Summary of Collaboration at Ames Lab from June 11 to July 3, 1997

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The purpose of my second visit to Ames (first visit July 17 to Aug 1 '96) is to continue the collaboration between Ames Lab (K. M. Ho, C. Z. Wang) and MIT (S. Yip, J. Li, L. Porter) to develop a unified tight-binding model for Si/C systems. In the previous year we have generated a sufficient LDA database for SiC in various crystalline phases which combined with the established model for pure Si and C [1], will enable us to start the work. New TB fitting codes were developed based on the scaffold of a Generic Parameter Table (see report I, page 12) which is the obvious extension of pure system models. The complete table will have more than 200 parameters, but most of them (at least at the initial stage of fitting) are treated as degenerate to the pure systems, that in the end we only have 21 new parameters to fit for the electronic band structure part, and seperately another 15 parameters or so for the repulsive terms.

The program for fitting the band structure was written by me. Dr. Lisa Porter used it (/home/porter/main.dir/finalcodes.dir/fitbands.3rcuts.f) during her visit to Ames (Aug '96) and got an average error of about 0.72 eV for the band structure of SiC in 3C (5 volumes), 2H, CsCl, NaCl, NiAs and anti-NiAs phases, which included several conduction bands with smaller weights. She then revised a code from Ames Lab to get the Fermi energy of each phase, by sampling weighted **k**-points (100 $\sim$ 300 of them) to get a discrete spectrum, and then Gaussian broaden each eigenvalue to width δ into a continuous spectrum. After the Fermi level was located, integration was carried out below ϵ_F to get the band structure energy E_{BS} at 0K (./calc.ebs3.f). She then feed these information into a similiar optimization program (./fitrep.newSi.3rcuts.f) to fit the repulsive term E_{rep}. Prelinminary results gave an average error of about 0.66 eV for the total energy curve of these structures. However, a few bugs were later found in the program.

The first task I faced was to understand the codes calculating ϵ_F and E_{BS}, and if necessary revise to make them work better. This is detailed in section 1; Due to charge transfer between

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[1] *Environment-dependent tight-binding potential model* by M. S. Tang, C. Z. Wang, C. T. Chan and K. M. Ho, Phys. Rev. B **53** 979 (1996)

Si and C, long range Coulomb interactions may have to be taken into account in the model in order to display, beside many things, lattice dynamical effects such as LO-TO splitting. Thus partial charges Z_i^* on atomic sites were calculated using the optimized electronic band parameters for each phase. An easy-to-use, high-accuracy Ewald summation routine was developed to calculate the total energy, force, stress tensor and the dynamical matrix of a general PBC triclinic rigid-ion system. However, the Coulomb term we invoke in the total energy functional is not a rigid-ion model, additional care should be taken in this aspect. This part is detailed in section 2 and 4; The nonlinear optimization subroutine we are currently using is MINA, developed in 1978 and may be obsolete. Many public domain optimization packages exist nowadays on the web, so I took some time to look for alternatives. One of them, Adaptive Simulated Annealing (ASA) developed by Lester Ingber 1993-1997 seems up to date and was successfully ported to our programs: it is certainly working, but its effectiveness needs to be benchmarked. And then the next step was to combine all the work above into a single code which can do both the optimization and all the following property calculations (its output files **.out* directly feed into the repulsive term optimization). This part is detailed in section 3. And then in the end total energy fitting is discussed, in section 4, where an average error of about 0.2 eV is obtained for the five crystalline structures of SiC with composition ratio 1:1.

One remark about interaction cutoffs: currently we are using a direct cutoff method for interaction strength $H(r)$, of the form

$$\tilde{H}(r) = \begin{cases} H(r) & 0 < r < r_1 \\ H(r)\cos^2\left(\frac{\pi(r-r_1)}{2(r_2-r_1)}\right) & r_1 < r < r_2 \\ 0 & r_2 < r \end{cases}$$

which is continuous in both value and derivative. A unified set of (r_1,r_2), 4.8 and 5.2 $\dot{A}$ for Si-Si, 3.2 and 3.6 $\dot{A}$ for C-C, 3.8 and 4.2 $\dot{A}$ for Si-C pair are being used for all kinds of interaction strengths (they are chosen to be a little smaller than the lattice constant of respective diamond cubic phase). Theoretically, a similiar smoother should also be applied to the screening contributions in order to completely avoid discontinuities in the Hamiltonian; however since the effect is so small it is neglected. There is another kind of cutoff scheme, the indirect kind, which applies to R(the reduced distance) instead of r, because atoms in low coordination structures (such as surfaces) naturally "see" farther. This arrangement sounds very convincing to me.

I am grateful to the Ames Lab for dispensing the travelling and local expenses of this visit, and for providing this wonderful collaboration opportunity. Special thanks to C.Z. whose intellectual guidance and hospitality as host make this visit a great experience for me.

