Density Functional Description of $CoSi_2$ on Si (100)

Steven Kenny
Ilan Goldfarb, Elena Akhmatskaya,
Andrew Horsfield and Andrew Briggs

OxfordMaterials

Outline

- Schrödinger's equation and Density Functional Theory
- Approximations!
- Periodic Boundary Conditions
- How an STM works
- Results from Experiment
- Surface Energies and Chemical Potentials
- The $\mathrm{CoSi_2}$ Surface Reconstructions
- Simulated STM images
- Co on Si (100)
- Conclusions

Density Functional Theory I

- What we are trying to solve is the Time Independent Schrödinger's equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

- This is a many-body equation and is VERY expensive to solve exactly, e.g. CI, QMC. These methods can typically treat only a few atoms.

- For any materials problem of interest we need to employ another approach.

Density Functional Theory II

- The Density functional theory of Hohenberg, Kohn and Sham[1] states:

The total ground state energy of a system is a unique functional of the electron density, ρ. The minimum energy of this functional is the ground-state energy of the system and the density that yields this is the exact single particle density.

- With this statement they replaced the many-electron problem with an equivalent set of self-consistent one-electron equations, the Kohn-Sham equations.

---

[1] P. Hohenberg and W. Kohn, *Physical Review* **136B**, 864-871 (1964); W. Kohn and L.J. Sham, *Physical Review* **140A**, 1133-1138 (1965)

Self-consistent Kohn-Sham Equations I

- The Kohn-Sham energy functional is:

$$\begin{aligned} E &= 2\sum_{\mathrm{occ}} \varepsilon_i + E_{\mathrm{ion-ion}} - \frac{e^2}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ & \quad + \int \rho(\mathbf{r})(E_{xc} - V_{xc}) d\mathbf{r} \end{aligned}$$

- The Kohn-Sham equations are:

$$\begin{aligned} \varepsilon_i \psi_i(\mathbf{r}) &= \left[-\frac{\hbar}{2m}\nabla^2 + V_{\mathrm{ion}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right] \psi_i(\mathbf{r}) \\ \rho(\mathbf{r}) &= 2\sum_i |\psi_i(\mathbf{r})|^2 \\ V_H(\mathbf{r}) &= e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \\ V_{xc}(\mathbf{r}) &= \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \end{aligned}$$

- These Kohn-Sham equations represent the mapping of the interacting many-body equation onto a system of non-interacting electrons moving in an effective potential due to all the other electrons.

Self-consistent Kohn-Sham Equations II

- The general scheme for solving the equations is:

1. Make an initial guess at the charge density; typically a superposition of atomic charge densities.
2. Construct the potentials with this.
3. Solve for the eigenvalues and eigenvectors, ψ_i's.
4. Construct a new density from these.
5. Mix the old and new densities together to form a new input density.
6. Repeat from step 2 until the input and output densities agree within some criteria.

Approximations:-
Exchange-Correlation Functional

- The only thing we do not know is what the exact exchange-correlation functional is.

- If we knew the exact exchange-correlation functional then we could solve the problem exactly. Density functional theory is not an approximation.

- We do not, however, know what the functional is so we must make a guess for this.

- The guess we make in general is the so called *local-density approximation*:

The exchange-correlation per electron at a point in space is the same as for a homogeneous electron gas of the same electron density.

$$E_{xc}[\rho(\mathbf{r})] = \int \varepsilon_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

- This is still the most widely used functional although a lot of calculations now use the generalised gradient approximation[2].

---

[2] A.D. Becke, *Physical Review A* **38**, 3098 (1988)

Approximations:- Pseudopotentials I

- When atoms bond together it is the valence (outer) electrons that take part in the bonding.

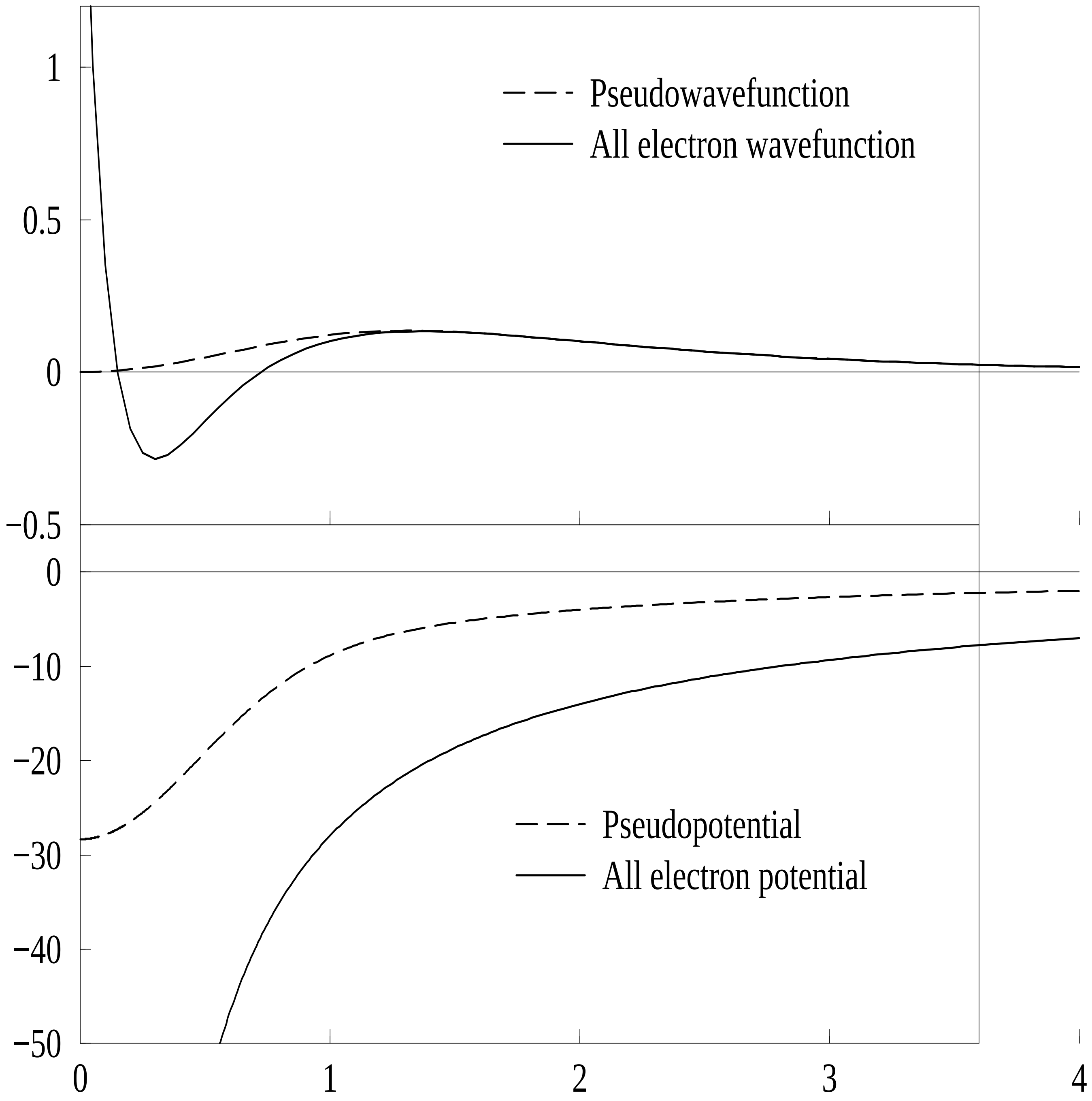
- What pseudopotentials do is replace the full potential (due to the nucleus) with one due to a combination of the nucleus and the core electrons.

- So pseudopotentials are an effective potential constructed so as to mimic the potential a valence electron feels due to the combination of the ion core and the core electrons [3].

---

[3] M.L. Cohen and V. Heine, *Solid state physics* **24**, 37 (1970)

Approximations:-
Pseudopotentials II



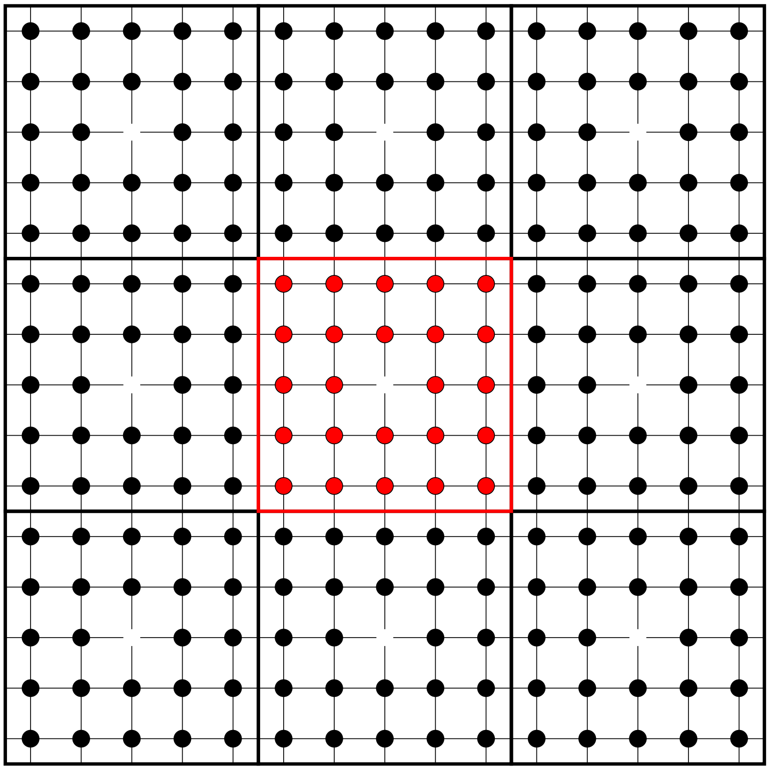
Periodic Boundary Conditions I

- In order to perform calculations of interest we need to perform calculations on systems which are not periodic; such as surfaces and vacancies.

- The methods we typically use can only deal with periodic systems.

- What we do is create a periodic cell from the nonperiodic system.

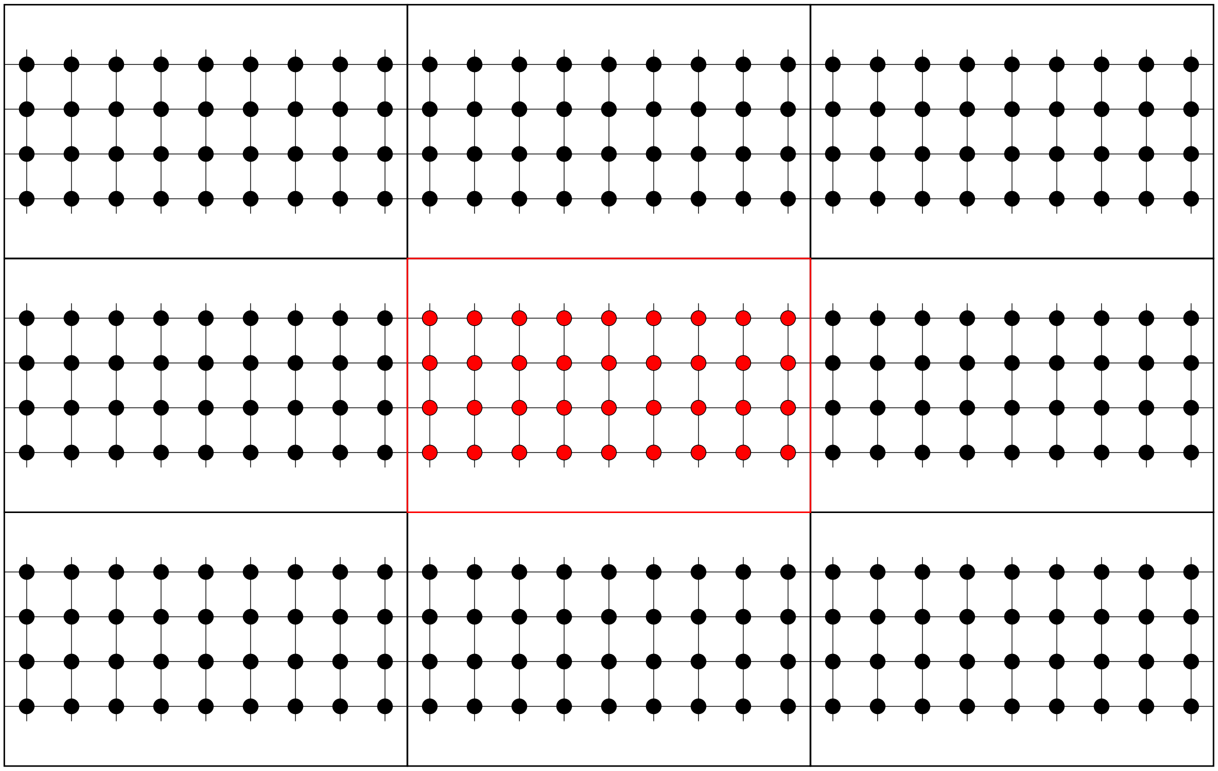
Vacancy:



