Silicon

A Journey of the full-potential KKR method towards semiconductors and functional materials

Yang Wang
Pittsburgh Supercomputing Center, Carnegie Mellon University

Categorizing the Ab Initio Methods

All-electron or Pseudo-potential

- In all-electron methods, both the valence and core electronic states are calculated, at each SCF iteration, by solving the Kohn-Sham equation
    - Atom centered local basis (e.g., KKR, LMTO, EMTO)
    - Local basis in the atomic volume and plane wave basis in the interstitial region (APW, FLAPW)
- In pseudo-potential methods, the core states are usually “frozen” and the valence states are calculated from a the Kohn-Sham equation with a pseudorized potential
    - Plane wave basis
    - No basis: adaptive grids, finite elements, etc

Band structure or Green function

$$\rho(\mathbf{r}) = \sum_{\varepsilon_\alpha \le \varepsilon_F} \left|\psi_\alpha(\mathbf{r};\varepsilon_\alpha)\right|^2, \text{ with } \alpha = (n,\mathbf{k})$$

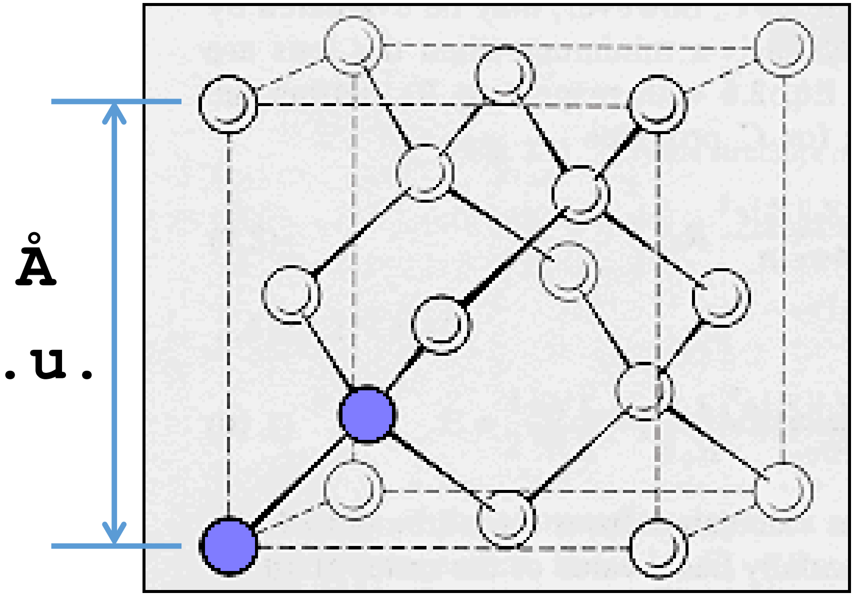
- The majority of the *ab initio* methods take band structure calculation approach that solves the Kohn-Sham equation and calculates the electron density based on the normalized Bloch wave functions
- The Green function approach focuses on calculating the Green function, instead of solving the Kohn-Sham equation. The electron density is then determined from the Green function using

$$\boxed{\rho(\mathbf{r}_n) = -\frac{2}{\pi}\operatorname{Im}\int_{-\infty}^{\varepsilon_F} G(\mathbf{r}_n,\mathbf{r}_n;\varepsilon)\,d\varepsilon}$$

$$\boxed{\rho_n(\varepsilon) = -\frac{2}{\pi}\operatorname{Im}\int_{\Omega_n} G(\mathbf{r}_n,\mathbf{r}_n;\varepsilon)\,d^3\mathbf{r}_n}$$

where $G(\mathbf{r}_n,\mathbf{r}_n;\varepsilon)$ is the Green function of the Kohn-Sham equation with $\mathbf{r}_n = \mathbf{r} - \mathbf{R}_n$

Crystal Structure of Silicon



$\boldsymbol{a_0} = 5.43$ Å

$= 10.21$ a.u.

Bravais lattice basis vectors (the same as the FCC Bravais lattice):

$\mathbf{a} = a_0 \times (1/2,\ 1/2,\ 0)$

$\mathbf{b} = a_0 \times (1/2,\ 0,\ 1/2)$

$\mathbf{c} = a_0 \times (0,\ 1/2,\ 1/2)$

Two atoms per lattice point:

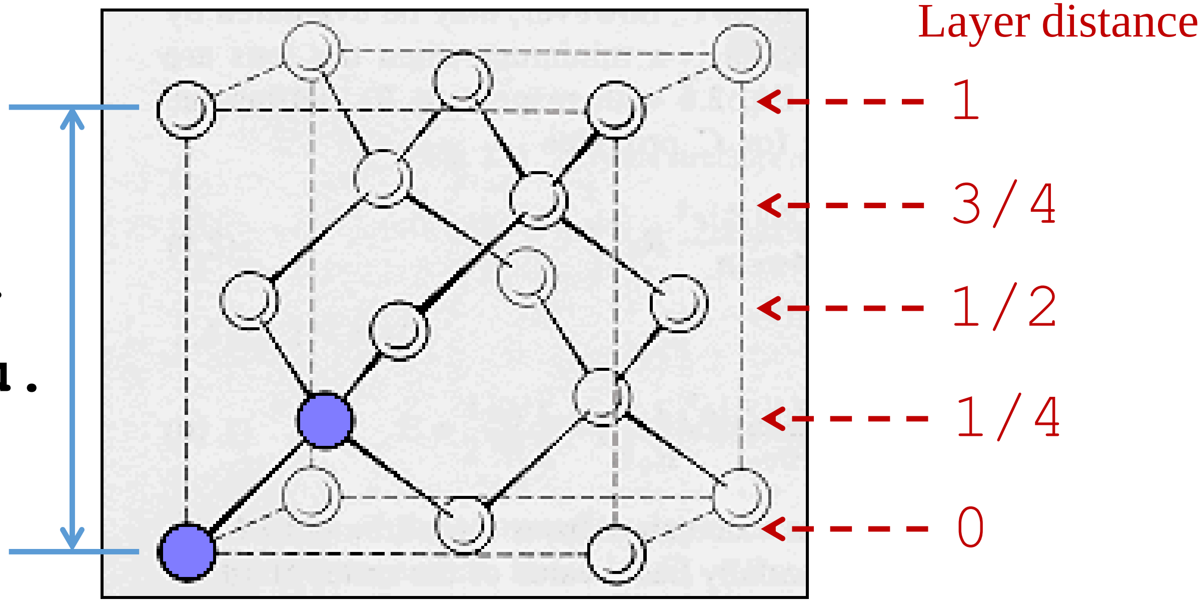
Si: $a_0 \times (0,\ 0,\ 0)$

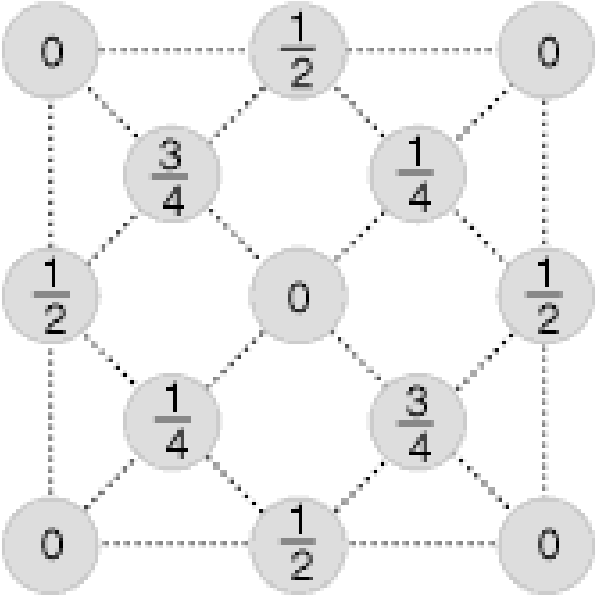
Si: $a_0 \times (1/4,\ 1/4,\ 1/4)$

Crystal Structure of Silicon – cont.

a_0 = 5.43 Å

= 10.21 a.u.

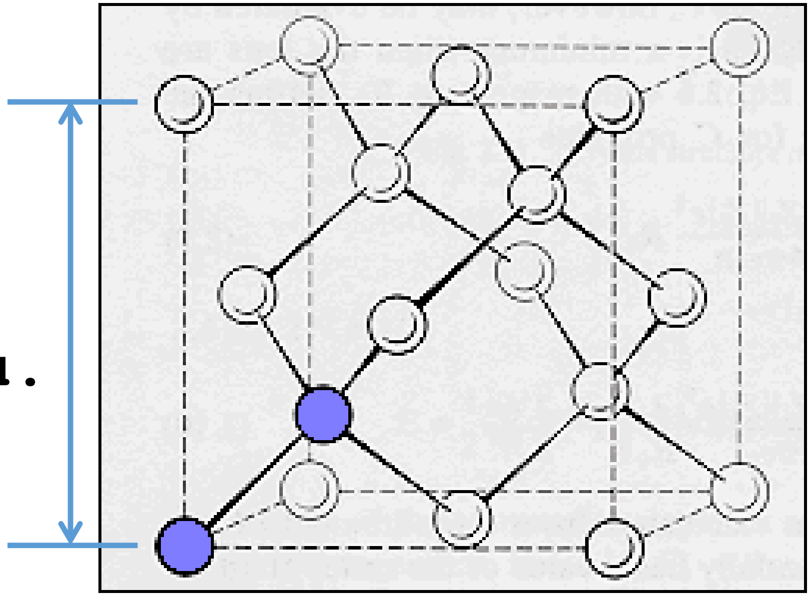




For the ab initio methods with atom centered local basis, each Si atom can be considered to occupy a spherical volume

- With such atom-centered volume construction, large empty voids appear in the Si structure
- With atom-centered local basis to expand the Bloch wave functions, the wave function representation in the large empty volumes becomes problematic
- A easy solution is to add “virtual” atoms (Va), or empty cell volumes, to fill the voids

Crystal Structure of Silicon – cont.



$\boldsymbol{a_0}$ **= 5.43 Å**
= 10.21 a.u.

Bravais lattice basis vectors:

$\mathbf{a} = a_0 \times (1/2,\ 1/2,\ 0)$

$\mathbf{b} = a_0 \times (1/2,\ 0,\ 1/2)$

$\mathbf{c} = a_0 \times (0,\ 1/2,\ 1/2)$

Two Si atoms + two Va “atoms” per lattice point:

Si: $a_0 \times (0,\ 0,\ 0)$

Si: $a_0 \times (1/4,\ 1/4,\ 1/4)$

Va: $a_0 \times (1/2,\ 1/2,\ 1/2)$

Va: $a_0 \times (3/4,\ 3/4,\ 3/4)$

Band Structure Approach: FP-LMTO and FP-KKR

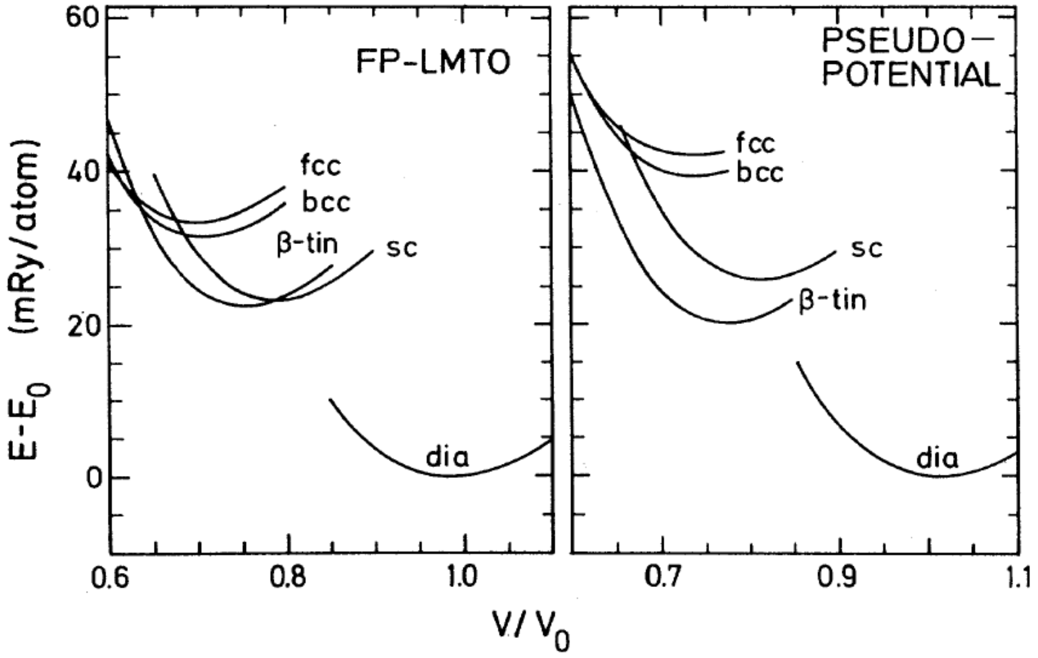
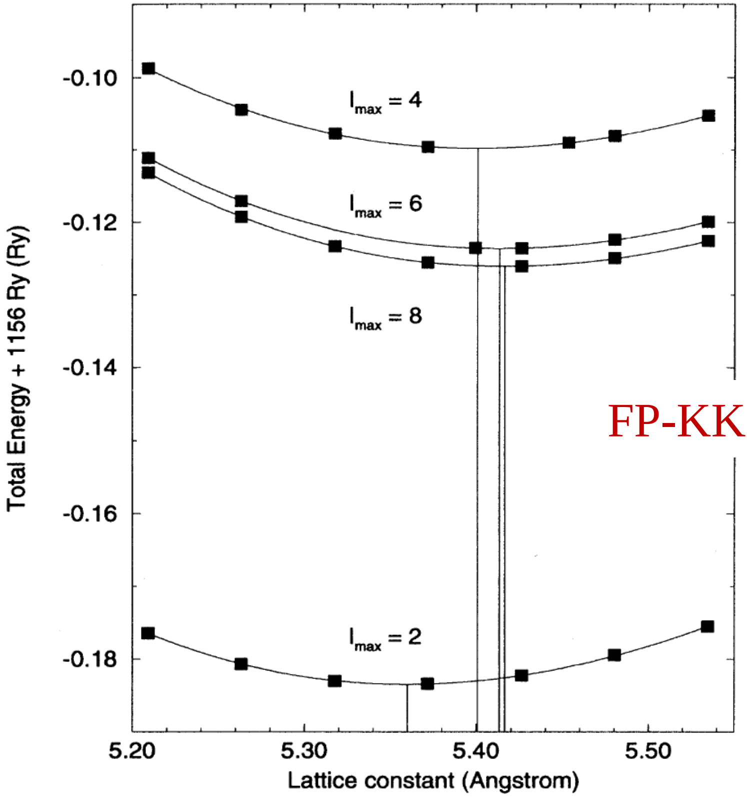


FIG. 2. Energy-volume curves for crystalline phases of Si calculated by Yin and Cohen using the pseudopotential method (Ref. 19) and by us using the FP-LMTO method. V_0 is the experimental equilibrium volume and E_0 is the calculated minimum energy in the diamond structure.

M. Methfessel, C. O. Rodriguez, and O. K. Andersen, “Fast full-potential calculations with a converged basis of atom-centered linear muffin-tin orbitals: Structural and dynamic properties of silicon,” Phys. Rev. B **40**, 2009 (1989)



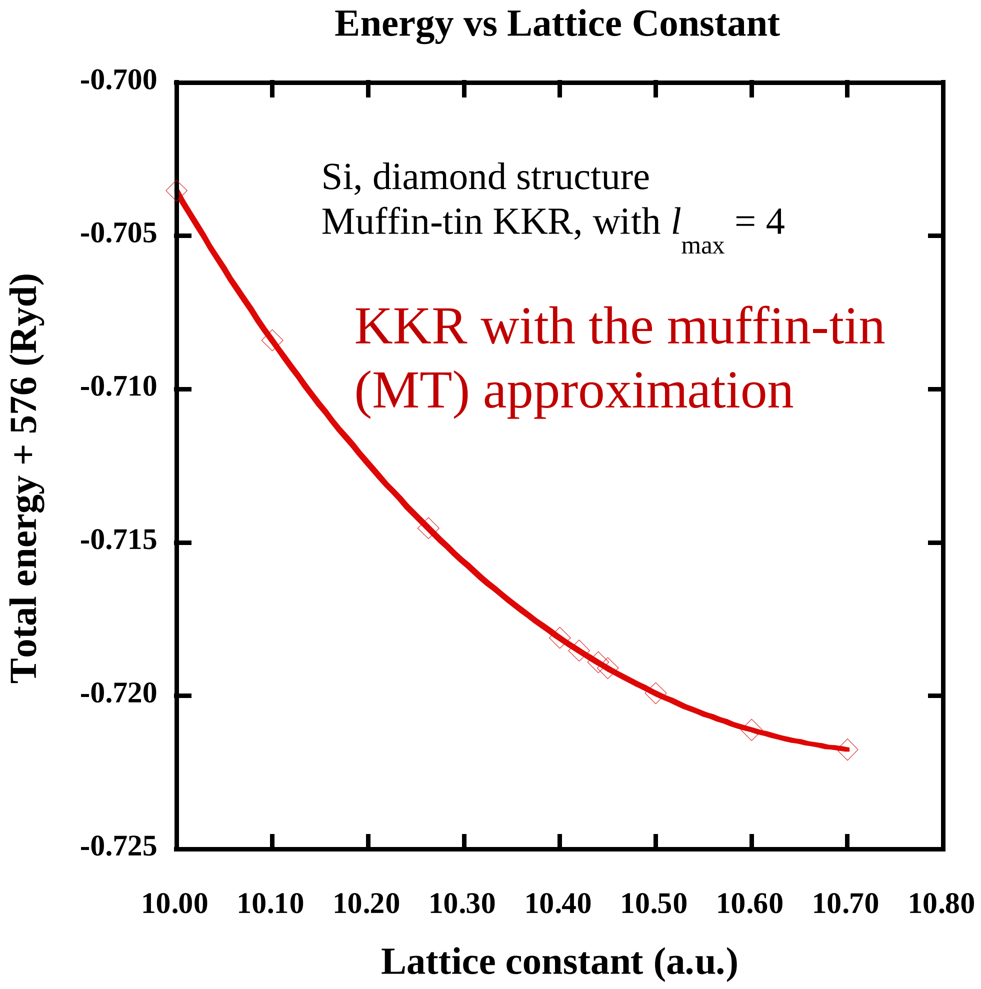
FP-KKR method

FIG. 9. Total energy as a function of lattice constant for several different $l_{\max}$. The lines represent least square fits to the calculated values marked by filled squares. For each $l_{\max}$ the location of the energy minimum is indicated by a vertical line.