1 Fermi Level and the Band Structure Energy

The band structure energy E_{BS}, due to electron occupation, is the unique feature of TB model. It corresponds to the single-(quasi)particle energy under self-consistent field in DFT: the total energy functional indeed includes a term which is the summation of all quasi-particle eigenvalues below the Fermi level. All other terms in the functional are local (EAM-like) except for possible dipole-dipole Ewald summation. Were we to directly model (parameterize) the effect of the summation of occupied eigenvalues, as classical potentials try to do, it will be rather difficult, as anyone who has dealt with matrices knows the tricky ways eigenvalues can vary. Sometimes the change is not even smooth, such as in level crossing. Spontaneous symmetry breaking may happen as in Jahn-Teller distortion. All these mean that it will require a lot of parameters, and sometimes quite impossible, for classical potential to model these strange effects. It will be easier to parameterize the matrix elements instead of the eigenvalues because matrix elements vary much more regularly; and if we have the intuition to tell roughly how the trend goes, we often get surprisingly good results.

In order to get E_{BS}, we have to sample **k**-points in BZ of the periodic cell (although in MD simulation often only Γ-point is needed because we have a large supercell). The way we do it here is regular meshing. If the system has certain symmetry (rotational part α of any space-group operation $\{\alpha|\mathbf{R}\}$) then only sampling the irreducible BZ will be enough. For discrete mesh there is the problem of weights because certain high symmetry **k**-point should have smaller weight.

A set of programs to automatically identify group symmetry [2] and generate corresponding **k**-points in the irreducible BZ are stored in "/farm2/liju/TB/Lisa/kpts.dir/". The ready to use **k**-point files are stored in "/farm2/liju/TB/Fitband/Kpts/", where the four column are (k_x, k_y, k_z) in terms of π/A (A is the characteristic length such as lattice constant in cubic structures or the equilateral triangle edge of the basal plane in hexagonal structure) and the weight of that **k**-point.

We shall collect all the eigenvalues of those **k**-points (K of them and the cell has N atoms) $\{\epsilon_i\}, i = 1..4NK$. Under Gaussian broadening with linewidth δ, let us define continuous density of states

$$\rho(\epsilon) = (4NK)^{-1} \sum_{i=1}^{4NK} \frac{1}{\sqrt{2\pi}\delta} \exp(-\frac{(\epsilon - \epsilon_i)^2}{2\delta^2})$$

such that

$$\int_{-\infty}^{+\infty} \rho(\epsilon) d\epsilon = 1$$

The Fermi level ϵ_F is defined to be where

$$\int_{-\infty}^{\epsilon_F} \rho(\epsilon) d\epsilon = \frac{1}{2}$$

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[2] The idea seems to be first extending the structure in three dimensions, and then look for possible atom to atom mappings (finite number of them) which conserves norm.

for 4-4 semiconductors. LHS can be explicitly written as

$$P(\epsilon_F) = (8NK)^{-1} \sum_{i=1}^{4NK} [1 + \mathrm{erf}(\frac{\epsilon_F - \epsilon_i}{\sqrt{2}\delta})]$$

where the error function is defined as

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-\eta^2) d\eta$$

and ranging from -1 to 1 as x goes from $-\infty$ to $+\infty$.

Theoretically, solving this nonlinear equation with non-decreasing $P(\epsilon)$ calls for the use of Newton's method (which has quadratic convergence) because the derivative of $P(\epsilon)$ is simply

$$P'(\epsilon) = \rho(\epsilon)$$

The problem is that it may (often) occur that $\rho(\epsilon)$ is very very small and $P(\epsilon)$ has a stair-like behaviour. We can combine the more stable "partition" algorithm with Newton's method to produce a fast yet robust routine: we shall first bracket ϵ_F between two ϵ_i's (called ϵ_L and ϵ_H, respectively). If a Newton's search exceeds either brackets we will suggest the new guess to be $(\epsilon_L + \epsilon_H)/2$, and we shall always update ϵ_L and ϵ_H.

After ϵ_F is located, we can calculate E_{BS}. For consistency we should stick to the same continuous $\rho(\epsilon)$. Thus,

$$\begin{aligned} E_{BS} &= 8N \cdot \int_{-\infty}^{\epsilon_F} \epsilon \rho(\epsilon) d\epsilon \\ &= 8N \left\{ -\delta^2 \rho(\epsilon_F) + (8NK)^{-1} \sum_{i=1}^{4NK} \epsilon_i [1 + \mathrm{erf}(\frac{\epsilon_F - \epsilon_i}{\sqrt{2}\delta})] \right\} \qquad (1) \end{aligned}$$

2 Coulomb Interactions

There are a lot of subtleties involving Coulomb interaction which even today I do not fully understand. One reason is that we have to simulate an infinite system (well, $\sim 10^{23}$ atoms with complicated boundaries) with a small cell ($\sim 10^3$ atoms), most often under PBC. The prodecure which relates simulation results to real world is often overlooked, thus leading to wrong or irrelevant conclusions. The rationale for using PBC is because in the limit of stacking infinitely many replicas of the small cell, the surface to volume ratio of the entire system decreases, which usually means that the exact condition of the surface and the "surface energy" will become relatively less important and we can only account for the bulk. Not so for Coulomb interactions, where macroscopic electric field might be set up throughout the bulk depending on surface conditions, which induces total energy change on the order of volume, not (volume)$^{2/3}$. In terms of mathematics, Coulomb interactions are *conditionally convergent*, while short ranged interactions such as the Lennard Jones potential are *absolutely convergent*. This is understood as follows: consider stacking identical copies of small cell of ions (with total charge summed to zero) in empty space (vaccum). The ions interact with each other through $q_i q_j / r_{ij}$. At any specific stage of the stacking the system is finite, and we can sum over all the interactions to get the total energy, and then divide by the number of cells to get the average energy, or energy per cell. Was the interaction to be short-ranged such as the Lennard Jones potential, this average energy would *not depend on the ways of stacking* as long as the span in any direction goes to infinity, i.e., it wouldn't matter if we stacks the cells as a big cube, a big sphere (roughly) or a big ellipsoid (roughly). But with Coulomb interactions the three stacking configurations lead to three different limits of energy per cell.