OxfordMaterials

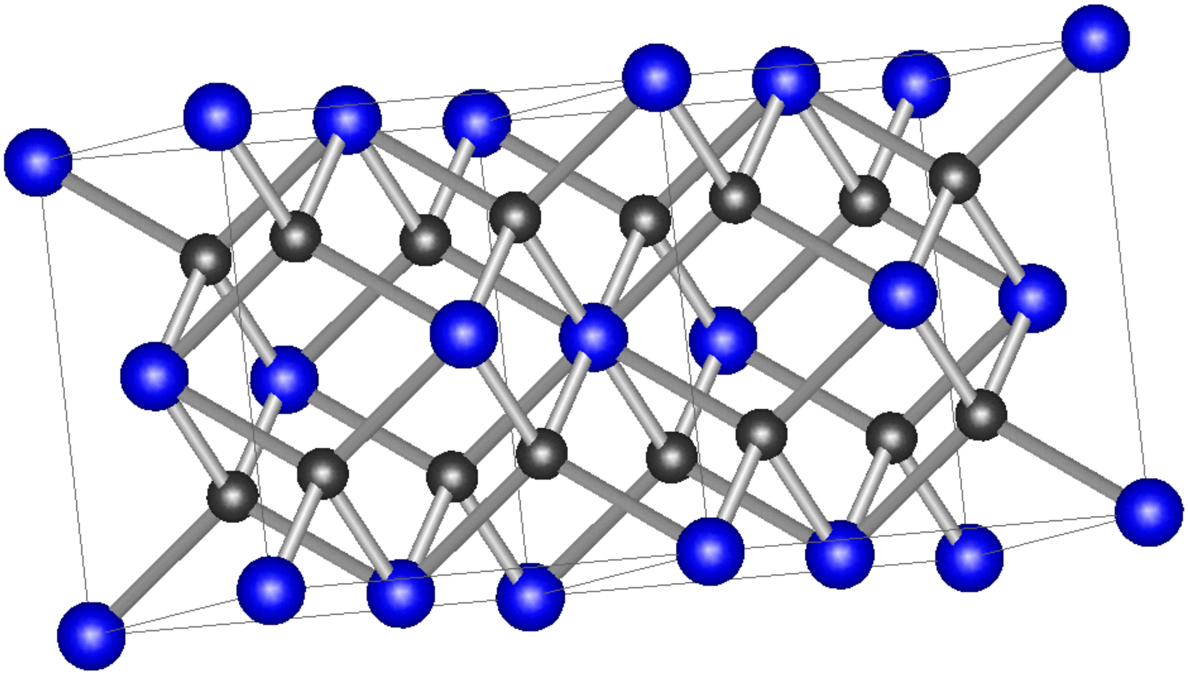
Periodic Boundary Conditions II

Surface:

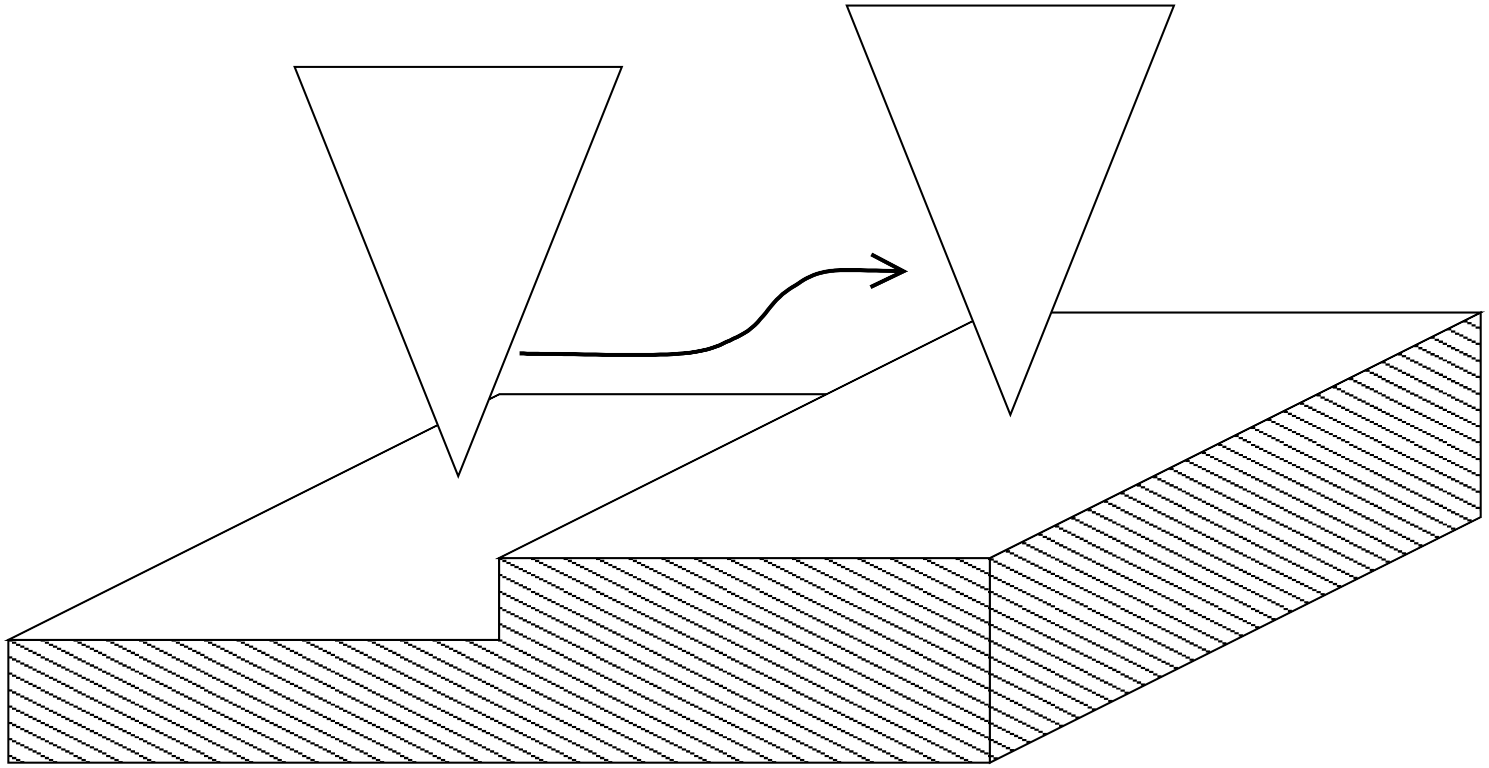


- Have to be careful that cell is large enough that there is little interaction between periodic images of the vacancy or surface.