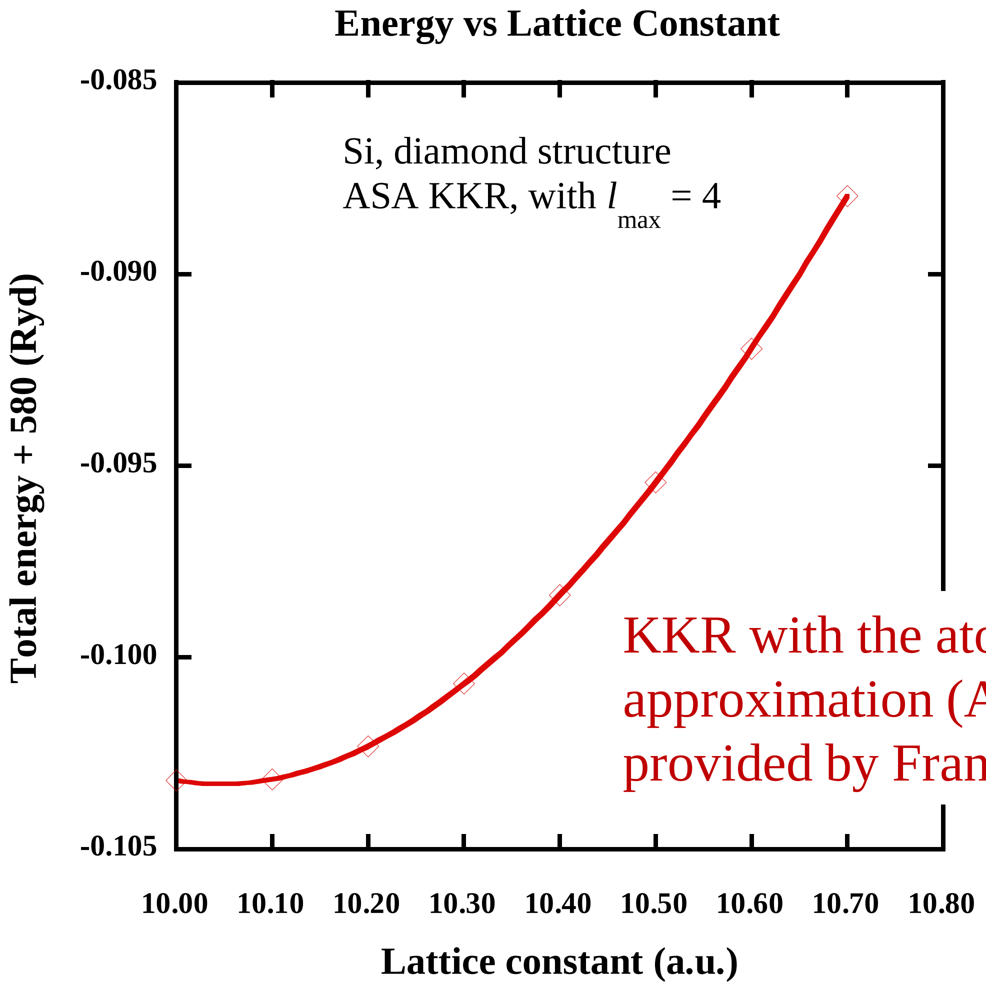
S. Bei der Kellen, Yoonsik Oh, E. Badralexe, and A.J. Freeman, “Self-consistent full-potential total-energy Korringa-Kohn-Rostoker band-structure method: Application to silicon,” Phys. Rev. B **51**, 9560 (1995)

What about the Green function approach?

The first try



KKR with the muffin-tin (MT) approximation

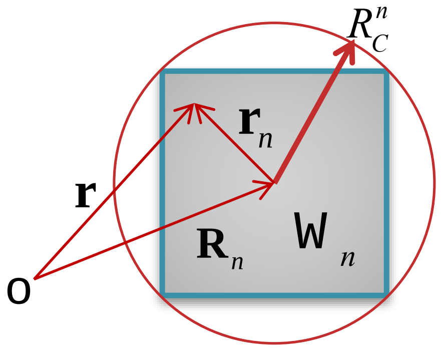


KKR with the atomic sphere approximation (ASA) provided by Franco Moitzi

The Green function approach to Silicon

A full-potential scheme is needed

- For systems dominated by covalent bonding, e.g., Si, the muffin-tin approximation to the potential is no longer appropriate



Despite the Green function method is mathematically elegant, and more importantly its solution is formally exact, its numerical calculation for the full-potential case turns out to be very difficult.

$$G(\mathbf{r}_n,\mathbf{r}_n;\varepsilon)=\sum_{L,L'}Z_L^n(\mathbf{r}_n;\varepsilon)\tau_{LL'}^{nn}(\varepsilon)Z_L^{n\bullet}(\mathbf{r}_n;\varepsilon)-\sum_{L}Z_L^n(\mathbf{r}_n;\varepsilon)J_L^{n\bullet}(\mathbf{r}_n;\varepsilon),\quad \text{where } L=\{l,m\},\ \mathbf{r}_n\in\Omega_n.$$

$Z_L^n(\mathbf{r}_n;\varepsilon)$ and $J_L^n(\mathbf{r}_n;\varepsilon)$ are the single site regular and irregular solutions, respectively, corresponding to local potential, which is $V_{\text{eff}}(\mathbf{r})$ inside of Ω_n and 0 outside of Ω_n.

The irregular solutions involved in the Green function are numerically difficult to calculate. Specifically, the numerical error of the irregular solutions becomes uncontrollable as, $\mathbf{r}_n \to 0$.

