

INTRODUCTION

Crystals are regions of ordered matter. A perfect crystal has no imperfections. A 3D crystal can be treated as a collection of atoms whose distribution is homogenous and isotropic in all three directions. It is the discrete equivalent of a homogenous, isotropic, continuous medium (like an infinite vacuum). A copper crystal exists as a repeating FCC (Face centered cubic) lattice as shown in fig 1.

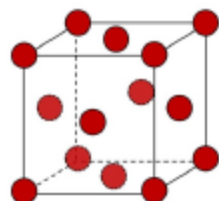


Figure 1: Face Centered Cubic Structure - The smallest repeating unit in a Copper crystal

The homogenous, isotropic nature of crystals means that no atom in a crystal is distinguishable from another. Hence, an electron wavefunction if shifted by a lattice constant would be unchanged; this leads to a very powerful tool - Bloch's Theorem. Bloch's Theorem states that basis wavefunctions ψ for electrons in a perfect crystal have the following properties.

$$\begin{aligned} \psi(\vec{r}) &= e^{i\vec{k}\cdot\vec{r}} u(\vec{r}) \\ u(\vec{r}) &= u(\vec{r} + n\vec{a}) \end{aligned}$$

where $\vec{k} = (k_x, k_y, k_z)$ is the wavevector, \vec{a} is the lattice vector, and n is an integer.

BULK COPPER

We define \hat{H} as the Hamiltonian for a Copper crystal. It is a 6×6 matrix (one for the s orbital, 5 for the d orbitals). As for the crystal wavefunction, we must work in a basis that is both complete and satisfies Bloch's Theorem. Consider $|\phi(\vec{r})\rangle = \sum_n e^{i\vec{k}\cdot\vec{n}} \sum_m b_{m,n} |\psi_m(\vec{r} - \vec{n})\rangle$. Where ψ_m represents electron wavefunctions and subscript n for the various orbitals (s,y,x,z etc.); \vec{n} represents the position of an atom in the crystal. Essentially, the wavefunction of the crystal at some point \vec{r} is the summation of the influence of every individual atom's wavefunction at that point. Realistically, we only work with nearest neighbours, not every atom. We then operate the Hamiltonian on $|\phi\rangle$, and eventually end up with the following eigenvalue equation:

$$b_{m,n}(e - E_n) = \sum_{m',n'} b_{m',n'} \langle \psi_{m'} | \hat{H} | \psi_m \rangle$$

The term $\langle \psi_m | \hat{H} | \psi_{m'} \rangle$ is the energy interaction term between the n and m orbital on neighbouring atoms (again, we only consider nearest neighbours). We can work out these terms using the orbitals' explicit wavefunctions, and using cubical harmonics. This enables us to solve the eigenvalue equation and plot the energy along the k-point path $(0,0,0)$ to $(0,0,\pi)$ as shown in fig 2

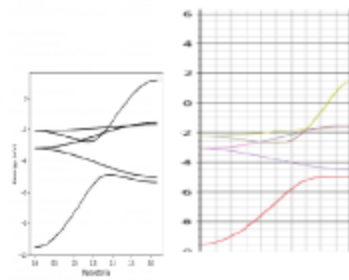


Figure 2: Band Structure of Copper obtained with the tight binding method (left) compared to that of Density Functional Theory (right)

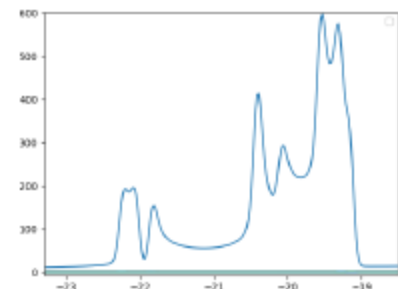


Figure 3: Density of States of bulk Copper

The Density of States refers to the proportion of states occupied by a system at each energy. In the context of the eigenvalue equation, this is done by counting every eigenenergy for every value of \vec{k} in the Brillouin Zone as shown in fig 3.

COPPER NANOPARTICLES

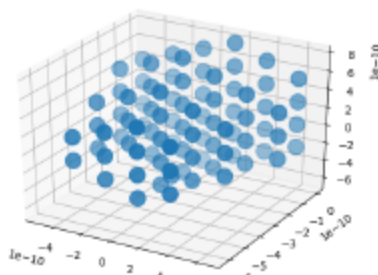


Figure 4: Atoms of the nanoparticle plotted in a 3D plot. The more opaque the sphere, the closer they are to the observer.

A nanoparticle or ultrafine particle is usually defined as a particle of matter that is between 1 and 100 nanometres (nm) in diameter. They exhibit properties different to that of their bulk equivalent because of a high surface to volume ratio. A nanoparticle cannot be considered a crystal, hence we can no longer use Bloch's Theorem (the atoms are not indistinguishable). In the context of this article,

consider the 88 atom nanoparticle shown in fig 4 (Real nanoparticles have billions of atoms). Using similar formalism as that of the earlier section, we got the following eigenvalue equation:

$$b_{m,n}(e - E_n) = \sum_{k,m',n'} \langle \psi_{m'} | \hat{H} | \psi_{k,m} \rangle$$

Since the atoms are now no longer indistinguishable, the Hamiltonian will now be a 528×528 matrix (88*6). Note that we now need two indices - k denoting the atom; and m,n denoting the orbital. Once again, using the explicit mathematical form of the orbitals and cubical harmonics, we can find the energy interaction term for every atom with its nearest neighbours. Due to its non-repeating nature, the wavevector \vec{k} has no relevance here. We have plotted the density of states in figure 5.

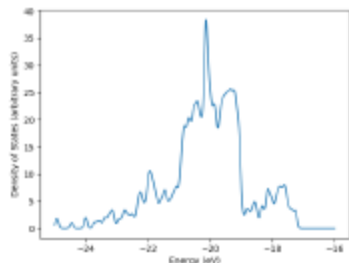


Figure 5: Density of States of the 88 atom nanoparticle.

Intuitively, one would expect that as the nanoparticle gets bigger, its density of states should tend towards that of bulk Copper. Note how the DoS of just this 88 atom nanoparticle is already quite qualitatively similar to that of bulk Copper (the peaks are at similar energies).

CONCLUSION

We have built up a formalism using Tight Binding and developed a Python code that enables us to study any nanoparticle of arbitrary size and atom positions (as much as computational costs allow). We have just mentioned one such system in this poster. Nanoparticles exhibit properties that are very different to their bulk equivalents, and building up a theory to simulate nanoparticles is an important step in understanding more about how they behave. In spite of its relative simplicity, tight binding continues to prove itself to be a very accurate and computationally efficient method to calculate intrinsic properties of any general many body atomic system even when compared to more complex techniques like Density Functional Theory.

WHAT COMES NEXT?

These results will now be used as a benchmark to develop a new analytic technique in Density Functional Theory that will help us study nanoparticles in a more accurate and computationally efficient way. This new technique is still currently in development and if valid, has the potential to help in making big strides in the study of systems using Density Functional Theory.

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