What is the case in nature? does a crystal have different energies depending on its geometrical shape? maybe, but we should keep in mind that the actual crystal, even if it doesn't have internal defects which disrupt the periodicity, will have much more complicated surface conditions by abrasion and chemisorption. It is not the perfectly stacked small cells at all.

The computational aspect of this is that if we indeed carry out the summation in the stacking experiment, its convergence is very slow. That was the reason Ewald summation technique was invented. The physical interpretation of Ewald summation[3] is that we screen each ion by a Gaussian charged cloud of the opposite sign: because of the screening the real space summation converges much faster. The extra interactions can be accounted for by transforming into a reciprocal space summation, which also has fast convergence. De Leeuw, Perram and Smith proved in 1980[4] that the original Ewald summation formula corresponds to stacking infinitely many replicas of the cell in a nearly-spherical manner, with conductive medium outside ($\epsilon_{\text{out}} = \infty$). Thus surface charge distribution is neutralized and there is no static *uniform* macroscopic electric field. It is the only self-consistent setup for both static and MD calculations using PBC.

For formulaes to calculate the total energy, force and stress tensor, see "/farm2/liju/Ewald/Doc/moldy.ps". However it is strongly believed that there is a typo in Eqn (2.19), (2.20) and (2.24), where a factor of 2 is missing and $\mathbf{k} > 0$ should be $\mathbf{k} \neq 0$ in the 2nd (the reciprocal summation) term, unless the author meant to utilize the inversion symmetry of the **k**-points and only sum over half of them.

A lattice wave is an issue decidedly different from the static calculations using PBC. None of the conditional convergence problem is present as long as $1/k$ is much smaller than the sample size, which would not be defined anyway by then. With that constraint but as $k \to 0$, another signature arises: LO-TO splitting [5]. For short ranged interactions, when $1/k >>$ the interaction range, one atom can not distinguish between longitudinal (variation

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[3] see *Computer Simulation of Liquids* by M. P. Allen and D. J. Tildesley, Clarendon, New York, (1987).

[4] S. W. de Leeuw, J. W. Perram and E. R. Smith, Proc. Roy. Soc. Lond. A, **373**, 27 (1980)

[5] see pg 218, *Electronic Structure and the Properties of Solids* by W. A. Harrison, Dover, New York (1989) for a lucid explanation

of distortion parallel to the distortion) or transverse (variation of distortion perpendicular to the distortion) modes. It is only concerned with the local distortion scenario and thus the restoration forces and consequently the eigen-frequencies are the same for LO and TO. Not so for Coulomb interactions: the lattice mode creates a polarization field $\mathbf{P}\exp(i(\mathbf{k}\cdot\mathbf{r}-\omega t))$[6]. A charge density wave could be induced by virtue of $\rho(\mathbf{r}) = -\nabla\cdot\mathbf{P}(\mathbf{r})$, depending on $\mathbf{k}\cdot\mathbf{P}$ is zero or not. The charge density wave in turn induces a macroscopic electric field[7] with *finite* wavelength, and alters the restoration force on the LO mode. This is the reason for LO-TO splitting.

The form of the force constant matrix due to Coulomb interactions in a rigid-ion model is given in pg 209, *Theory of Lattice Dynamics in the Harmonic Approximation* by A. A. Maradudin, E. W. Montroll and G. H. Weiss, Solid State Physics Supplement 3, Academic Press, New York (1971). Our macroscopic electrostatics argument in the above paragraph has been rigorously confirmed by lattice summation calculations using the Ewald method in $k \to 0$ limit.

A high precision, easy-to-use routine (/farm2/liju/Ewald/ewald.c) to do the Ewald summation was developed. An example driver program (./driver.f) was also given, where we calculated the Madelung constant for several structures, all of which agrees with known results (pg 228, Maradudin) to the last digit. For compilation details see ./Makefile, or type

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% make help
```

The *make* utility is used to specify machine dependencies and to avoid repetitious compilations. To compile, type

```
% setenv SYS ‘uname‘; make
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To run, type

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% make run
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A parameter α is needed to specify the relative importance between real and reciprocal space summations. The bigger the α is, the faster (slower) the convergence of real (reciprocal) space summations. Depending on the rate of convergence, cutoffs need to be chosen for both summations. A formula was given by D. Fincham, Molecular Simulation **13** 1-9

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[6] Note that although $k \to 0$, $e^{i\mathbf{k}\cdot\mathbf{r}}$ can not be treated as 1 because $\mathbf{r}$ varies on the range of sample size.

[7] This electric field is actuated by polarization density caused by atomic displacements, but once it becomes established the electrons are further relaxed. So the actual forces on atoms are proportional to the *screened* electric field, scaled by the electron dielectric constant $1/\epsilon_{\mathrm{electron}}(\omega = 0)$. Here $\omega = 0$ is with respect to the electrons.