Green Function of Single Site Scattering

- Single site Green function

$$G_S(\mathbf{r}_n,\mathbf{r}_n;\varepsilon)=\sum_{L,L'}Z_L^n(\mathbf{r}_n;\varepsilon)t_{LL'}^n(\varepsilon)Z_L^{n\bullet}(\mathbf{r}_n;\varepsilon)-\sum_{L}Z_L^n(\mathbf{r}_n;\varepsilon)J_L^{n\bullet}(\mathbf{r}_n;\varepsilon)$$

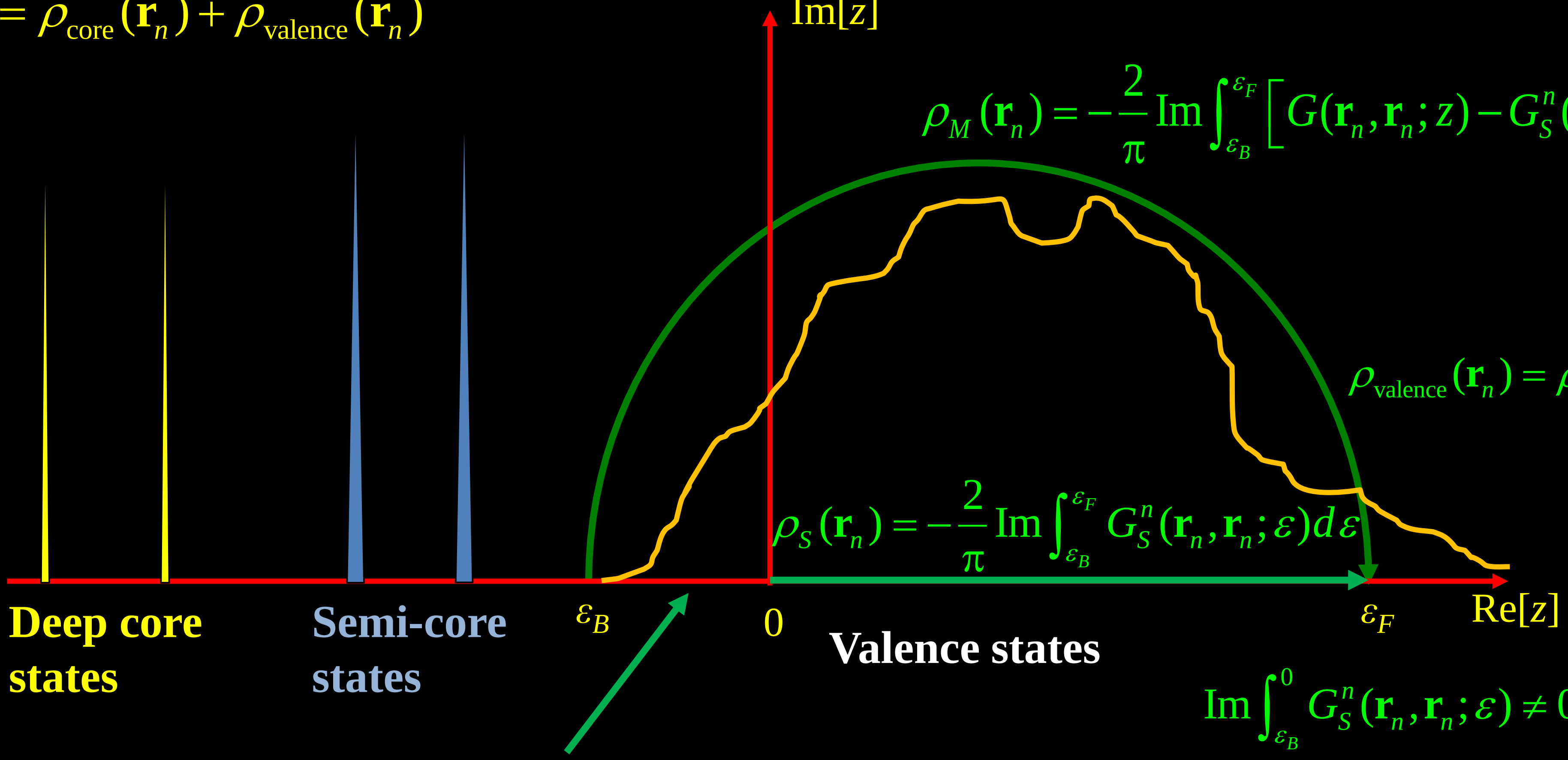
- For ε on the real energy axis, the imaginary part of the 1st term is non-zero if $\varepsilon > 0$
- For ε on the real energy axis, the 2nd term is real
- The imaginary part of the single site Green function on the real energy axis is thus given by

$$\operatorname{Im} G_S(\mathbf{r}_n,\mathbf{r}_n;\varepsilon)=\operatorname{Im}\sum_{L,L'}Z_L^n(\mathbf{r}_n;\varepsilon)t_{LL'}^n(\varepsilon)Z_L^{n\bullet}(\mathbf{r}_n;\varepsilon).$$

$$= 0,\ \text{if}\ \varepsilon < 0$$

Green Function Method and Contour Integration – cont

$$\rho(\mathbf{r}_n) = \rho_{\text{core}}(\mathbf{r}_n) + \rho_{\text{valence}}(\mathbf{r}_n)$$



$$\rho_M(\mathbf{r}_n) = -\frac{2}{\pi}\,\mathrm{Im}\int_{\varepsilon_B}^{\varepsilon_F}\left[G(\mathbf{r}_n,\mathbf{r}_n;z) - G_S^n(\mathbf{r}_n,\mathbf{r}_n;z)\right]dz$$

$$\rho_{\text{valence}}(\mathbf{r}_n) = \rho_S(\mathbf{r}_n) + \rho_M(\mathbf{r}_n)$$

$$\rho_S(\mathbf{r}_n) = -\frac{2}{\pi}\,\mathrm{Im}\int_{\varepsilon_B}^{\varepsilon_F} G_S^n(\mathbf{r}_n,\mathbf{r}_n;\varepsilon)\,d\varepsilon$$

Deep core states

Semi-core states

Valence states

$$\mathrm{Im}\,G_S^n(\mathbf{r}_n,\mathbf{r}_n;\varepsilon) = 0, \text{ for } \varepsilon < 0$$

$$\mathrm{Im}\int_{\varepsilon_B}^{0} G_S^n(\mathbf{r}_n,\mathbf{r}_n;\varepsilon) \neq 0$$

Si calculation failed!