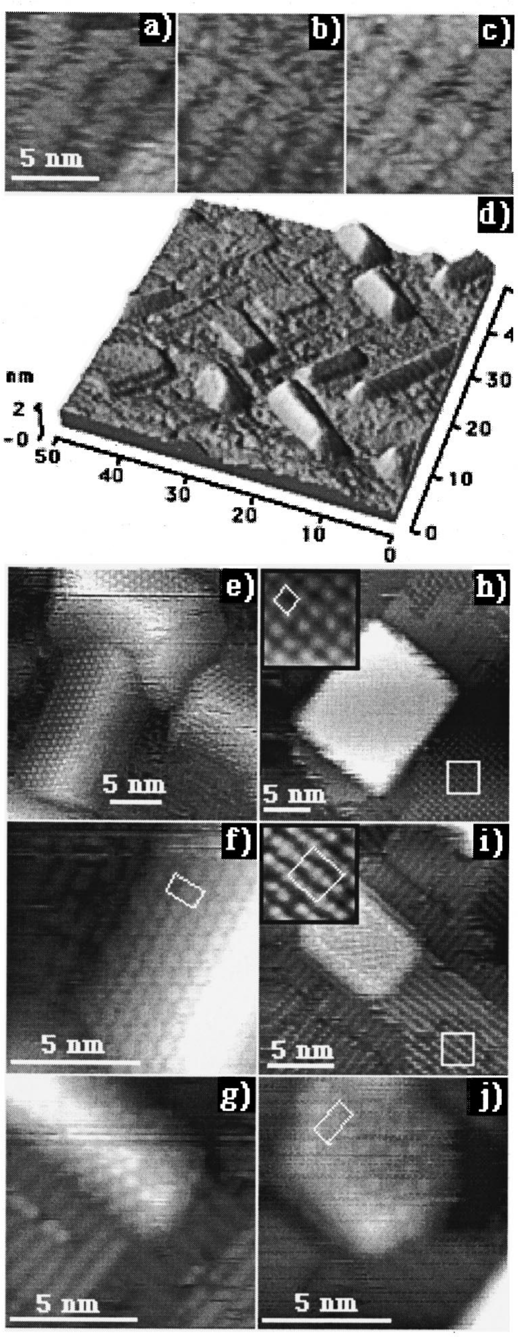
$CoSi_2$ Structure



Principal of an STM

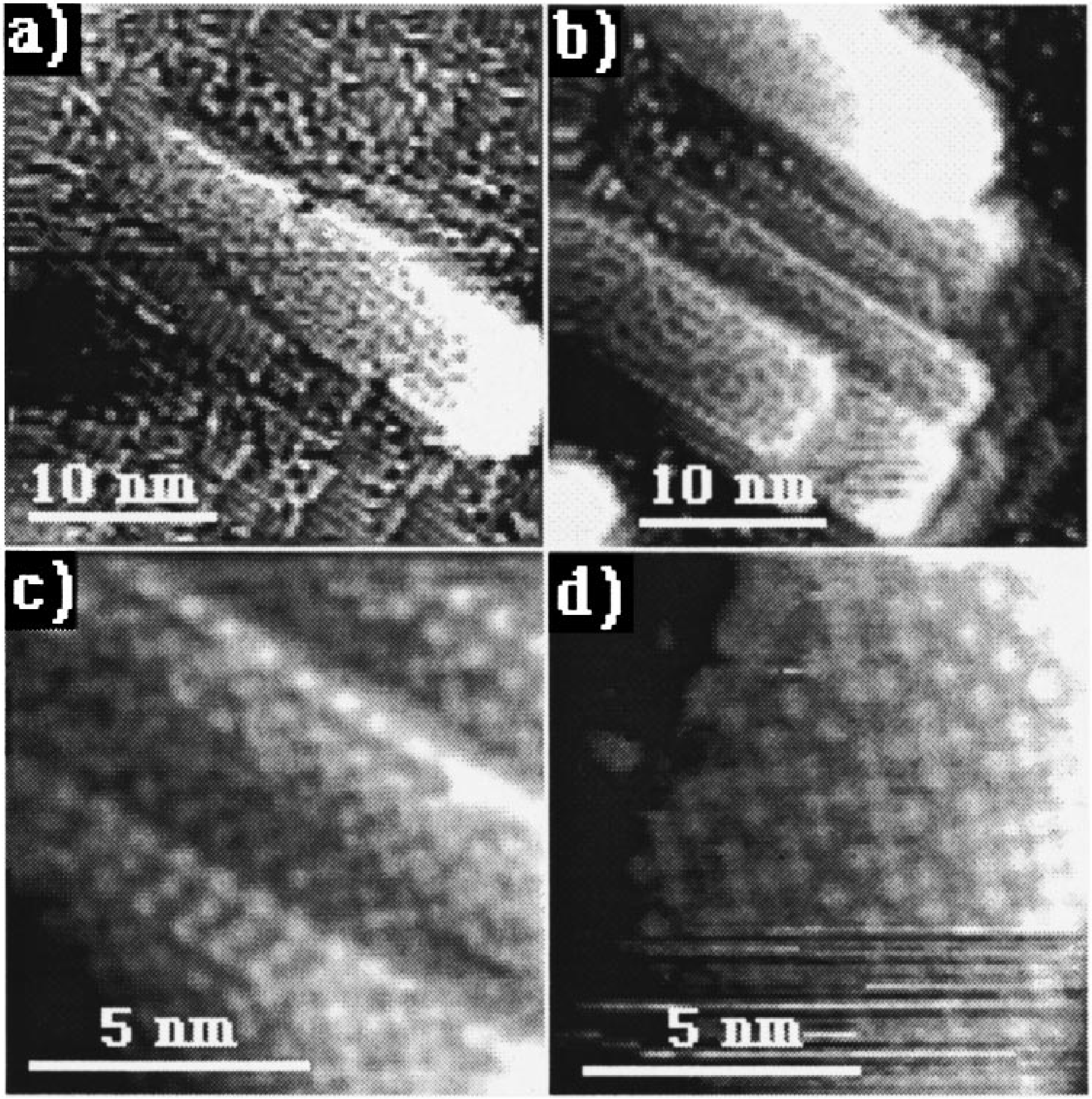


STM image of CoSi$_2$ on Si (100)

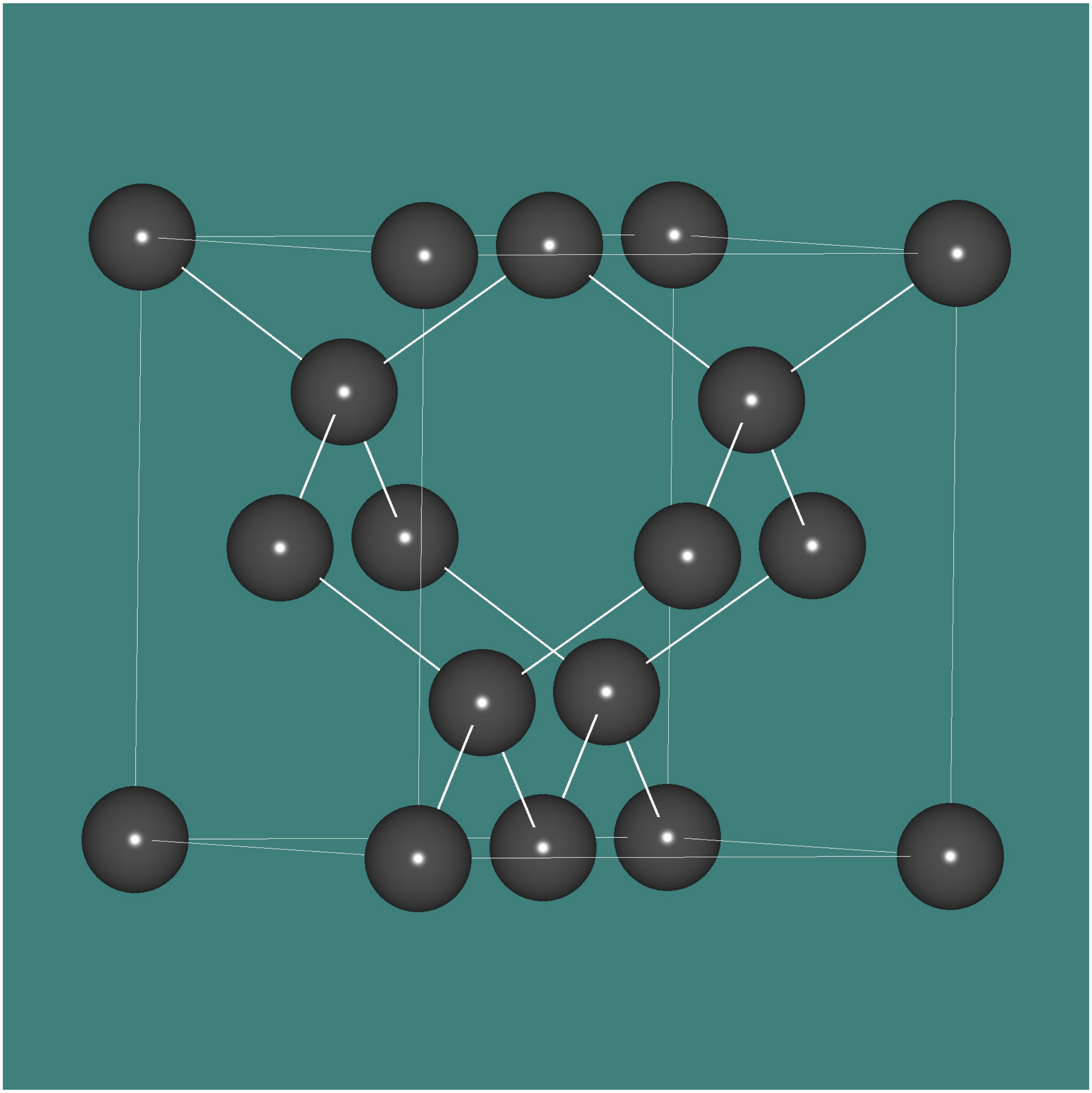


OxfordMaterials

STM image of (100) $CoSi_2$ on Si (100)



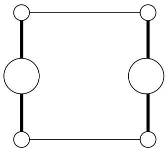
Surface Reconstructions

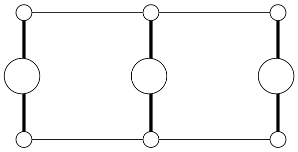


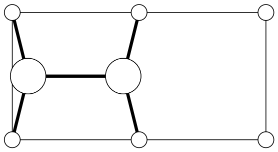
Surface Reconstructions

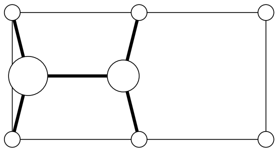
- Most simple metal surfaces do not reconstruct but lots of semiconductor surfaces do.

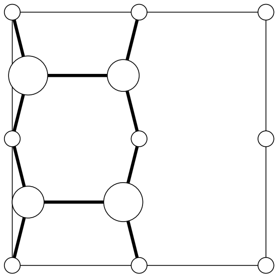
- Silicon does forming a dimerised surface thus reducing the number of dangling bonds.


1x1


2x1






2x2

- Reconstructions such as tilted dimers only happen if you break the symmetry.

Surface Energies

- When surfaces reconstruct they do so to lower their surface energy.

- This might be to try and saturate dangling bonds or it may be more preferable to put one atom species on the surface rather than another.

- Many other factors also influence what the most stable surface reconstruction is.

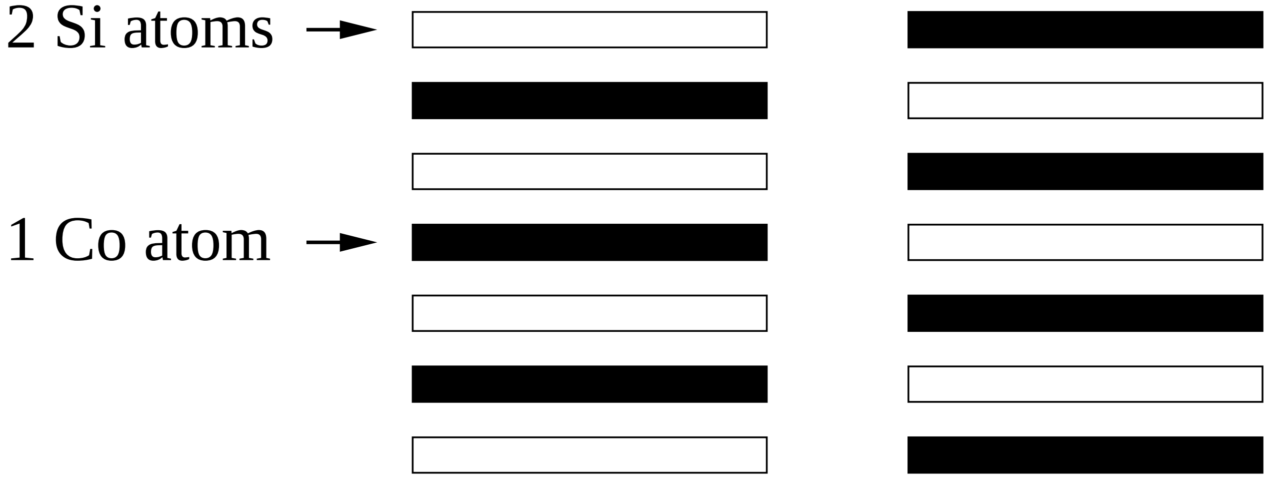
- An understanding of the energetics of the surface reconstructions is essential for understanding the equilibrium driving forces for a system.

Chemical Potentials

- For systems containing more than one atomic species we need to address the problem of defining a chemical potential.

- Why?