(1994) to minimize the computation time for a given numerical accuracy (total time has $N^{3/2}$ scaling). However, I found that to achieve the claimed accuracy for certain types of quantities, additional coefficients need to be multiplied in front. They can be specified at compilation time by setting flags _ALPHA, _RCUT or _KCUT to desired ratios. If not, default will be used which usually guarantees satisfactory accuracy. You can also chose to save computation time sometime by defining _TABULATE_SIN and _TABULATE_ERFC to tabulate the sin/cos and error functions.

Because the method is complicated, the code can not be considered bug free yet. However it did pass several sanity checks. The Madelung constant calculations confirm the potential energy summation is correct; A mini-MD program (./driver2.c) was written to test the force calculations: the total energy is conserved to the 7th digit as the potential energy varies to the 2nd digit; A special theorem was used to test the stress calculation: because $V(r) \propto 1/r$, there must be $V/\Omega = \sum_{i=1}^{3} \tau_{ii}$; The dynamical matrix calculation and the diagonalization subroutine in $\mathbf{k}$-space was tested in two ways: first the LO-TO splitting formula was verified[8]; the second test is the so called Blackman's sum rule (pg 228, Maradudin), as $\sum_j \omega_j^2(\mathbf{k}) = 0$ because $1/r$ potential is harmonic.

We now come to the question of how to account for the Coulomb interactions in our TB model. From the physical picture of LCAO, the first thing we calculate is the partial charge Z^* (charge transfer) on each atomic site by summing over occupied states. This leads to $Z^* \approx 1.7$ for zero pressure 3C-SiC using our current parameters. In the limit of infinite lattice constant, Z^* will goes to 2 with our model because Si p-level is the highest, so occupied orbitals will be $\mathrm{C}(2s^2 2p^4)$ and $\mathrm{Si}(3s^2)$, which means that the big volume limit of the total energy curve for SiC is $\mathrm{Si}^{2+}/\mathrm{C}^{2-}$, not neutral Si/C. This would not happen in nature, as the first and second ionization energy of Si are 786.5 kJ/mol and 1577.1 kJ/mol respectively, while the (first) electron affinity energy is only 121.9 kJ/mol for C[9]. It is not clear to me what would happen in LDA calculations: theoretically as long as the HOMO of isolated Si and C are not equal (in fact they are not, for atoms), there will be charge transfer. Does this mean that there will be fractional charge transfer? Reconsidering our TB model, it seems that in order to avoid the (in reality) incredibly high energy $\mathrm{Si}^{2+}/\mathrm{C}^{2-}$ state would require the u-term in self-energy expression, to set up a negative feedback mechanism, as in LDA.

When atoms move, there will be another problem: dynamic charge transfer (see pg 219, Harrison). The so-called *transverse charge* e_T^* is different from Z^*, linked by relation (9-24) in Harrison (of course the formula is not exact but from his simple TB model). We see that the long range effect (change of forces on other atoms) of infinitesimal charge transfer occuring in a finite region, due to the infinitesimal displacement of one atom, is equivalent to that of the displacement itself, both by creating a small dipole upon the original structure. For a tetrahedral system or systems with high symmetry, that dipole created by dynamic

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[8] Because we are using a rigid-ion model, the electronic dielectric consant in (9-22) of Harrison is 1.

[9] This information can be obtained from http://www.shef.ac.uk/uni/academic/A-C/chem/web-elements/, along with other properties.

charge transfer must also be in the direction of the displacement, thus defining an effective charge e_T^* is entirely legal.

Formally, the polarization density of $\mathbf{k} \to 0$ phonon can be written as

$$\begin{aligned} \mathbf{P}(\mathbf{r}) &= e_T^*(\mathbf{u}_1 - \mathbf{u}_2)e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)}/\Omega \\ &= e_T^*\mathbf{u} \end{aligned} \tag{2}$$

where we use $\mathbf{u}$ to denote the lattice displacement coordinate. Everything could be explained by a simple Hamiltonian model for the system

$$\mathcal{H} = \frac{1}{2\chi}(\mathbf{P} - e_T^*\mathbf{u})^2 - \mathbf{E}\cdot\mathbf{P} \tag{3}$$

where $\mathbf{E}$ is taken to be a *constant* electric field[10], and χ is the electron dielectric susceptibility. $\mathbf{P}$ is used to denote the collective electron behavior, it is always relaxed first. We see that when $\mathbf{E}$ is zero, $\mathcal{H}$ takes minimum at $\mathbf{P} = e_T^*\mathbf{u}$, and the minima is always 0 (no force constant contribution to $\mathbf{u}$). When $\mathbf{u}$ is fixed at 0, the minimum happens at $\mathbf{P} = \chi\mathbf{E}$, conforming to the definition of electron dielectric susceptibility.

