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Mobile Electron Pairs on Lattices in the UV Model

by

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of

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S.Jackson April 2011

Abstract

We investigate the conditions under which the ground state of a low-density quasi-twodimensional electron (or hole) system is a Bose-Einstein condensate of mobile dimers. Such a ground state would require an effective attraction between electrons but an effective repulsion between dimers to prevent clustering. A UV model is assumed; this is not specific to the pairing mechanism but can be obtained from a Fröhlich-Coulomb model by the Lang-Firsov transformation. We survey the parameter space for each lattice restricting the dimer Hilbert spaces to the low-energy sector since we are interested in low-lying states and low densities. Singlet dimers are mobile on a triangular lattice; in the simplest case the effective Hamiltonian for dimer hopping is that of a kagome lattice. However, a dimer condensate is never the ground state in the triangular lattice, as dimers will either cluster or dissociate. For a square lattice with nearest- and next-nearest-neighbour hopping we find a substantial region in which dimers form a ground state. These dimens turn out to be very light since they can propagate by a "crab-like" motion without requiring virtual transitions. For a perovskite layer we find a substantial region in which dimers, which are also light and mobile due to crab-like motion, form a ground state. Our findings indicate that the existence of stable small mobile bipolarons is very sensitive to the lattice structure.

We secondly identify circumstances under which triplet dimers are strictly localised by interference in certain one- and two-dimensional lattices. We find that strict localisation is possible for the square ladder and some two-dimensional bilayers. We thirdly investigate the electronic properties of Graphene. We identify the origin of Graphene's Dirac points and subsequently identify Dirac points in other two- and three-dimensional lattices. We finally investigate the dynamics of electrons and dimers on various oneand two-dimensional lattices by the use of Green's functions.

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Contents

1	Intr	oduction	1
	1.1	History of Superconductivity	1
	1.2	High Temperature Superconductors	3
	1.3	Applications of Superconductors	4
	1.4	Theories of Superconductivity	4
	1.5	Bipolaronic Theory of High Temperature Superconductivity	8
	1.6	Resonating Valence Bond Theory	10
2	For	malism and motivation	13
	2.1	Bloch Theorem	13
	2.2	Tight Binding Approximation	14
	2.3	The Hubbard Model	18
	2.4	UV Model	20
	2.5	Dimer Lattice Formalism	22
	2.6	Motivation	24
	2.7	Overview of chapters	26
3	The	e Diatomic Molecule	27
	3.1	Finite U	27

	3.2	Small and Large Coupling Expansion	30
	3.3	Strong and Weak Coupling Perturbation Theory	32
4	$\mathrm{Th}\epsilon$	e Triangular Molecule	35
	4.1	Single Electrons	35
	4.2	Dimers with $U = \infty$	36
	4.3	Dimers with Finite U	38
	4.4	Small Coupling Expansion	40
5	The	Staggered Ladder	41
	5.1	Staggered Ladder Electrons	41
	5.2	Staggered Ladder Dimers	42
	5.3	Effective Mass	47
6	$\mathrm{Th}\epsilon$	e Triangular Lattice	49
	6.1	Objectives and Method	49
	6.2	Nearest-Neighbour Dimers	50
	6.3	Feasibility of a Nearest-Neighbour-Dimer Ground State	52
	6.4	Stretching Dimers and Trimers	54
	6.5	Feasibility of a Stretching-Dimer Ground State	55
7	The	Square Lattice	59
	7.1	Square Lattice Dimers	59
	7.2	Feasibility of a Dimer-Based Ground State	61
	7.3	Effective Mass	63
8	$\mathrm{Th}\epsilon$	e Perovskite Layer	66
	8.1	Introduction	66