- Surface reconstructions on the $\mathrm{CoSi_2}(100)$ surface

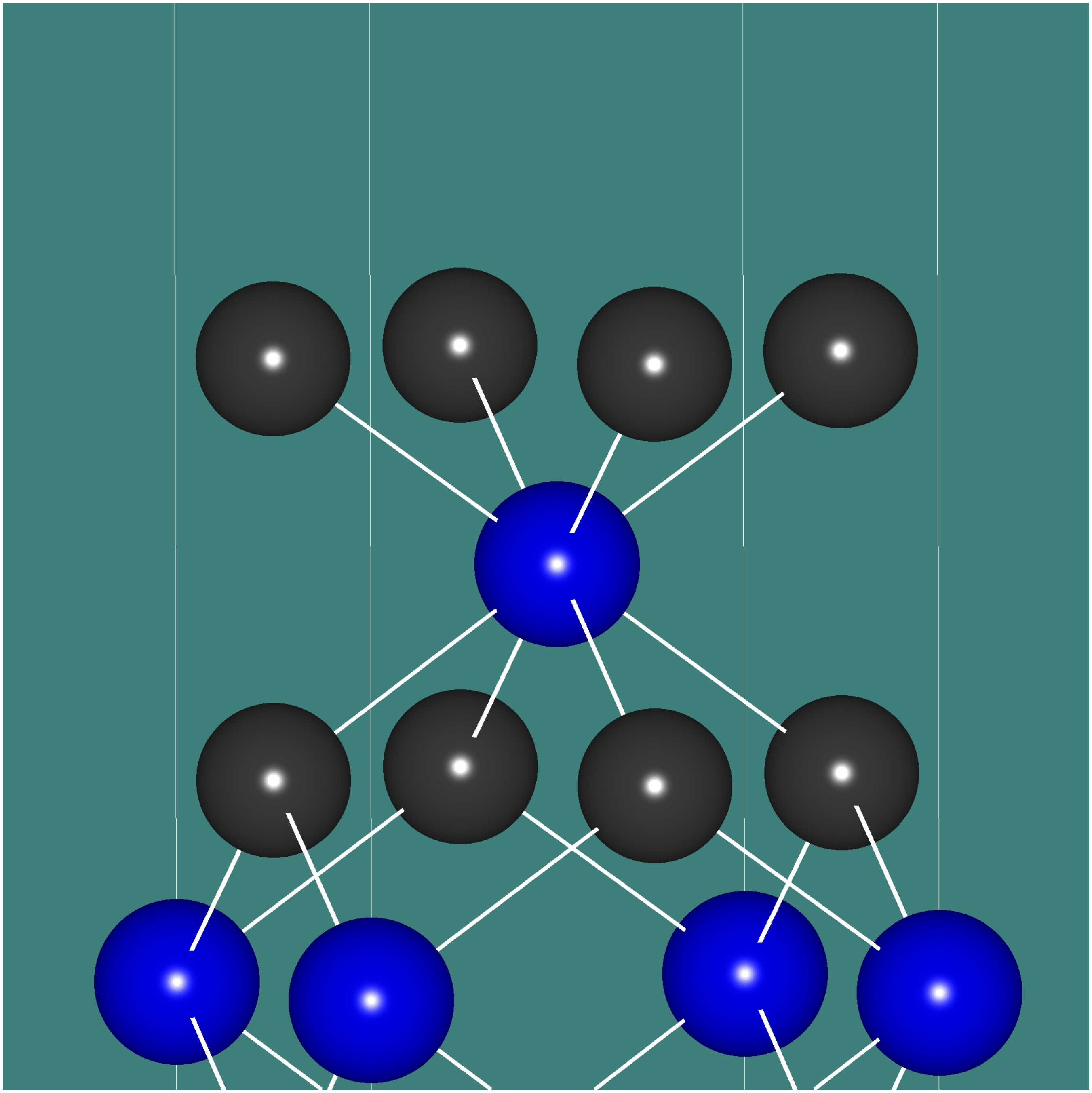


- Cell on the left has 3 Co's and 8 Si's the one on the right 4 Co's and 6 Si's; neither is stoichiometric.

- If we want to calculate the surface energy of either cell we need to define the chemical potential of the Co and Si atoms.

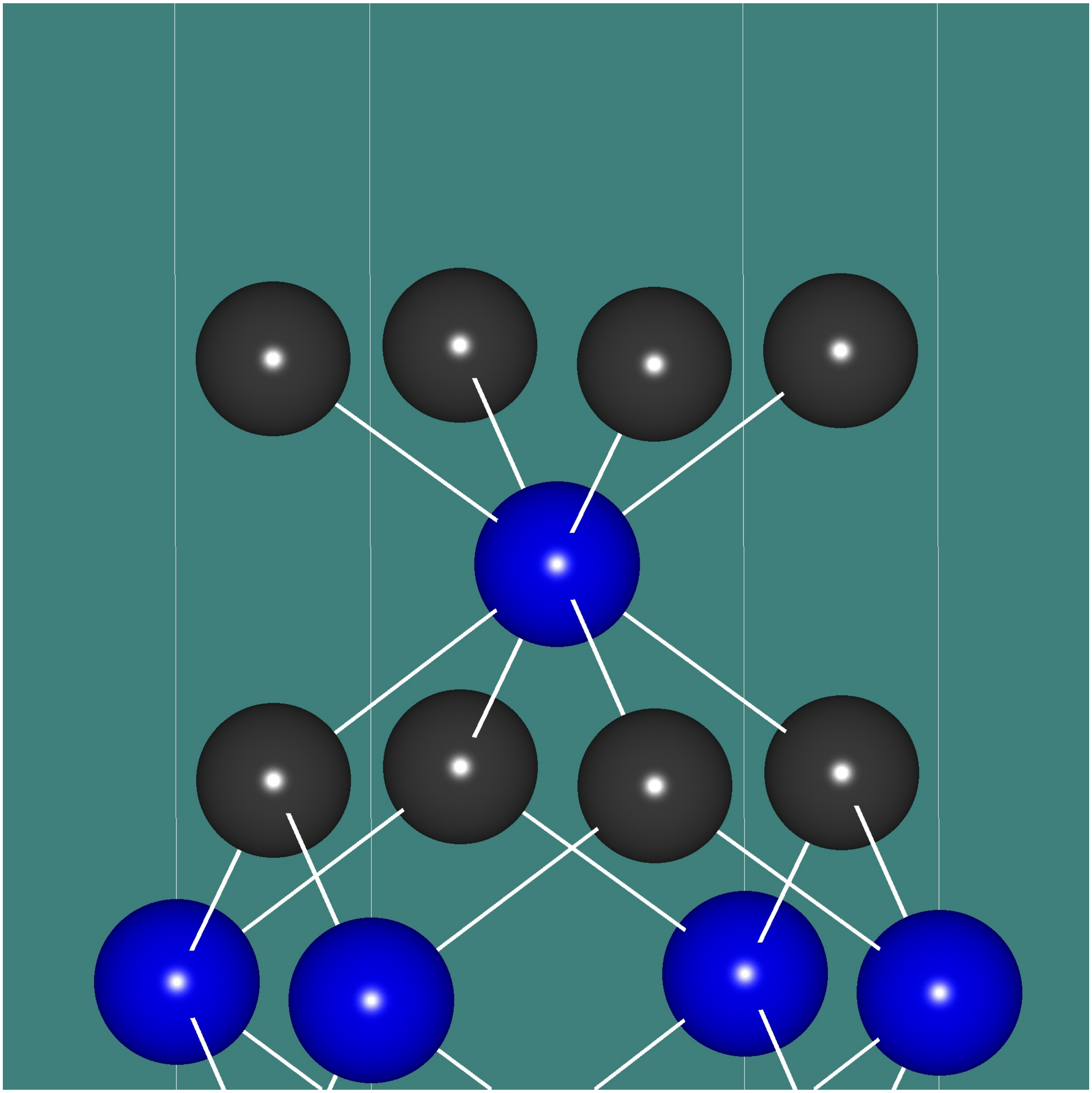
$$\mu_{\mathrm{CoSi_2}} = \mu_{\mathrm{Co}} + 2\mu_{\mathrm{Si}} + H_{\mathrm{CoSi_2}}$$