The situation for phonon is a little different. $\mathbf{E}$ now depends on $\mathbf{P}$ itself, and on $\mathbf{k}$. If $\mathbf{k}$ is perpendicular to $\mathbf{P}$, $\mathbf{E} = 0$; if parallel then $\mathbf{E} = -4\pi\mathbf{P}$. Also because it is self-interaction, the second term of (3) should be divided by 2. Thus,

$$\mathcal{H} = \frac{1}{2\chi}(\mathbf{P} - e_T^*\mathbf{u})^2 + 2\pi\mathbf{P}\cdot\mathbf{P} \tag{4}$$

For a given $\mathbf{u}$, the minimum happens at

$$(1 + 4\pi\chi)\mathbf{P} = e_T^*\mathbf{u}$$

and the minima is by then

$$\mathcal{H} = \frac{1}{2}\frac{4\pi(e_T^*\mathbf{u})^2}{\epsilon}$$

contributing to the force constant in $\mathbf{u}$ that splits LO-TO modes.

Returning to the TB model, we want to *construct* something which can quantitatively reproduce the LO-TO splitting. If we use the simplest rigid-ion model with constant point charges on atoms, like in some classical potential for H_2O and SiO_2, that charge would have to be

$$q = e_T^*/\sqrt{\epsilon}$$

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[10] In electrostatics $\mathbf{E}$ denotes the *actual* field, $\nabla\cdot\mathbf{E} = 4\pi\rho_a$; by definition $\nabla\cdot\mathbf{P} = -\rho_P$, where ρ_P is the induced or polarization charge density; thus $\nabla\cdot(\mathbf{D} = \mathbf{E}+4\pi\mathbf{P}) = 4\pi\rho_t$ where ρ_t is the *true* or external charge, which activate the field. Susceptibility is defined by $\mathbf{P} = \chi\mathbf{E}$; dielectric constant is defined by $\mathbf{D} = \epsilon\mathbf{E}$; thus $\epsilon = 1 + 4\pi\chi$.

in order to correctly reproduce the splitting. If we take the experimental values[11] for 3C-SiC in: $e_T^* = 2.57$, $\epsilon = 6.7$, we get $q \approx 1.0$. However, in general both e_T^* and ϵ are environmental dependent and sometimes directional dependent. We can not get a transferable TBMD potential model using the rigid-ion approach.

On the other hand if we want a more basic model, we have to deal directly with the electron dielectric constant ϵ. We can proceed by following the procedure in calculating the electron thermal conductivity[12], which perhaps involves matrix elements of the type $\langle \phi_i^\alpha | \mathbf{r} | \phi_j^\beta \rangle$. By adding some empiricism we can expect a reasonable model for ϵ. Even by itself this work will be interesting and useful.

The total energy will then include the term:

$$E_C = \sum_{i>j} \frac{\tilde{Z}_i^* \tilde{Z}_j^*}{r_{ij}} \tag{5}$$

where

$$\tilde{Z}_i^* = Z_i^* + \sum_j \Delta_{ij}(\mathbf{E}) \tag{6}$$

such that

$$\sum_{i>j} \mathbf{r}_{ij} \Delta_{ij}(\mathbf{E}) = \chi \mathbf{E} = \frac{\epsilon - 1}{4\pi} \mathbf{E}$$

(5) corresponds to the Hartree term in the total energy functional of DFT. The first term of (6) is the partial charge on site i when there is no $\mathbf{E}$, setting up a reference; the second term corresponds to the polarization charge transfer if there *is* $\mathbf{E}$. This way we can avoid $\mathbf{E}(\mathbf{r})$ directly entering the band structure part of the calculation (no self-consistent iteration), which in essence is doing a perturbation theory. $\mathbf{E}(\mathbf{r})$ can be obtained by, for instance, averaging over the electric field inside the Wigner-Seitz polyhedra around each atom.

In the LCAO picture, no matter how distorted the local orbital might become (for instance due to the renormalization from the overlap matrix $\mathbf{S}$), its center should be considered to be situated on the atomic site always. If so, the polarization density or the dipole moment per cell is exactly represented by $\sum_i \tilde{Z}_i^* \mathbf{r}_i$, in going from the charge density picture (LDA) to TB. Thus, the long ranged part of the Hartree interaction is in fact equal to that of a dipole lattice, other terms are short-ranged which can be absorbed into E_{rep}. The catch is that the dipole moment is dependent on both atomic positions (accounted for by term 1 in (6)), and possible electric field $\mathbf{E}$ (term 2).

In a phonon frequency calculation, this formula (5) will give the correct LO-TO splitting, because $\mathbf{E}(\mathbf{r})$ is just the coarse-grained effect of many lattice charges (dipoles) combined. As

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[11] pg 220 and 114 of Harrison.

[12] *Relationship between structure and conductivity in liquid carbon*, J. R. Morris, C. Z. Wang and K. M. Ho, Phys. Rev. B **52**, 4138 (1995).

we mentioned before, a straight forward lattice sum calculation[13] agrees with macroscopic electrostatics arguments in the $\mathbf{k} \to 0$ limit.

It is worth mentioning that since (5) is not a rigid-ion model, the program ./ewald.c can not account for all the terms that is occurring in force, stress and Hessian expressions. In general if we write

$$E_c = E_c(.., q_m, q_n, .., \mathbf{x}_m, \mathbf{x}_n, ..)$$

it is sufficient only if $\{q_m\}$ doesn't depend on $\mathbf{x}_n$'s. There is one extra term entering the first derivative and two extra terms entering the second derivative and unfortunately they are both long ranged. In the $\mathbf{k} \to 0$ limit the extra effect is summarized by the screening constant ϵ.