Due to a "shallow" bound state at the Si site that contributes a pole to the single site Green function G_S in $(\varepsilon_B, 0)$.

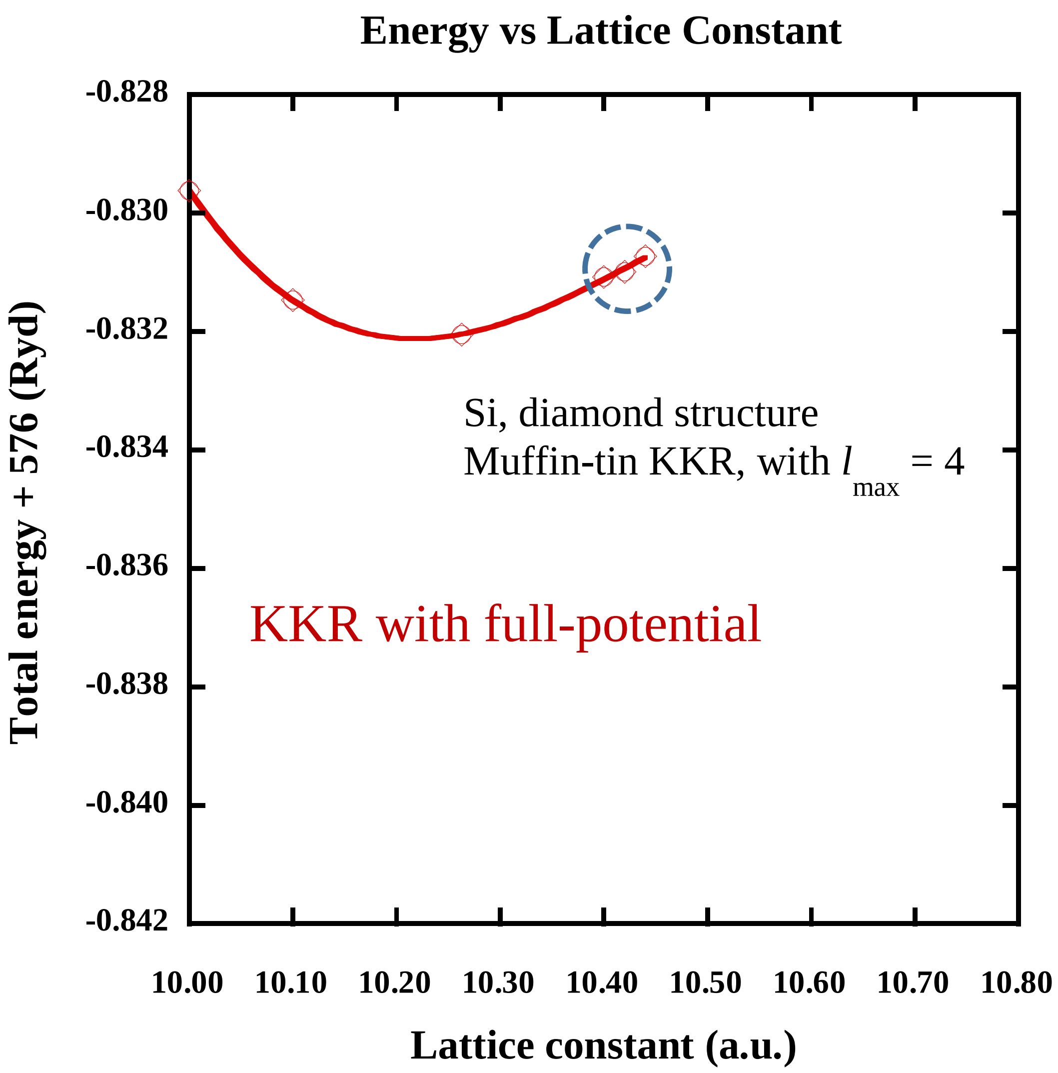
Green Function Method and Contour Integration – cont.

We take the following steps to improve the Green function integration:

- Determine if there are the shallow bound states associated with each atom
  - This is a single site scattering problem
  - The same technique can be used to calculate the core states, which are the “deep” bound states, from the scattering theory approach
- If there are shallow bound states, determine the bound state energy
  - Create a small (~ 5 Gaussian quadrature points) energy contour around the bound state energy and perform the integration
  - Add the integration result to the single site Green function integrated over $(0, \varepsilon_F)$

What about the full-potential Green function approach?

The next try



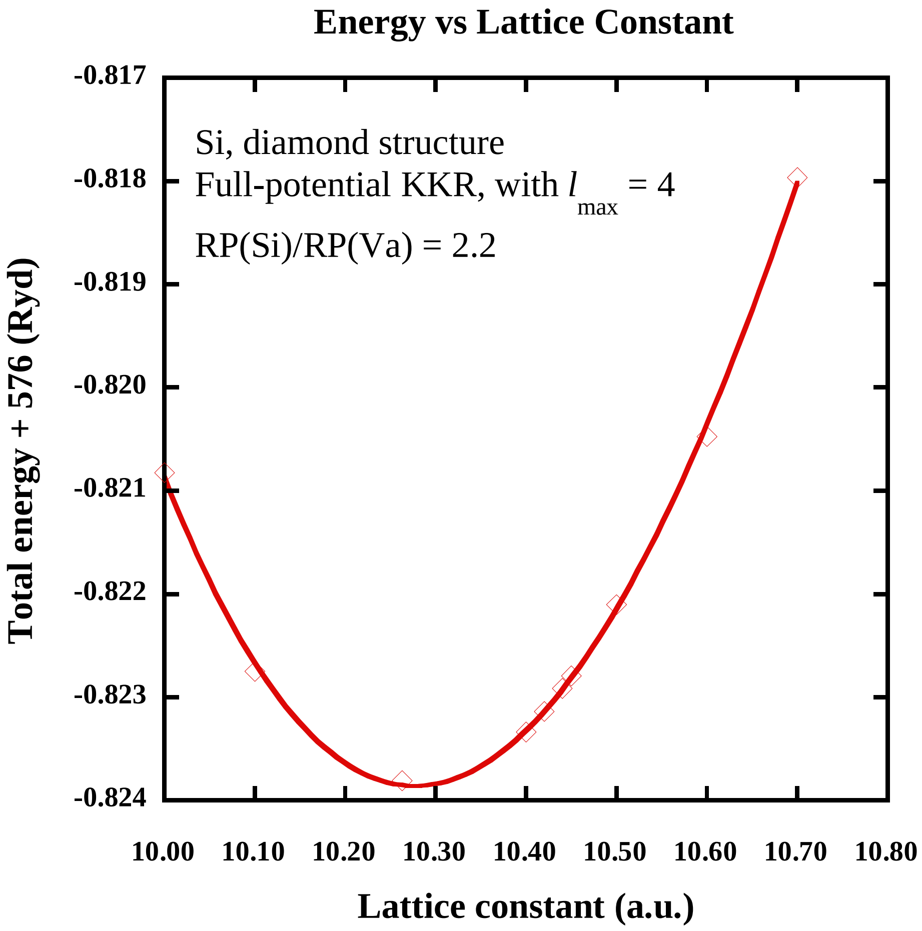
The calculation failed to converge for $a_0 > 10.45$ a.u.