p(1×1) Si terminated Surface

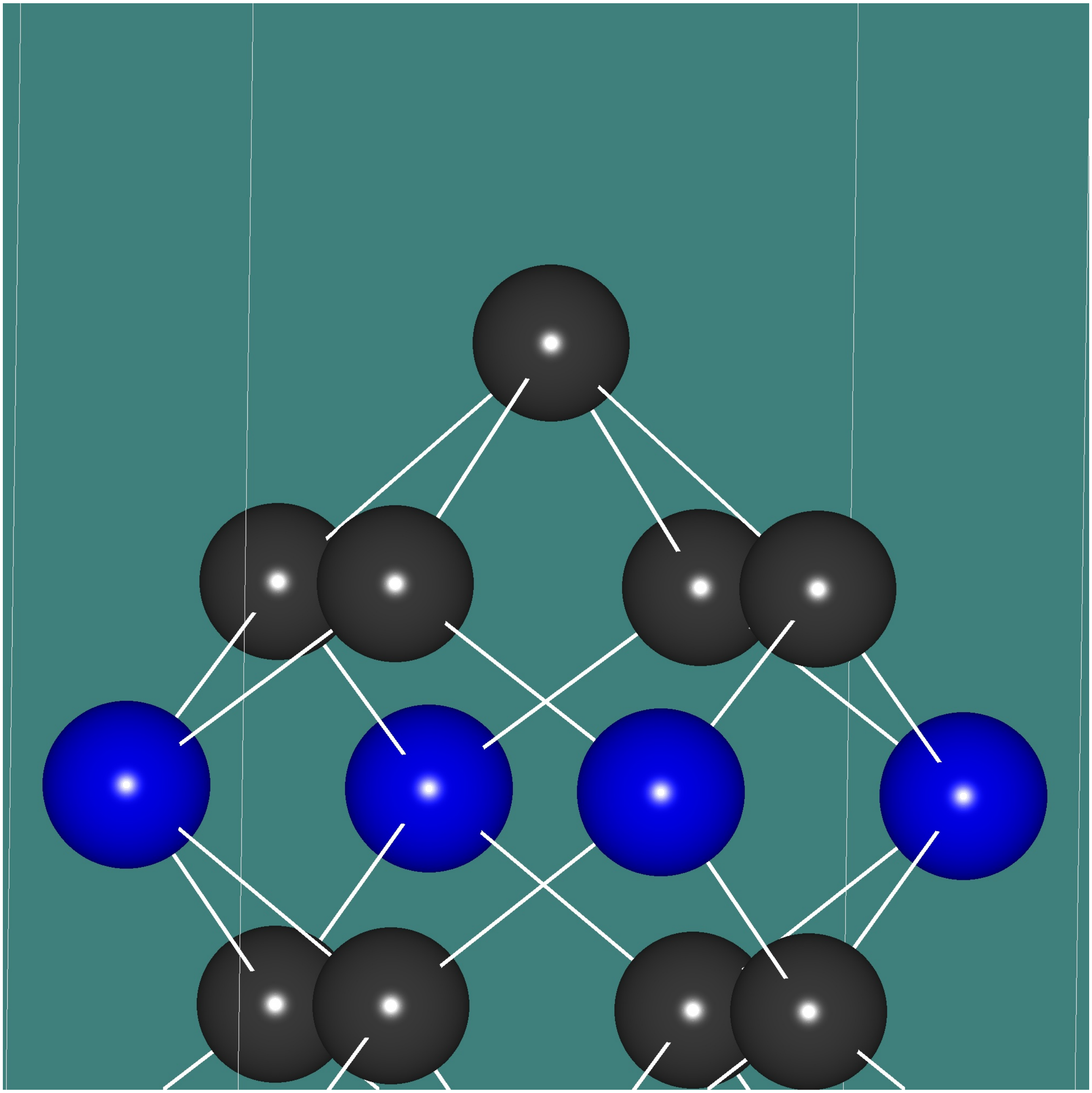


OxfordMaterials

p(1×1) Co terminated Surface

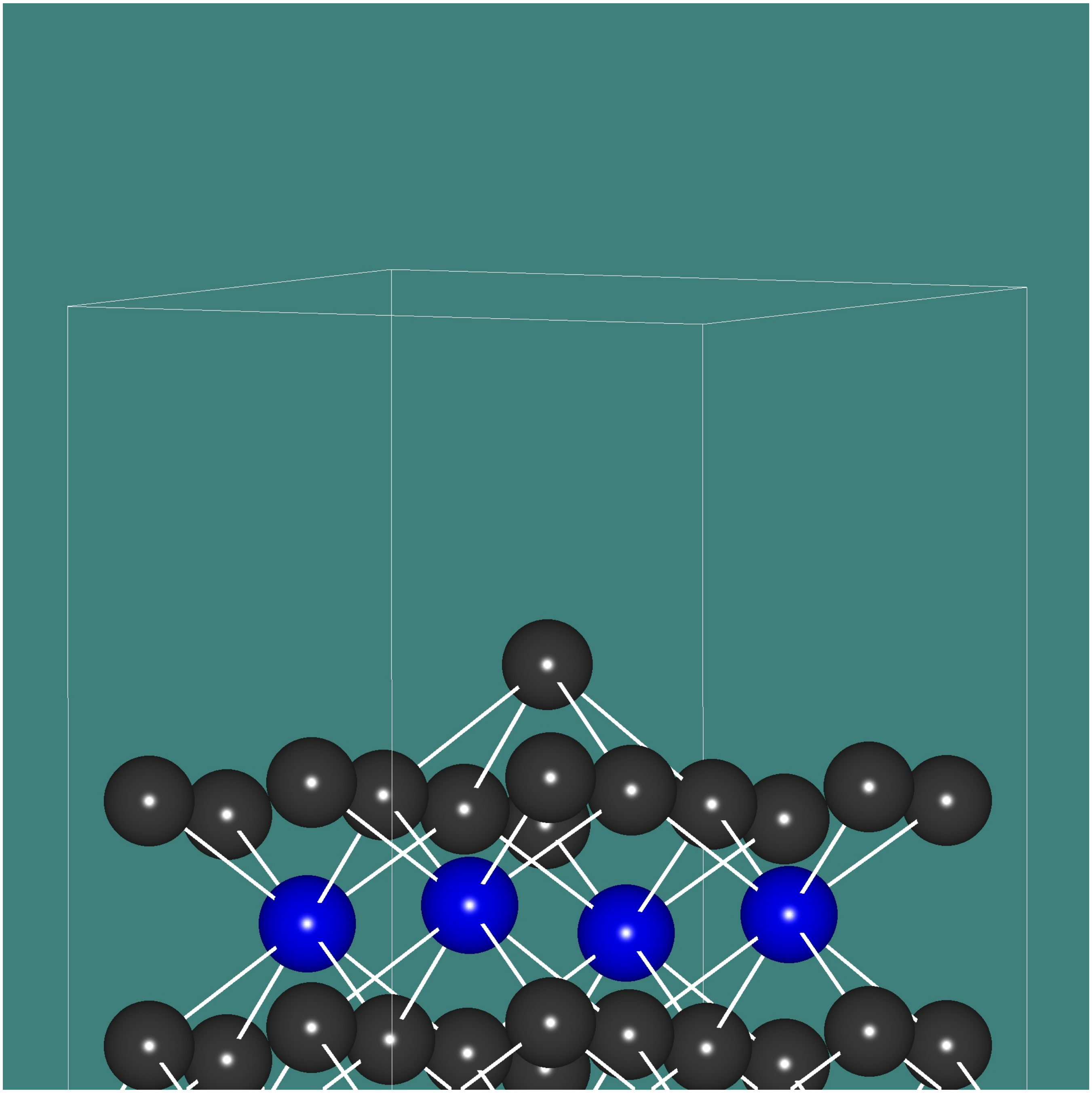


c(2×2) Si terminated Surface

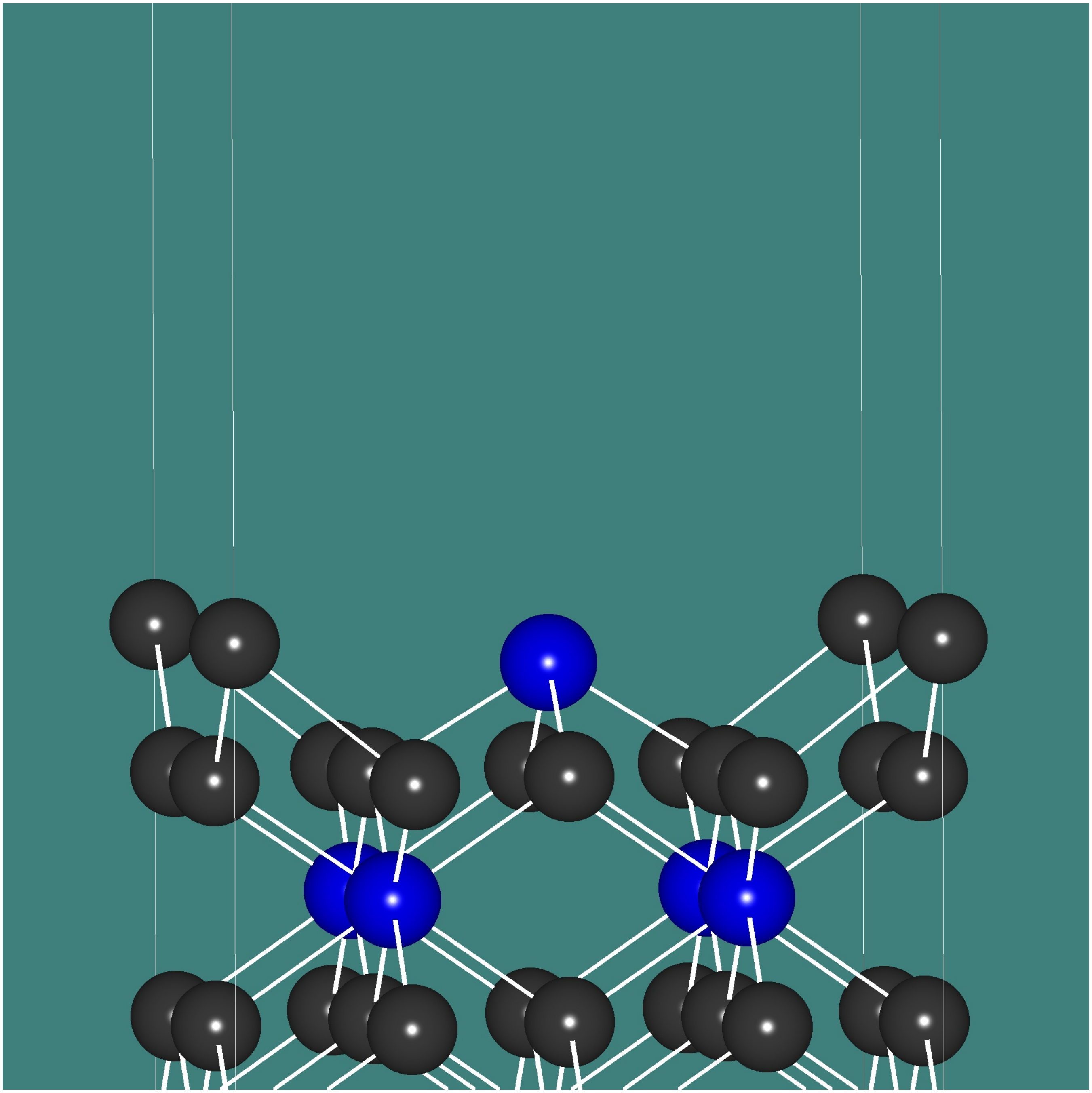


OxfordMaterials

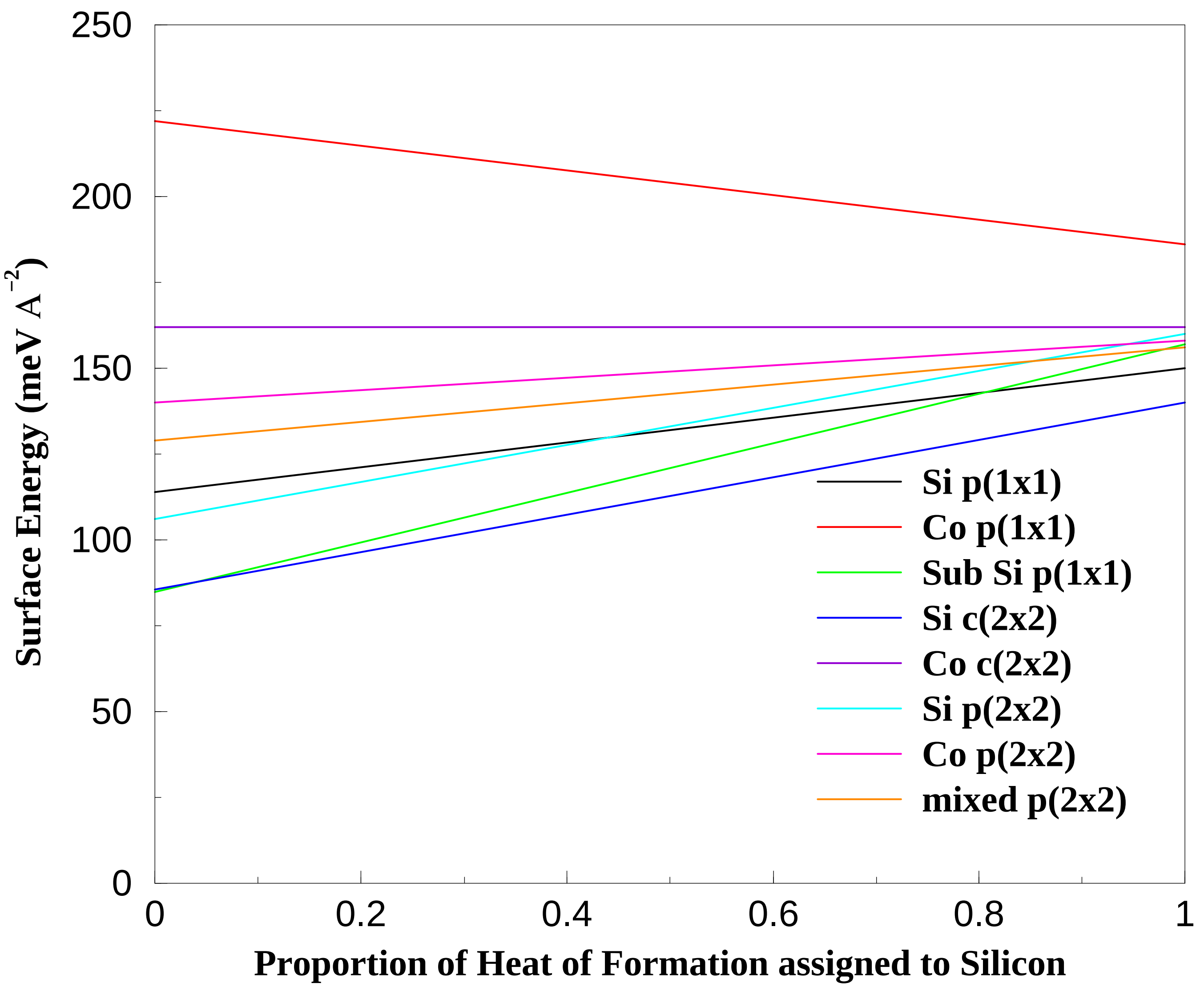
p(2×2) Si terminated Surface



p(2×2) Mixed terminated Surface



Phase Diagram for CoSi$_2$ Surface

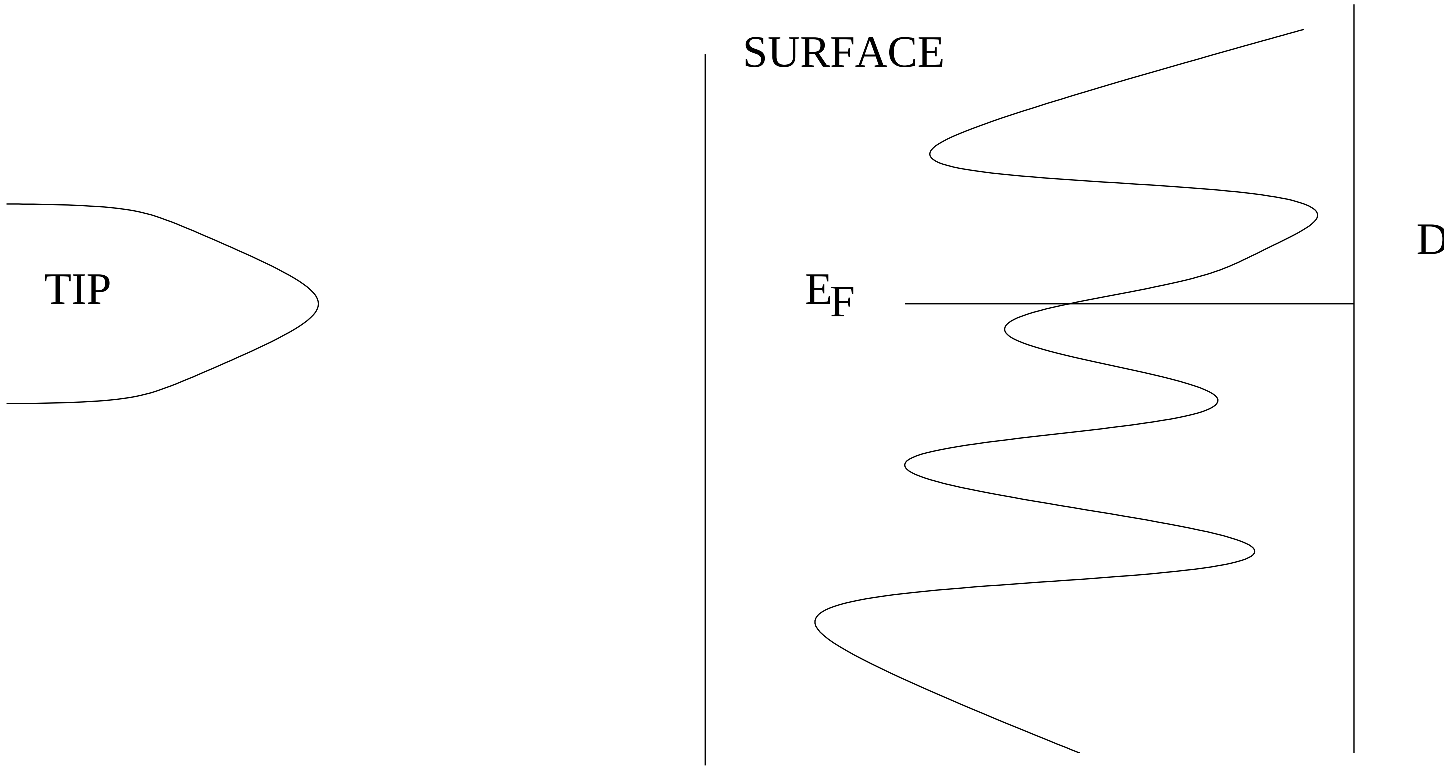


STM Image Simulation