The consistency of this approach can be examined by doing MD in a fairly large, but PBC, supercell. The allowed phonon modes are the discrete samplings of the continuous band with $\mathbf{k}$ being multiples of $1/L$. So if we integrate $\mathbf{E}(\mathbf{r}) \sim e^{i\mathbf{k}\cdot\mathbf{r}}$ over the supercell, we get zero, in accordance with the claim that the super-supercell is surrounded by conductive medium and there is no *uniform* macroscopic electric field. However if we average $\mathbf{E}$ over volumes with size around that of a primitive cell, then we would observe the $e^{i\mathbf{k}\cdot\mathbf{r}}$ behavior if, of course, the displacements in the supercell are LO.

3 Simulated Annealing and the Integration of Band Structure Optimization

There are plenty of public domain optimization codes on the web[14]. Adaptive simulated annealing (ASA)[15], developed by Lester Ingber, seems to be the most up to date. I have ported the code to our IBM RS6000 platform (/farm2/liju/Asa/), made it callable as a subroutine by changing MY_TEMPLATE in asa_user.h, and it works fine. Look at ./mine.c to see how it is called to minimize a 5-variable parabola. The code (user.c/cost_function()) looks for an error function named *fe* which takes in a double precision array *guess* and returns the error in double precision. The interfaces conform to Fortran calling conventions. Because some Fortran compilers like *xlf* on IBM RS6000 do not recognize front underline convention for function and variable names in both compiling and linking, a special macro *realname* is used in C programs like ./mine.c to conform with the Fortran compiler of that machine. Type "make help" or look at ./Makefile for details.

The power of the code has been compromised to simplify its usage, with most of the intrinsic parameters taking default values. Many options could be read in at run time from

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[13] Chap. VI, *Theory of Lattice Dynamics in the Harmonic Approximation* by A. A. Maradudin, E. W. Montroll and G. H. Weiss, Solid State Physics Supplement 3, Academic Press, New York (1971).

[14] Visit http://tonic.physics.sunysb.edu/docs/num_meth.html for a list, and other numerical softwares.

[15] Visit http://www.ingber.com/ for a free copy of the code and paper reprints.

"asa_opt", although this choice was nullified currently by setting OPTIONS_FILE_DATA in "./asa_user.h" to be FALSE. ASA can do a lot more, for instance, to do constraint minimization only requires setting **cost_flag* in user.c/cost_function() to be FALSE whenever the parameters take impermissible values. Read /farm2/liju/Asa/Doc/README.ps for details.

Currently the annealing process is controlled by a single parameter which I call *annea_rate* (default=1.0), which is the "Temperature_Ratio_Scale" in the original ASA program scaled by 10^{-5} (the default value). The bigger it is, the faster the system cools down, and the bigger the danger of being trapped in a local minima.

There are two output files from ASA: *usr.out* which contains the final results, and *asa.out* which shows the list of current best at various stages of the cooling.

A unified band structure optimization program (/farm2/liju/TB/Fitband/) was developed, which in the end does all the necessary property calculations using optimized parameters, such as band plot, evaluating ϵ_F, E_{BS}, Z_i^*, and deducing the repulsive term from LDA database. The source codes are

- *fitband.fh*: all the common variables and intrinsic parameters of the code.
- *fitband.F*: the main program, which includes I/O; structure initialization; interface to ASA or MINA (*fe*); construction of the overlap matrix (*overlap*); and property calculations (*wrapup*). This part is most frequently altered.
- *energetics.F*: diagonalizing the overlap matrix in **k**-space (*diag_k*); calculating the Fermi level, E_{BS} and Z_i^* (*sea*, *calc_ebs*); interface to Ewald summation routine to calculate the electrostatic energy (*calc_ec*) (ewald.(SYS).o need to be in the directory – source codes in /farm2/liju/Ewald/); and deducing the repulsive energy term from LDA database (*deduce_erep*).
- *mina.F*: the MINA optimizer. To use it choose OPTIMIZER in *con* to be 1. Otherwise ASA is used – asa.(SYS).o and user.(SYS).o must be in the current directory, the source codes are in /farm2/liju/Asa/.
- *Makefile*: Machine dependencies and shorthands. Type
  - `% make help`
    for help.
  - `% setenv SYS ‘uname‘; make`
    to compile.
  - `% make run`
    to run (input file is *con*).
  - `% make longrun &`
    to submit a long job. Screen output will be saved to file *output*.

- `% make kill`
  to kill the process.
- `% make clean`
  to remove the .o and .f files, such that next time everything will be re-compiled. Use when you are not sure that the Makefile dependencies are correct and want to watch the entire compilation.

Machine dependencies include special names for compilers on IBM RS6000[16], and different library environments. For instance, the subroutine name for the diagonalization of Hermitian matrix is *zhpev* in both *essl* (IBM RS6000) and LAPACK (DEC-alpha), but the arguments are different. To accommodate such variations to make the code as transferable as possible, Makefile is presented and the fortran programs are written with suffix .F, meaning that there could be *cpp* directives in the source, such as #include, #define and #ifdef. Before compilation, .F file is first pre-processed by *cpp* to be converted into a .f file, like

```
% /lib/cpp -P -D_$(SYS) fitband.F > fitband.$(SYS).f
```

where on IBM RS6000 the environmetal variable SYS should be set to AIX (=‘uname‘), and it creates the real fortran source program “fitband.AIX.f”, customized for this machine, which is subsequently fed into the fortran compiler[17].

