Understanding the Electronic Structure of Organometallic Sandwich Complexes and Graphene Based Nanomaterials

A Thesis

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by

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CERTIFICATE

I hereby certify that the matter embodied in this thesis entitled "**Understanding the Electronic Structure of Organometallic Sandwich Complexes and Graphene Based Nanomaterials**" has been carried out by Mr. Ershaad Ahamed Basheer at the Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India under my supervision and that it has not been submitted elsewhere for the award of any degree or diploma.

Prof. Swapan K. Pati
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CHAPTER 1

INTRODUCTION

Systems in which the motion of microscopic degrees-of-freedom such as electrons, phonons, or orbitals are restricted from interacting in full three-dimensional space are called low-dimensional systems. Numerous discoveries over the past decades have fuelled interest in such systems. Most notable among these discoveries are the experimental isolation of zero-dimensional fullerenes, one-dimensional nanotubes and molecular wires, and most recently, the discovery of two-dimensional graphene.

Low-dimensionality has given rise to several new fields of research. This is due to the fact that, unlike normal materials, low-dimensional systems exhibit quantum phenomena that arise out of disorder, electron-electron interactions and restricted boundary conditions [1–7]. Thus the physics in low-dimensional systems is often different than that in three dimensions. Any study of a low-dimensional or mesoscopic system requires a fully quantum mechanical treatment of the confined degrees of freedom. Thus low-dimensional systems exhibit quantum effects such as Aharonov-Bohm effect, persistent currents, phase-coherent transport and Luttinger liquid. Current research efforts also focus on the metal-insulator transition, quantum Hall effect, composite fermions and high-temperature superconductors in which confinement effects have a primary role.

Advancements in experimental techniques such as thin film deposition [8–15], mechanically controlled break junction [16–19], scanning tunneling microscopy [20–23], transmission electron microscopy [24–26], atomic force microscopy [27–32] and angle resolved photoemission spectroscopy [33–37] have provided impetus to research by enabling the fabrication and characterization of a host of new low-dimensional materials.

In this chapter, we include brief overviews of the low-dimensional materials that are studied in this thesis. We also introduce the theoretical and computational methods that are used to study these materials. Our primary aim is to explore the interesting electronic and magnetic properties of these systems. These systems can potentially have conduction properties that are of value in future electronic and spintronic devices. In the following, section we introduce graphene and graphene

nanoribbons (GNRs) which are two-dimensional and quasi one-dimensional respectively. The next section describes a class of one-dimensional compounds known as organometallic sandwich complexes. The following sections will give an outline of the theory and computational methods used in this thesis to study these systems. The chapter ends with an outline of later chapters.

1.1 Low-dimensional Systems

1.1.1 Graphene

Carbon is one of the most interesting elements in nature. It forms several allotropes each of which shows diverse properties. Well known among the allotropes are amorphous carbon, diamond and graphite. In recent decades more exotic allotropes have been discovered including fullerenes [38] and nanotubes [39, 40]. Fullerenes and nanotubes which are the zero-dimensional and one-dimensional allotropes of carbon respectively continue to receive focus from physicists and chemists alike. It was only recently that the two-dimensional allotrope had been isolated. But its elusiveness to experimental observation did not stop it from being the best theoretically studied carbon allotrope [41–44]. This two-dimensional allotrope, named graphene, is a lattice of sp^2 bonded carbon atoms arranged on a honeycomb lattice. Prior to the discovery of graphene, it was firmly established that a strictly two-dimensional crystal cannot exist [41–45].

In 2004, physicists from Manchester University, led by Andre Geim and Konstantin Novoselov extracted a single layer of graphene from three-dimensional graphite by the technique of micromechanical cleavage [46, 47]. This simple approach enabled the production of high quality graphene crystallites, encouraging further experimental activity [48, 49]. Theoreticians demonstrated that the existence of two-dimensional graphene, despite earlier predictions to the contrary, can be justified by the presence of ripples in its structure. Indeed, these ripples were observed in graphene which affect its properties [50].

Graphene displays several striking electronic properties. The electronic structure of graphene can be derived from simple nearest-neighbour tight-binding approximation [51]. In the vicinity of two high symmetry points K and K′ in the Brillouin zone, the electron energy is linearly dependent on the wave vector. Thus