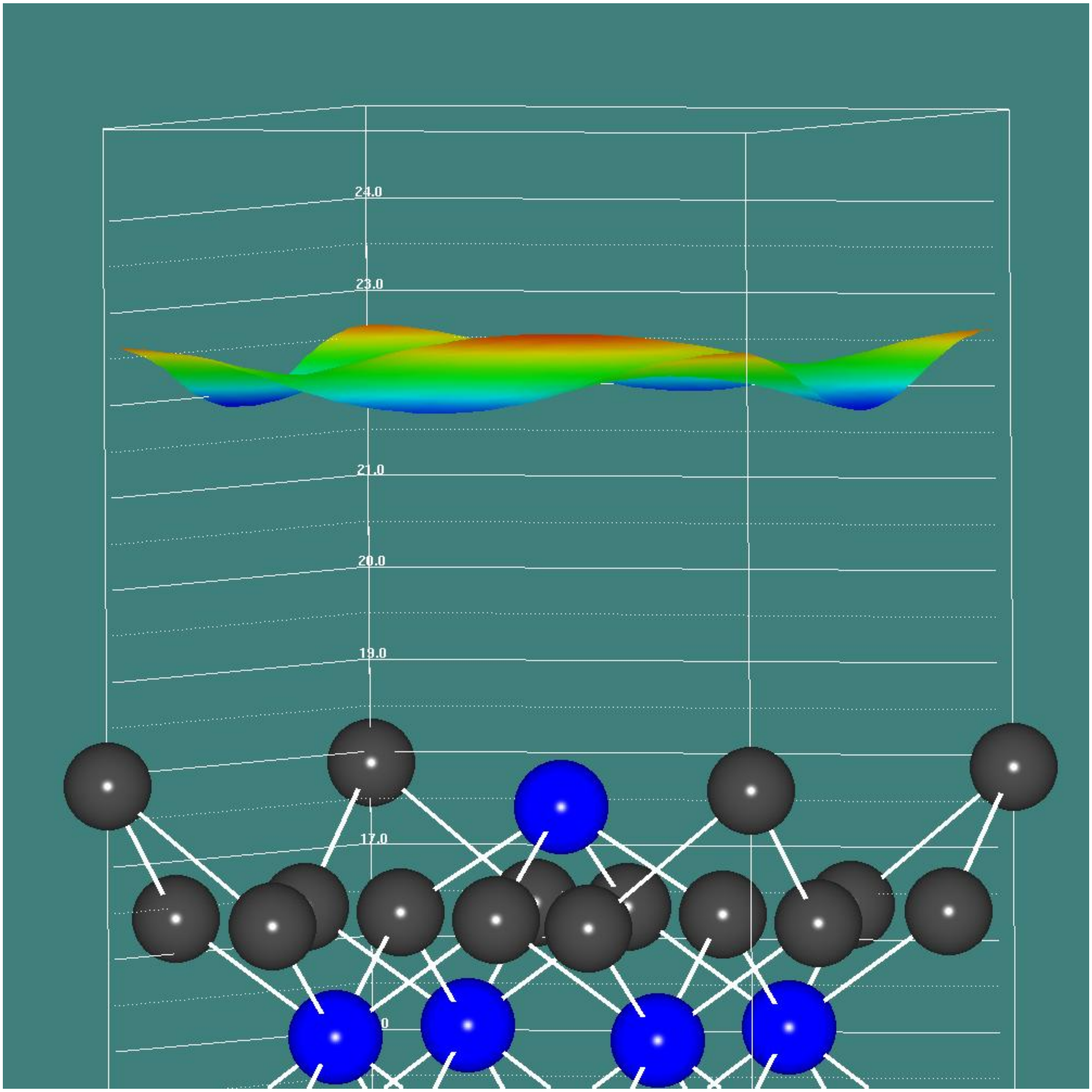
- What an STM tip sees is the surface electronic structure, this is not always the same as the underlying physical surface.

- A simple model can be used to produce simulated STM images from an electronic structure calculation.

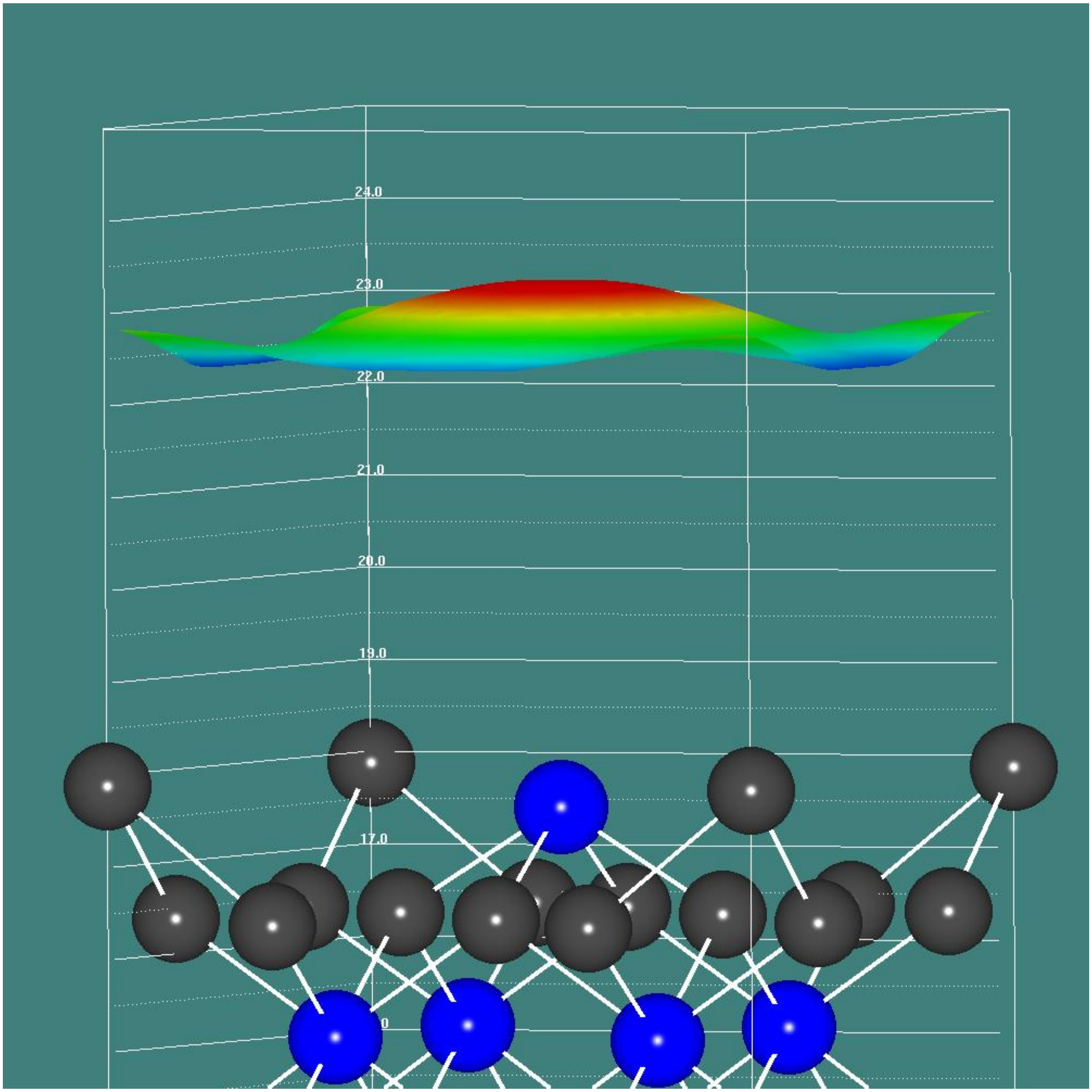
- By taking eigenstates within the energy window of the tunnelling a simulated STM image can be produced that gives at least a qualatative description of what is observed.