The TB bands will be stored in *.band after execution. Band structure plot is detailed in report I, where I use Matlab script to do the graphs. A more refined, dialog-driven version (/farm2/liju/TB/Fitband/band.m) is written where the LDA results (/farm2/liju/TB/ Fitband/LDA/*.LDA.band) are plotted on the same graph for comparison (both set zero-level to be the lowest eigenvalue of Γ-point). The way to use *band.m* on Vincent (because the IBM’s do not have Matlab) is to copy *.m, *.band files and the LDA/ directory to the current machine, type “% mat” (csh script at ~/liju.dir/Shell/mat) and then at Matlab prompt type “⟩⟩ band”.

The LDA total energy is stored in ./LDA/Coh_LDA_Raw/ and ./LDA/Coh_LDA_Fitted/. The first directory stores the raw data points from LDA calculations (/farm2/liju/SiC/) and the second one stores the smooth curves fitted to universal binding model[18]. Because raw data points usually contain some noise, here we use results from ./LDA/Coh_LDA_Fitted/. The .coh.original files contain data for a pair of Si-C, the left column being the volume per pair (in a.u.[3]), the right column being the total energy per pair (in Rydberg)[19]. *convert.m*

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[16] Many of the softwares and libraries only exist on ssibm9.ssp.ameslab.gov, like *xlf*, *xlc*, *essl*, *xmol* and *ghostview*.

[17] Most Fortran compilers nowadays can directly handle .F files, but not *xlf*. Besides it might be desirable to have the .f files on hand for error checking.

[18] In a sense they are the best fits which agree with experiments, because usually the results depend sensitively on the range of fitting. See /farm2/liju/TB/liju.dir/SiC.m.

[19] 1 a.u. = Bohr radius = 0.529177249 angstrom; 1 Rydberg = 13.605826 eV.

sorts the .coh.original file according to volume, convert the data to angstrom and eV, and stored them in .coh file: the first column of the .coh file are the characteristic lengths (lattice constants for cubic systems and basal plane lattice for hexagonal systems) of the structure, the second column are the volumns per atom and the third column are the total energy per atom. The .coh files are what is directly used by our program.

In order for the code to be able to deduce the "correct" repulsive term, LDA total energy for that volume must be in the database. If not then an error message "*Error (deduce_Erep): the piece AA=* is not found in LDA database LDA/Coh_LDA_Fitted/**" will appear. This feature can be easily changed at later stages.

The major output of *Fitband* are the *.out* files, each for different structure, which are written at the end of optimization (if MAXITER is set to 0 in *con*, then property calculation immediately starts using the current parameter set in *con*). The meaning for each column in the *.out* files are, sequentially,

1. characteristic length ($\dot{A}$).
2. volume per atom ($\dot{A}^3$).
3. Fermi level (eV).
4. E_{BS} per atom (eV).
5. E_C per atom (eV).
6. $E_{\rm rep}$ per atom (eV), deduced from LDA database.
7. $4 - Z_i^*, i = 1..N$.

The *.out* files should be directly included in the *con* input file of *Fitrep*, for the next stage of optimization.

4 Total Energy in a Unified Model

For pure element potential models, the zero-point is not important. Suppose we are only interested in a finite volume range of the various condensed phases, we can even neglect what is happening at the infinite volume limit and let the zero-point be a floating constant that minimizes the error in the volume region of interest[20]. It is not so for a unified multi-element model: using the same potential we should be able to get a total energy curve for pure C, a

---

[20] In fact C.Z. has proposed a scheme to give the correct limit, by smoothly distorting the embedding function of $E_{\rm rep}$ at small $\sum_j \phi_{ij}$.

total energy curve for pure Si and a total energy curve for SiC (let's say all of them are in the diamond structure). The difference of the last minima to the average of first two should be 6.34 eV, the definition of cohesive energy. By inheriting the parameters for cohesive energy in both pure Si and C potentials, and *only* fit the new parameters in various SiC phases (with a floating zero-point) without referencing to the pure Si or C curves, can we hope to get this difference right? It seems unlikely that we will get it exactly correct the first time, and that value becomes a prediction.

Currently the following model is being used:

$$\begin{aligned} E_{\text{total}} = \quad & E_{BS} + \sum_{i>j} \frac{Z_i^* Z_j^*}{r_{ij}} + \sum_i (4 - Z_i^*) \Delta E_s(i) \\ & + \sum_{i \in \text{Si}} f_{\text{Si}} (\sum_{j \in \text{Si}} \phi_{ij}^{\text{Si}-\text{Si}} + \sum_{j \in \text{C}} \phi_{ij}^{\text{Si}-\text{C}}) \\ & + \sum_{i \in \text{C}} f_{\text{C}} (\sum_{j \in \text{C}} \phi_{ij}^{\text{C}-\text{C}} + CK \sum_{j \in \text{Si}} \phi_{ij}^{\text{Si}-\text{C}}) \\ & + \sum_i f_{\text{Si}-\text{C}} (\sum_{j \text{diff}.i} \phi_{ij}^{\text{Si}-\text{C}}) \end{aligned} \tag{7}$$

where f_{Si}, f_{C}, $\phi_{ij}^{\text{Si}-\text{Si}}$ and $\phi_{ij}^{\text{C}-\text{C}}$ are from pure Si and C models. The things to be fit are $f_{\text{Si}-\text{C}}$ (order-4 polynomial), $\phi_{ij}^{\text{Si}-\text{C}}$ (screened interaction strength) and parameter CK. CK is the ratio of "charge density projection" from Si to C to that of from C to Si.

