energy compensation

$$C_E = \Delta E - \sum_i \frac{\partial \Delta E}{\partial q_i} q_i \tag{35}$$

to E_{rep} after the iteration has converged.

The main assumptions of (17) are the reliance on Mulliken charges and the negligence of atomic polarizability; the major difficulty seems to be the large energy associated with bare Coulomb interactions, which perhaps can be assuaged by throwing away the second assumption and introduce an intrinsic, atomic dielectric constant ϵ_A.

Appendices

A Classification of Neighbors (Interactions)

We classify atom i's neighbors first by their species and then distances to i. But atoms which have the same bond length to i are not necessarily equivalent: for instance in 2H-SiC (Si ABAB stacking + C vertical shift), a Si has 12 "second-nearest neighbors", but only 6 are on the basal plane, the other 6 give a different coordination number contributions. Even those 6 are *inequivalent* as upper 3 + lower 3, although the 6 bonds themselves are equally screened for there is $i + j$ exchange symmetry.

The definition of equivalent neighbors is that if you look in the second direction, after an axial rotation the surrounding would looks exactly the same as in the first direction, which means that the two neighbors can be related by a point group operations centered on i. A full implementation of this definition is feasible (*Kpts/Bin/group.f*) but time-consuming. Instead, I implement in the code *fitall.F* a complicated checksum of screening atoms to ij bond that would remain invariant under axial rotations, so as to verify that j indeed looks the same to i as k to i. And if so j and k would belong to the same equivalent class of atom i's neighbors. This classification result is very helpful for thorough human understanding of the structure, such as frozen phonons. It is also an error-checker.

B Symmetrization of IBZ-summed Mulliken Charges

Although IBZ $\mathbf{k}$-point mesh with proper weights is sufficient for total energy summation, it can lead to erroneous results in LDOS (Mulliken charges) summation if the symmetry operations used in generating the IBZ $\mathbf{k}$-point mesh contain non-primitive translations (non-symmorphic); such as two Si atoms in a 2H-SiC cell, though physically equivalent, may have different IBZ-summed charges. The reason is that although $\mathcal{O}\psi(\mathbf{k}) \equiv \psi(\mathcal{O}\mathbf{k})$ has the same energy as $\psi(\mathbf{k})$, the partial charge on atom i due to $\psi(\mathbf{k})$ could shift to an equivalent but different atom after the $\mathcal{O}\psi(\mathbf{k})$ operation; thus although $\sum_{BZ} E(\mathbf{k}) = \sum_{IBZ} w_{\mathbf{k}} E(\mathbf{k})$, and $\sum_{BZ} \rho(\mathbf{k}, \mathbf{x})$ has the full symmetry of the crystal, $\sum_{IBZ} w_{\mathbf{k}} \rho(\mathbf{k}, \mathbf{x})$ may not.

The above problem admits a simple solution: one can show that charges belonging to one equivalent class of atoms (two Si above) never goes to other classes in any transformation, so one just needs to symmetrize within each class the IBZ-summed charges in order to obtain the actual charges that have full symmetry of the system. To determine equivalent atomic classes without going through the trouble of generating and applying space-group operations (*Kpts/Bin/group.f*), let me use a "quick and dirty" trick of comparing coordination numbers, defined by quantifying the screening concept[8]. An agreement to the sixth digit in both Si and C coordination numbers is a sound guarantee (against accident) that the two atoms are actually equivalent, and should have the same charge.

[8]Environment-dependent tight-binding potential model, Tang MS, Wang CZ, Chan CT, Ho KM *Physical Review* B **53** 979-982 (1996).