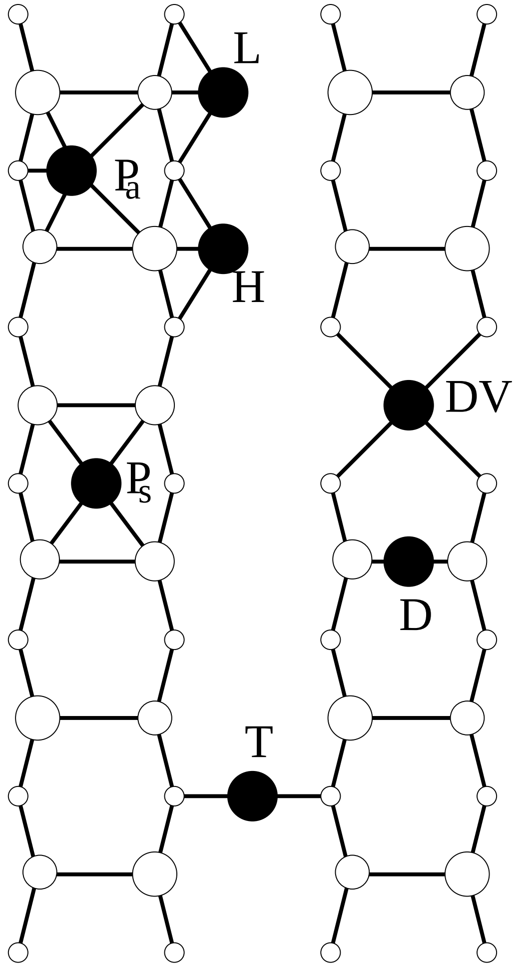
Simulated STM Image:- Relaxed V=0.5



Simulated STM Image:- Relaxed V=1



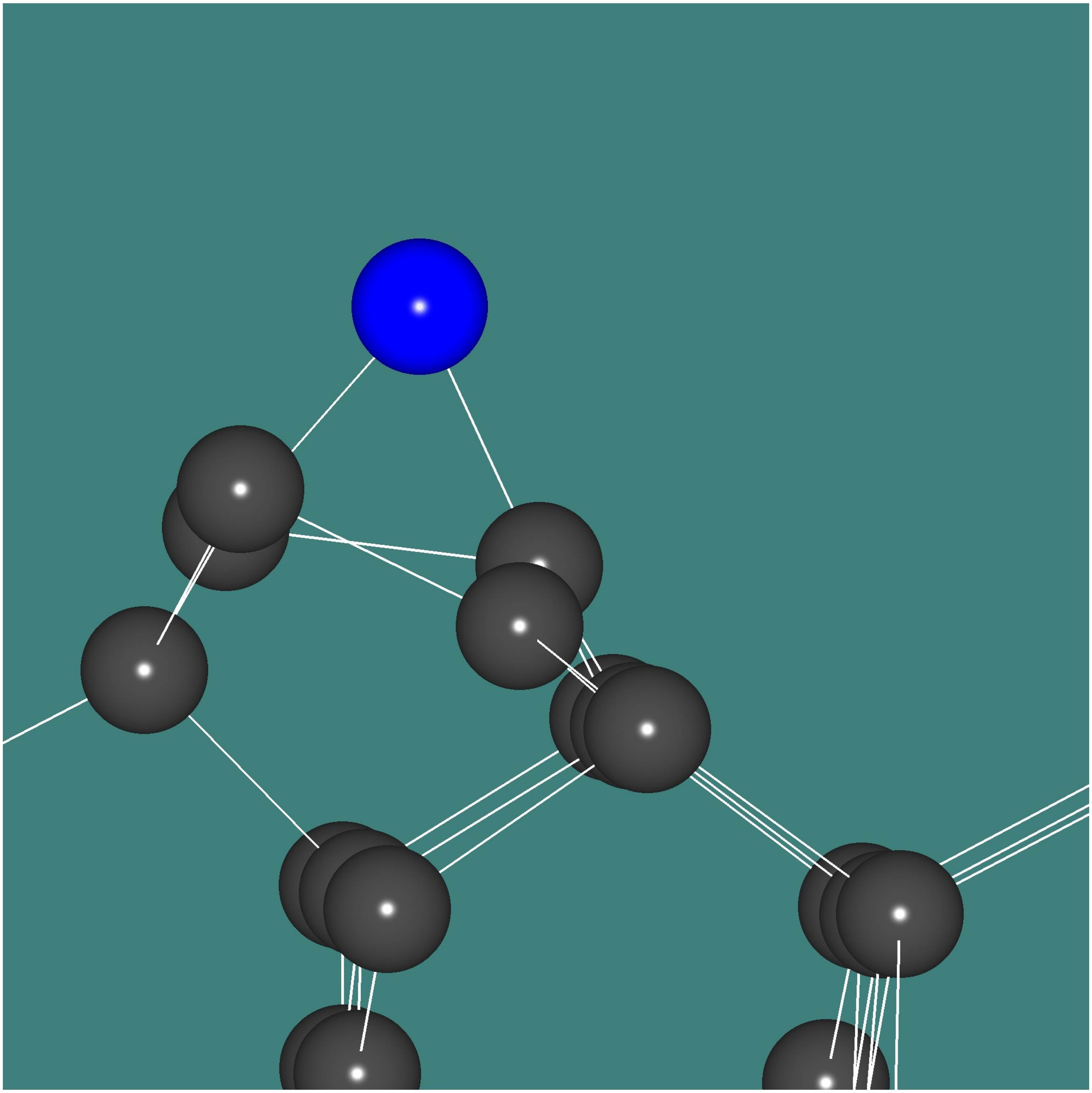
Co on Si (100):- Initial bonding Site



- The picture above shows a number of possible bonding sites for a Co atom on a Si(100) surface.

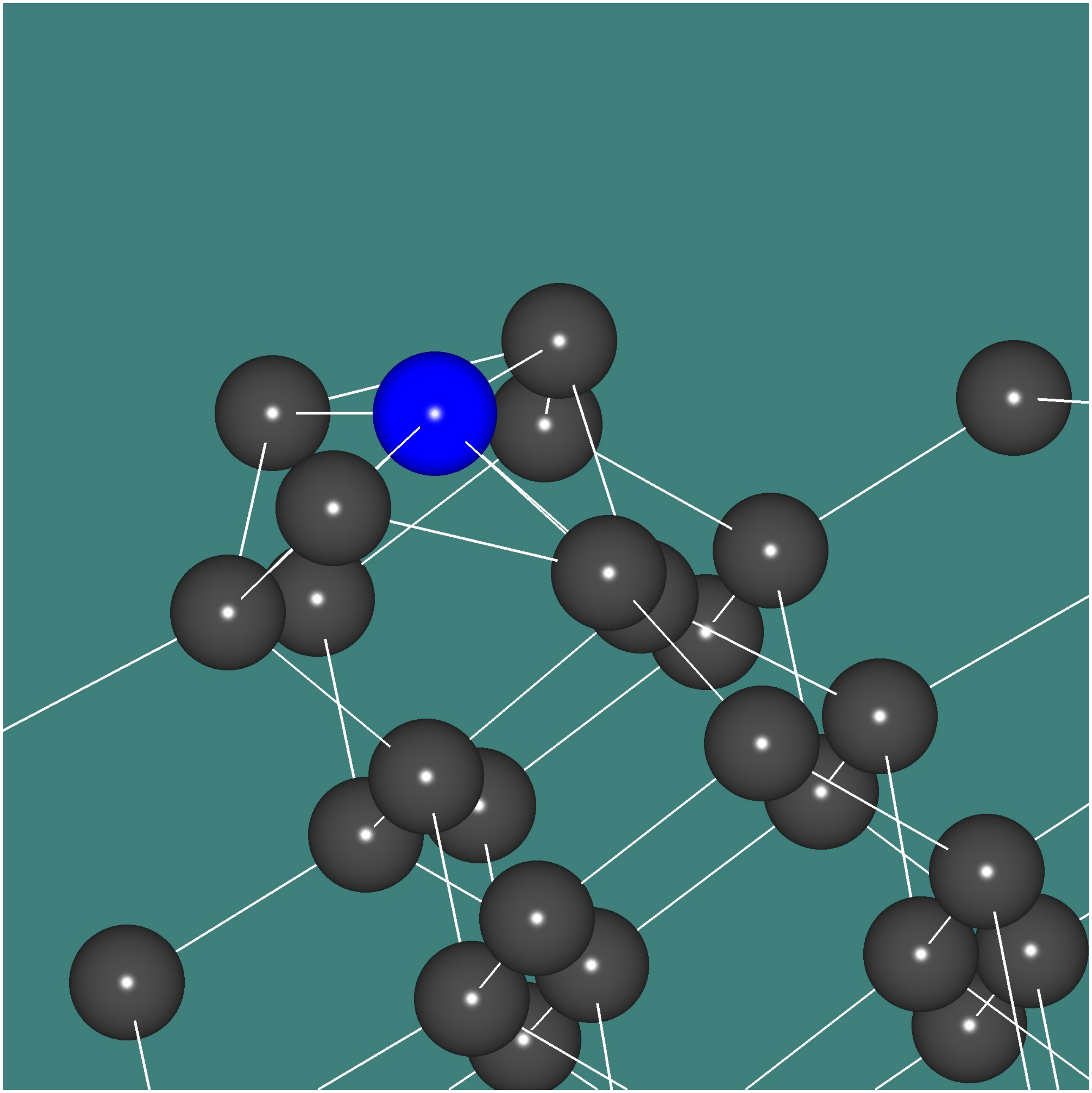
- To find the real site in which the Co atom sits it is necessary to perform calculations for all the sites to see which is most stable.