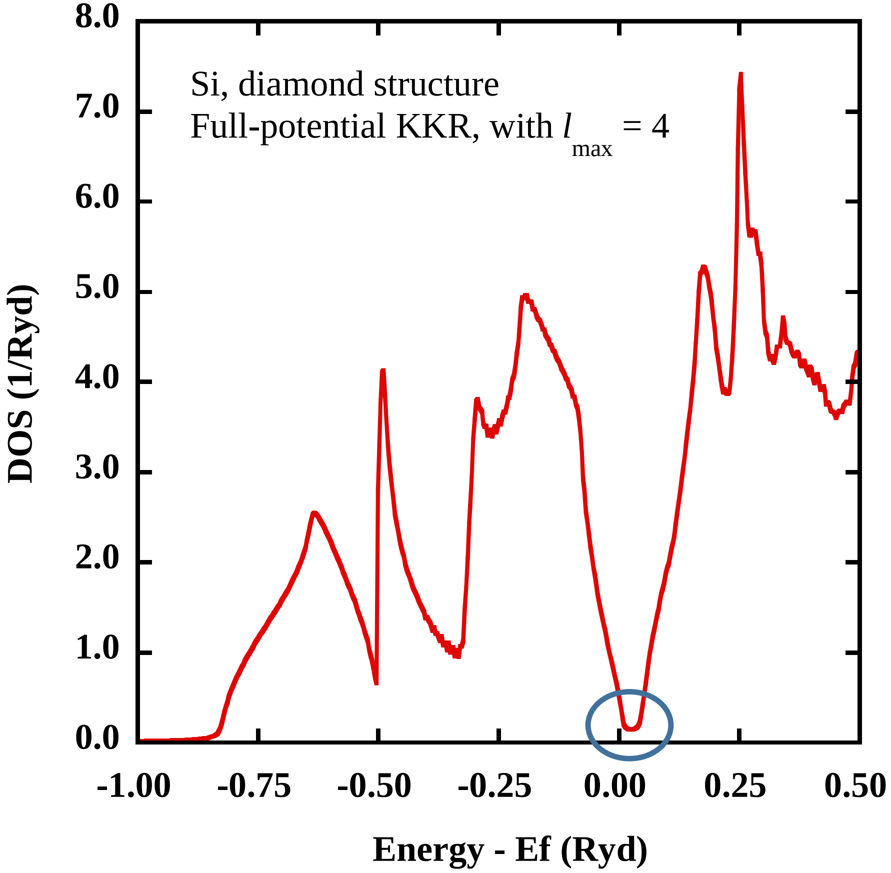
However, for $a_0 < 10.45$ a.u., the total energy does appear to be parabolic.

In the FP-KKR method, the unit cell is divided into non-overlapping atomic cells, each of which contains a single Si or Va atom at the center of the atomic cell.
In atomic cell construction process, we have given Si and Va the same atomic radius: R(Si)/R(Va) = 1.0

Full-potential Green function approach to Si – cont.