K. M. Ho pointed out that in order for the model to be variational, we can not simply add a term in E_{total} which involves wave functions without making corresponding changes in band structure calculations. If for instance

$$E_{\text{total}}^0 = E_{\text{total}}^0 (S, \{|\psi_n\rangle\})$$

where S genericly denotes atomic positions and $\{|\psi_n\rangle\}$ are the occupied electron wave functions. Then there is

$$\frac{\delta E_{\text{total}}^0}{\delta \langle \psi_n |} = \mathcal{H}_0 |\psi_n\rangle = \epsilon_n^0 |\psi_n\rangle$$

by orthonormalization constraints of eigenstates. But if we are to add a long ranged Coulomb term to the total energy functional (which apparently plays a role in $\mathbf{k} \to 0$ phonon of polar semiconductors),

$$E_{\text{total}} = E_{\text{total}}^0 + \sum_{i>j} \frac{Z_i^* Z_j^*}{r_{ij}} = E_{\text{total}}^0 + \sum_{i>j} \frac{(\sum_{n,\alpha} |\langle \phi_i^\alpha | \psi_n \rangle|^2)(\sum_{m,\beta} |\langle \phi_j^\beta | \psi_m \rangle|^2)}{r_{ij}} \tag{8}$$

where $\alpha(\beta)$ denotes local orbitals, then

$$\frac{\delta E_{\text{total}}}{\delta \langle \psi_n |} = \mathcal{H}_0 |\psi_n\rangle + \sum_i \left[\left(\sum_{j \neq i} \frac{Z_j^*}{r_{ij}} \right) (\sum_\alpha |\phi_i^\alpha\rangle \langle \phi_i^\alpha |) \right] |\psi_n\rangle = \epsilon_n |\psi_n\rangle \tag{9}$$

which simply means that the on-site elements of the electronic TB Hamiltonian must be raised by the electrostatic potential due to charge accumulation on other sites[21]. If previously there has been

$$E^0_{\rm total} = \sum_n \langle \psi_n | \mathcal{H}_0 | \psi_n \rangle + E_{\rm rep}(S) = \sum_n \epsilon^0_n + E_{\rm rep}(S)$$

Now there is

$$\begin{aligned} E_{\rm total} = & \quad E^0_{\rm total} + \sum_{i>j} \frac{Z^*_i Z^*_j}{r_{ij}} \\ = & \quad \sum_n \langle \psi_n | \mathcal{H}_0 | \psi_n \rangle + E_{\rm rep}(S) + \sum_{i\neq j} \frac{Z^*_i Z^*_j}{r_{ij}} - \sum_{i>j} \frac{Z^*_i Z^*_j}{r_{ij}} \\ = & \quad \sum_n \epsilon_n + E_{\rm rep}(S) - \sum_{i>j} \frac{Z^*_i Z^*_j}{r_{ij}} \end{aligned} \tag{10}$$

Now we come to the question of how to calculate the Madelung (electrostatic) potential at each atomic site:

$$E_M(i) = \sum_{j\neq i} \frac{Z^*_j}{r_{ij}} \tag{11}$$

There is a simple relation if we know the electrostatic energy per cell (from ewald.c) *and* if the atoms sit at equivalent positions. For instance in 3C-SiC, since we can think of each atom as having half of the potential energy for every pair of interaction involving it, there is

$$\text{energy per cell} = \frac{1}{2}(Z^*_{\rm Si} E_M({\rm Si}) + Z^*_{\rm C} E_M({\rm C}))$$

By symmetry there is $E_M({\rm Si}) = -E_M({\rm C})$ and $Z^*_{\rm Si} = -Z^*_{\rm C}$, so E_M can be known from energy per cell. But when the atoms do not sit at equivalent positions, such as in NiAs, there is no direct link. We have to look into the derivations for Ewald summation to know the answer.

There is a consensus among us that Z^* probably should take values below 1.0,[22] instead of the current 1.7; and probably it won't change much from structure to structure. So instead of doing a full-blown self-consistent optimization which might be expensive, perhaps we can first assume $Z^* \approx 1$, and let the shift

$$\Delta E_s(C) - \Delta E_s(Si) = w + E_M(S, {\rm C}) - E_M(S, {\rm Si})$$

where w is a constant to be optimized in the band structure optimization. Basic self-consistency can be achieved by calculating Z^* for 3C-SiC at zero pressure using 60 **k**-points, and define its deviation from 1.0 to be part of the error function.

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[21] It is in fact just the delocalized generalization of the on-site u-term, which should be iterated up to self-consistency. Its long-ranged effect can not be absorbed into any short-ranged environmental dependent term, which can never distinguish LO and TO. Just as the u-term effects can not be replaced by environmental dependent ΔE_s in the infinite volume limit for SiC.

[22] Integration of LDA charge density inside an atomic-volume sphere for CsCl gives $4 - Z^*_i \approx 2.99$ for Si, and Si should have a larger radius.