To do

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1 About Fitting Targets

Our primary fitting targets are two: band structure shape and cohesive energy. By band structure shape, we mean energy difference of excitations $E_n(\mathbf{k})$ with respect to $E_0(0)$. This target is only available from LDA. Let us define the band structure shape error function to be

$$e^b = \sum_{\mathrm{i} \in \mathrm{struc}}^{3C,2H..} w_{n\mathbf{k}}^i \left| \frac{E_n^{TB}(\mathbf{k}) - E_0^{TB}(0) - E_n^{LDA}(\mathbf{k}) + E_0^{LDA}(0)}{E_n^{LDA}(\mathbf{k}) - E_0^{LDA}(0)} \right| / \sum_{\mathrm{i} \in \mathrm{struc}}^{3C,2H..} w_{n\mathbf{k}}^i. \tag{1}$$

Cohesive energy is the energy cost to (adiabatically) extend the current structure to infinity. The final states are just isolated atoms in pure structures. For instance, diamond into a set of C atoms. But for multi-species compound, the final state *theoretically* may not be exactly that. Consider the final state to be made from by placing one electron in a Si^+/C system where the Si^+ and C are ∞ apart. In the LCAO picture, the electron can have wave function

$$\psi = a|\phi_{\mathrm{C}}\rangle + \sqrt{1-a^2}|\phi_{\mathrm{Si}}\rangle. \tag{2}$$

If $a = 0$, then it is a Si/C system, but that does not have to be the total energy minima. Since $|\phi_{\mathrm{C}}\rangle$ and $|\phi_{\mathrm{Si}}\rangle$ has no overlap, the total energy might be written as

$$E = E_{\mathrm{C}}(a^2) + E_{\mathrm{Si}}(1-a^2), \tag{3}$$

and ground state can only be achieved when

$$\frac{\partial E_{\mathrm{C}}}{\partial a^2} + \frac{\partial E_{\mathrm{Si}}}{\partial a^2} = 0. \tag{4}$$

This claim is rather counter-intuitive, I do not know if it is correct or not. But that is not critically important: the first ionization energy of Si is 786.5 kJ/mol while the first electron affinity of C is 121.9 kJ/mol, so a separated $\mathrm{Si}^+/\mathrm{C}^-$ system has higher energy than a separated Si/C system, thus the fractional charge transfer, if it exists, must be smaller than one. Also, I am sure that experimentally the reference state for the "cohesive energy" is taken to be Si/C. So, from now on let us take the reference state at infinity to be isolated atoms with no charge transfer.

By definition, a cohesive energy plot should go to 0 as $a \to \infty$, or at least be very close to 0 if there is actually some slight charge transfer. LDA results satisfy that. However, sometimes LDA cannot very accurately evalute the absolute magnitude of the cohesive energy minima E_{coh}^{min}, although shape of the curve is much better. Another consideration is that most high energy phases are non-existent in nature and their cohesive energies are unknown experimentally, and can only be evaluated by LDA. We can form a composite cohesive energy target (CPS) that is neither LDA nor experiment: it has the experimental value of E_{coh}^{min} for the lowest energy phase, but with the volume and curvature of LDA. Other phases sustain the same rigid shift as its lowest energy bother of the same chemical composition. Thus, the family of SiC LDA curves are shifted to make $E_{coh}^{min}(3C)$ agree with experiment, so are the family of C LDA curves shifted to make $E_{coh}^{min}(graphite)$ agree with experiment, etc.

Our primary error function in fitting the cohesive energy curve should be

$$e^p = \sum_{\text{i}\in\text{struc}}^{3C,2H..} w_i \left| \frac{E_{coh,min}^{TB} - E_{coh,min}^{CPS}}{E_{coh,min}^{CPS}} \right| / \sum_{\text{i}\in\text{struc}}^{3C,2H..} w_i. \tag{5}$$

where we go over all the phases and compare their lowest energies with those of the target curves. Since the actual TB minimum positions change with parameters and are unknown beforehand, we should use the target minimum position (volume) for each phase.

Our secondary targets are elastic constants and phonon energies, say, only for the lowest energy (3C) phase. The configurations are usually specified by a small deformation parameter δ, and

$$E_{coh}^{TB}(\delta) - E_{coh}^{TB}(0) \approx C_{TB}\delta^2/2, \quad E_{coh}^{CPS}(\delta) - E_{coh}^{CPS}(0) \approx C_{CPS}\delta^2/2. \tag{6}$$

Because we want to fit C_{TB} with C_{CPS}, our error function should pay equal attention to C's for each δ datapoint. The resultant secondary error function should be

$$e^s = \sum_{\text{d}\in\text{deform}}^{B,C_{44},\Gamma..} w_d \left(\sum_{\delta}^{n_d} \left| \frac{E_{coh}^{TB}(\delta) - E_{coh}^{TB}(0) - E_{coh}^{CPS}(\delta) + E_{coh}^{CPS}(0)}{E_{coh}^{CPS}(\delta) - E_{coh}^{CPS}(0)} \right| / n_d \right) / \sum_{\text{d}\in\text{deform}}^{B,C_{44},\Gamma..} w_d. \tag{7}$$

The total error function should be

$$e = \frac{w_b e^b + w_p e^p + w_s e^s}{w_b + w_p + w_s}. \tag{8}$$

Keeping the normalization lends e the meaning of average relative error for all properties.

2 TB model for band structure shape of SiC

We now have good parameters for the band structure shape of pure Si and C. There are $\Delta e_s \equiv \Delta e_p$ in those models, which should really be regarded as another contribution to E_{rep}. Since the environment does not alter the sp gaps there, it should not alter the sp gaps for Si-C interaction either. That is, we stipulate

$$\Delta e_s \equiv \Delta e_p \tag{9}$$

for Si-C interaction (16=15,18=17). The only handle we have here to influence the SiC band structure shape is (17-15), which should use four parameters but we now only use α_1. I suggest we use four. Then, row 15 itself does not influence the band structure shape, but it influences the total energy. Since it seemed necessary to have Δe_s there in pure Si or C, we should fit Row 15 during cohesive energy fitting (another four parameters).

For the hopping parameters, we have α_1, α_2, α_3, α_4 of $ss\sigma$, $sp\sigma$, $ps\sigma$, pp_sigma, $pp\pi$ (row 19-23) respectively. The screening contribution to ξ_{ij} are chosen to be solely dependent on the screening atom (l), which is reasonable. As long as the nearest neighbors are not strongly screened, I don't think this needs to be changed.

Thus, we have 24 parameters in band structure shape fitting for SiC.

3 TB model for cohesive energy of pure elements

The biggest problem right now is that at ∞ the pure element TB models do not give $E_{coh} = 0$. However, since there is no electronic structure (charge transfer) involved, this problem as CZ pointed out last year can be easily fixed by deforming E_{rep} at small coordination number, without influencing the condensed phase results. Yet, I think this needs to be done sometime.

4 TB model for cohesive energy of SiC

I plan to move the Ewald summation and LDA database parts to *Fitrep*, as right now we use a rigid ion model with $q \approx 1$, but q should be tunable. In the future we may use

$$q_i = \sum_{j \neq i} \Delta q_{ji} \tag{10}$$

with $\Delta q_{ji} = -\Delta q_{ji}$ the charge transfer term environment dependent.