Let us give Si and Va a different atomic radius: R(Si)/R(Va) = 2.2



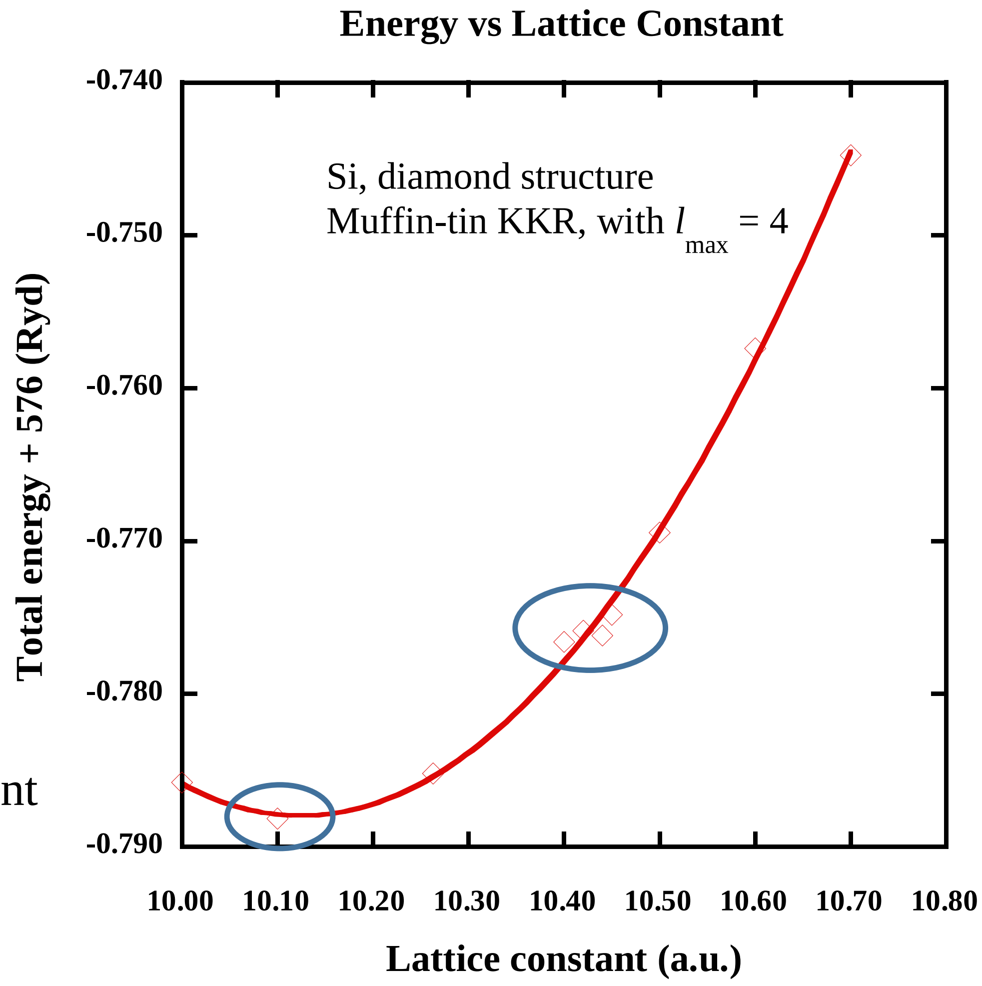


The experimental band gap is 0.086 Ryd (1.17 eV).

The FP-KKR calculation shows the LDA bandgap is around 0.033 Ryd, agreeing well with other band structure calculation results (~ 0.035 Ryd)

Green function approach to Si – cont.

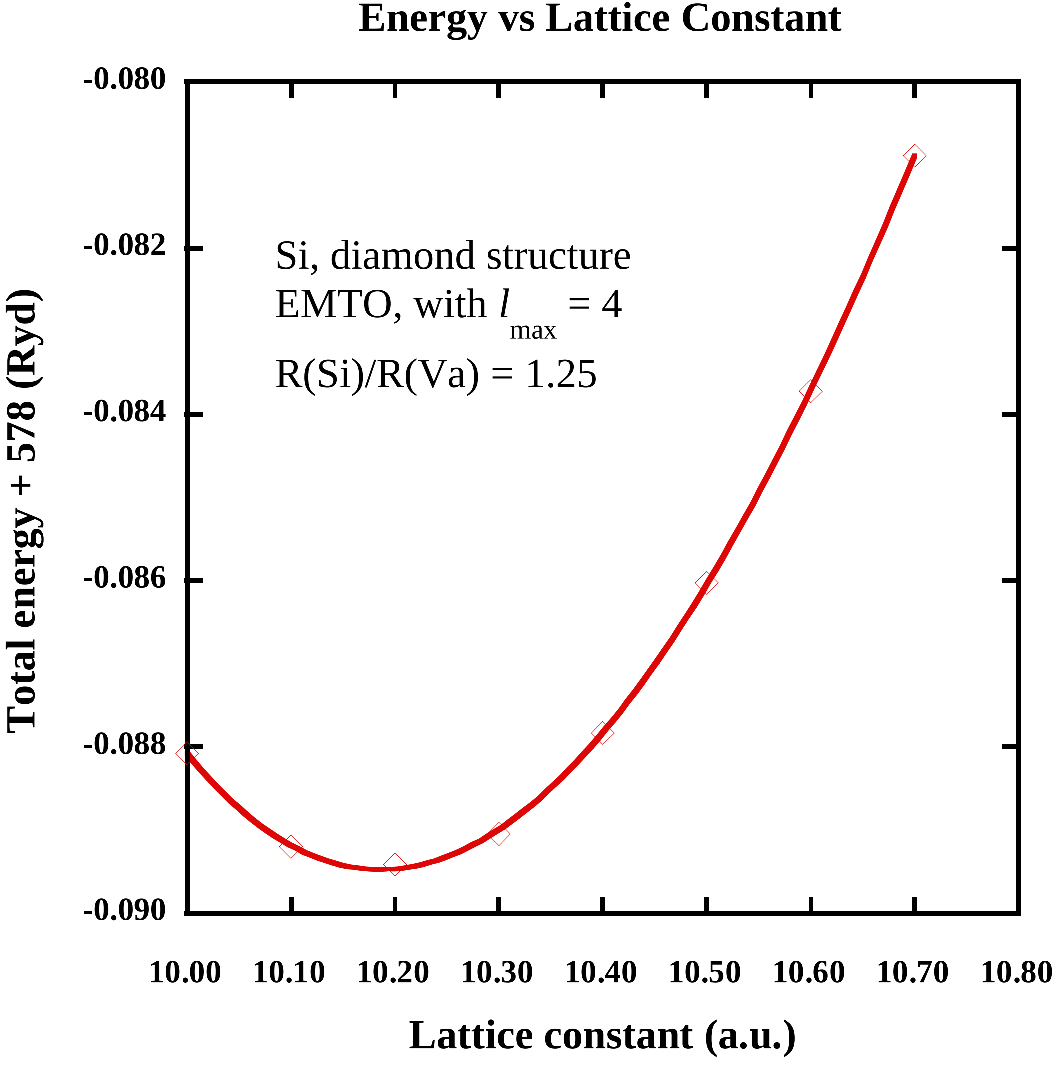
Let us give the muffin-tin KKR one more chance by assigning Si and Va a different atomic radius: R(Si)/R(Va) = 2.2



The equilibrium lattice constant is off by ~ 1%

Green function approach to Si – cont.

The EMTO results provided
by Franco Moitzi



In Summary

- Full-potential or full-charge density is needed for the ab initio calculation of Si and other covalent bonding systems
- Empty cell volumes are needed to fill the open structures, but the size of the empty cell needs careful examination
- It is necessary to consider a general approach to the atomic volume setup, especially different atoms can occupy different space volume
  - We can use atomic radius of the involved atoms to set up the radical plane
  - An alternative suggestion is to place the radical plane between two neighboring atoms at the point where the charge density is at its ext
    - The radical plane needs to be adjusted at each SCF iteration