Dimer Site



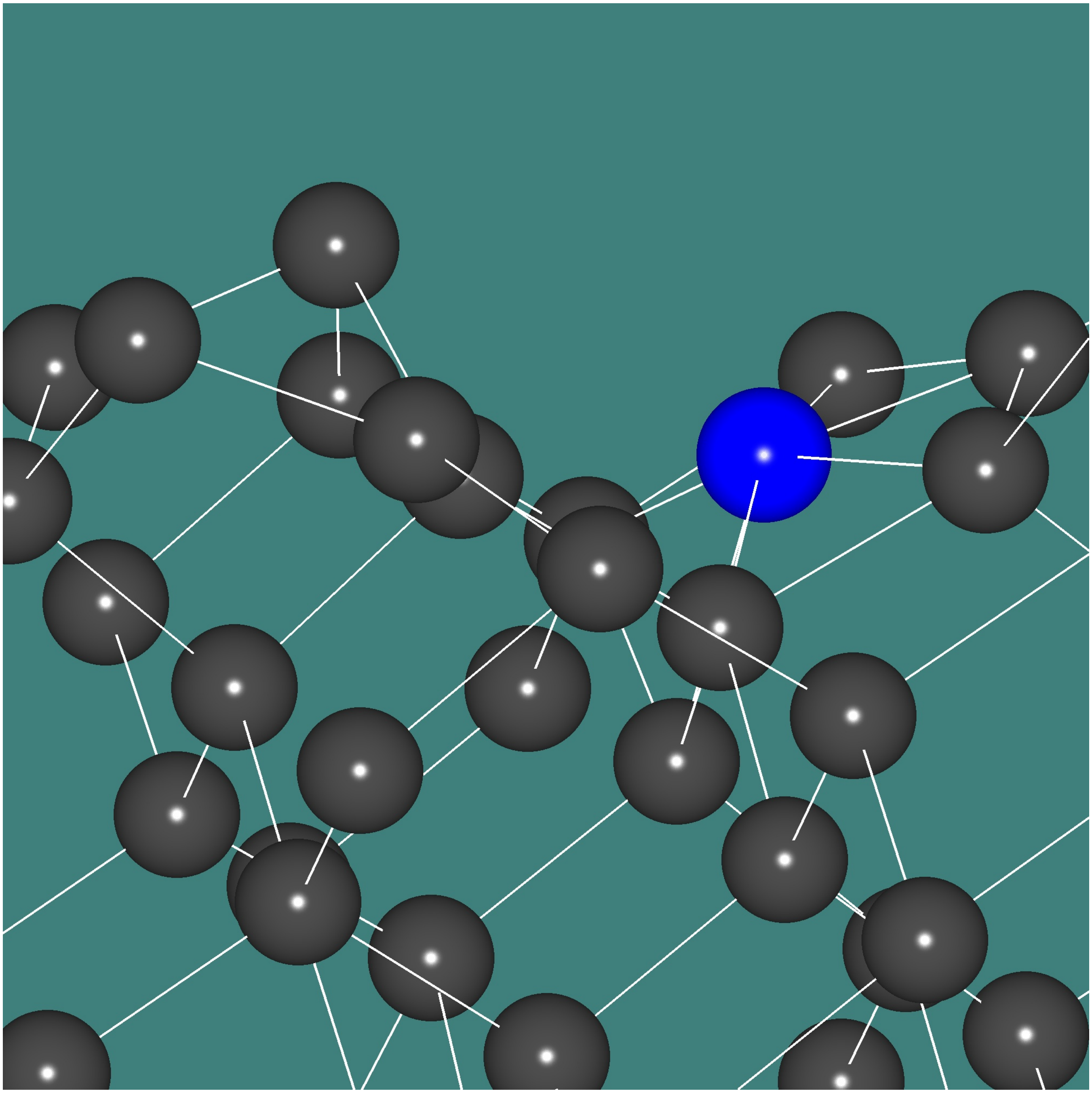
OxfordMaterials

Pedestal Site



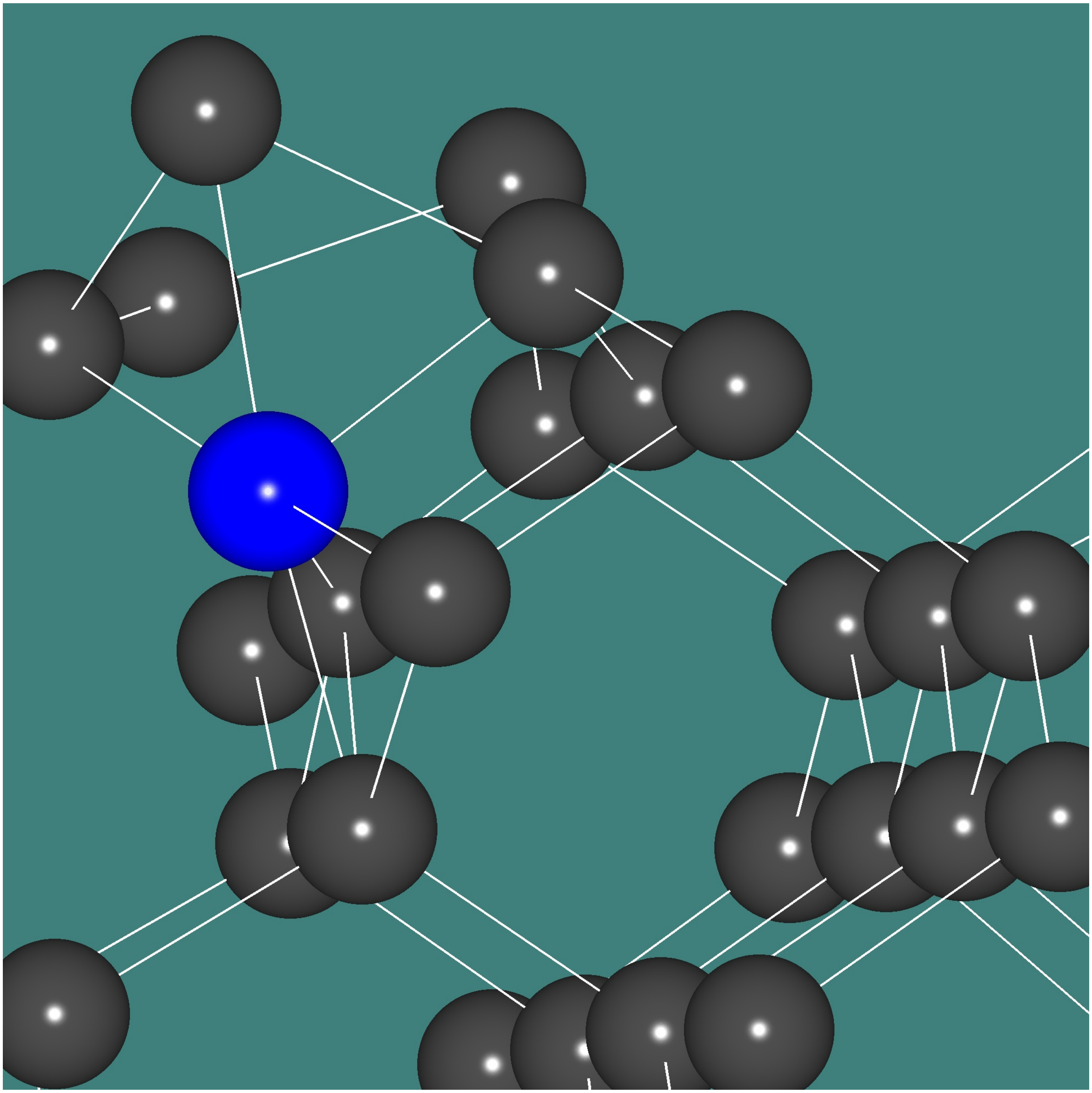
OxfordMaterials

Low Site



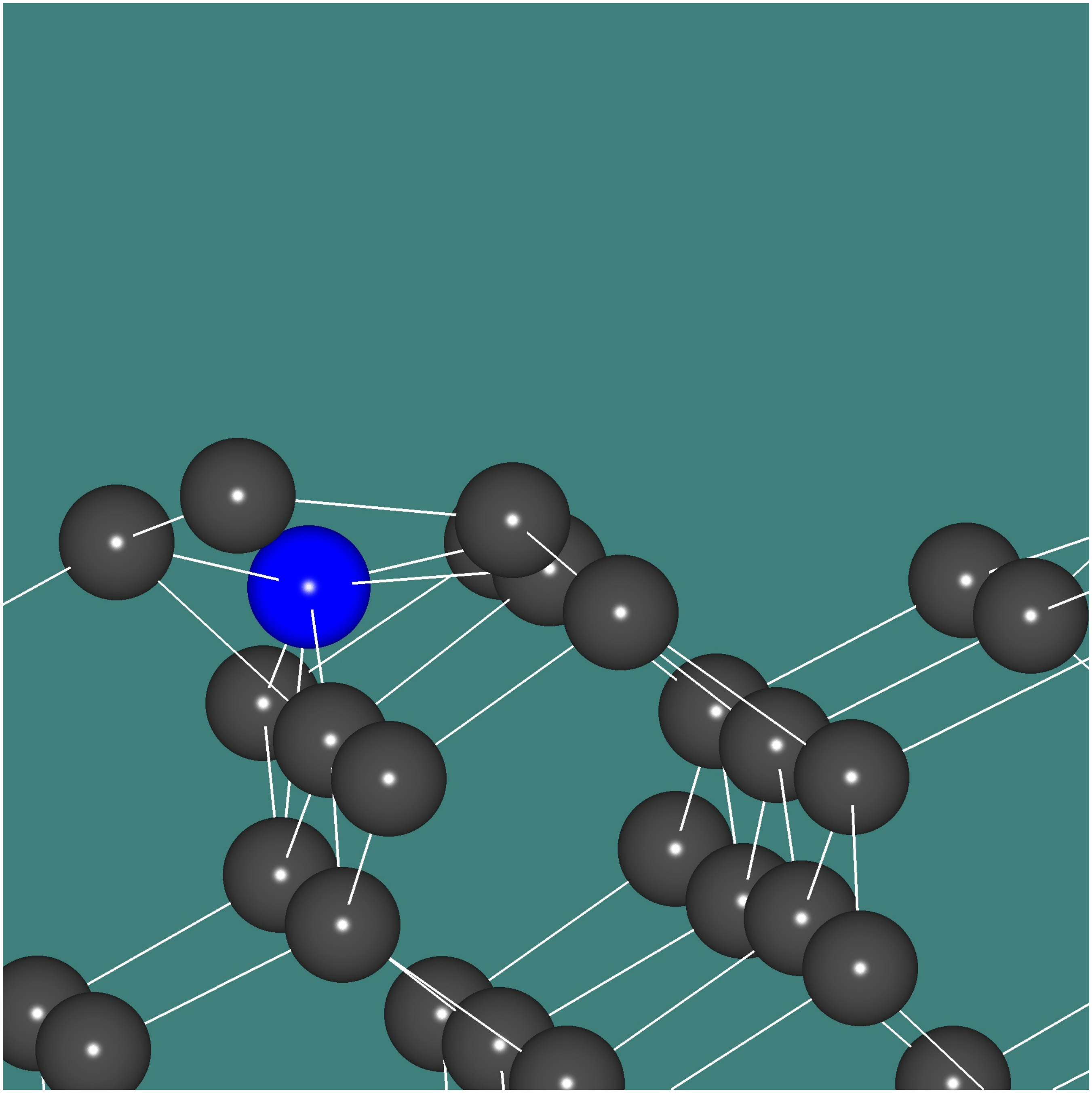
OxfordMaterials

Under Dimer Site



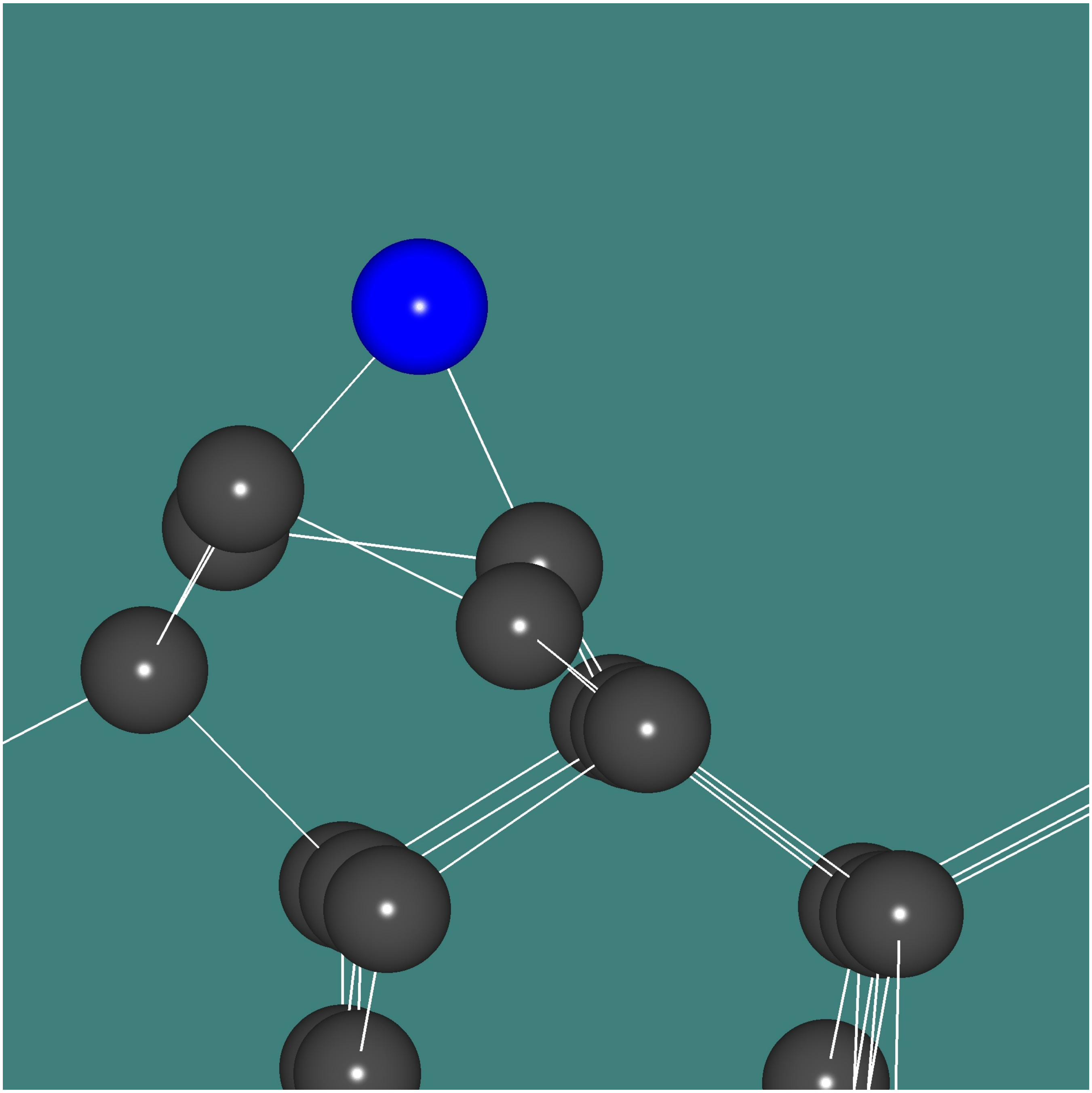
OxfordMaterials

Dimer Vacancy Site



OxfordMaterials

Dimer Site



Conclusions

- The calculations confirm the models that have been proposed that suggest that the surface is always silicon terminated.

- The calculations indicate that it is likely that the observed c(2×2) (100) surface reconstruction is one due to an extra half layer of silicon.

- The unusual bonding configuration for the silicon leads to a situation where saturating more dangling bonds is offset by the decrease in strength of the bonds due to the loss of the ability to relax.

- STM images show surface electronic structure which is not always the same as the physical structure.

- When Co bonds to Si (100) it wants to sit in a packed enviroment with lots of neighbours.