	8.2	Feasibility of a Dimer-Based Ground State	67
	8.3	Effective Mass	68
	8.4	Summary	70
9	Gra	phene and Dirac points	72
	9.1	Electronic Properties of Graphene	72
	9.2	Dimer Lattice of Graphene	76
	9.3	Graphene Bilayer	76
	9.4	Origin of Dirac Points	77
	9.5	Square Lattice Singlets	79
	9.6	Cubic Lattice Singlets	80
	9.7	Modified Triangular Lattice	81
	9.8	Conclusions	82
10	Stri	ctly Localised Triplet Dimers	84
	10.1	Introduction	84
	10.2	The Square Ladder	85
	10.3	The Square Bilayer	88
	10.4	The Honeycomb Bilayer	91
	10.5	Three-Dimensional Structures	93
	10.6	The Simple Cubic Lattice	94
	10.7	The Body Centred Cubic Lattice	95
	10.8	Conclusions	96
11	Tim	e Evolution of Wavefunctions	100
	11.1	Introduction	100
	11.2	Infinite Chain	101

11.3 Staggered Ladder Dimers	. 103
11.4 Including a Flat Band	. 106
11.5 Dispersionless Band Structure	. 107
11.6 Triangular Lattice	. 108
11.7 Modified Graphene Lattice	. 109
11.8 Conclusions	. 11(
12 Summary and Conclusions	113
12.1 Feasibility of a Ground State Consisting of Mobile Dimers $\ .\ .\ .$.	. 113
12.2 Graphene and Dirac Points	. 115
12.3 Strictly Localised Triplet Dimers	11:
· -	. 110

Chapter 1

Introduction

1.1 History of Superconductivity

Superconductivity was first observed in 1911 by Heike Kamerlingh Onnes while studying the electrical resistance of solid mercury at cryogenic temperatures. Onnes observed that at a temperature of 4.2 K the resistance of mercury drops to zero or an immeasurably small value. It was known that the resistance of metals decreases with decreasing temperature. However a sharp drop in resistance was not consistent with the smooth dependence on temperature that was expected.

Electrons in metals can be thought of as plane waves which propagate through the crystalline structure of the metal. If an electric field is applied the electrons will acquire a net momentum in a particular direction. However the electron waves are scattered from vibrating ions in the lattice, dissipating energy as heat. This is the concept of electrical resistance.

In this process the electrical resistance of an ideal sample, containing no impurities or defects, should decrease smoothly with decreasing temperature, and essentially vanish at near absolute zero temperature. However the observed sharp drop in resistance suggested that superconductivity is not simply a consequence of idealised conditions and that superconductivity is fundamentally different to conventional conductivity.

Many other superconductors were subsequently discovered including lead, which would superconduct at 7 K, and niobium nitride, which would superconduct 16 K. It is now known that superconductivity occurs in a wide variety of materials such as tin, alluminium, various metallic alloys and heavily doped semiconductors [1].

Superconductivity is characterised by exactly zero resistance and the exclusion of the interior magnetic field, an effect known as the Meissner effect. A magnetic field is however able to penetrate the surface of a superconducting sample down to a small depth know as the London penetration depth. The magnetic field decays exponentially from the surface of the superconductor down to the penetration depth. The physical properties of a sample change abruptly at the transition temperature T_c indicating that a phase transition takes place at T_c . For instance the specific heat undergoes a discontinuous jump at T_c and ceases to depend linearly on temperature below T_c [1].

A simple way to confirm that the resistance is indeed zero in a sample is to put the sample in a circuit so that a small current flows and measure the voltage V across the sample. Ohms law states that R = V/I, where R is resistance and I is current, so that if V = 0 then R = 0 and the sample is in the superconducting state. Once a current has been produced it will continue to flow indefinitely with no applied voltage. An alternative test would be to induce a small current in a closed superconducting ring, keep the material below its transition temperature for a long time and then measure whether there has been any detectable degradation in the current flow. Experiments have shown that superconducting currents could persist for at least 100,000 years [1].

In 1962 Brian Josephson predicted that supercurrent can flow between two pieces of superconducting material separated by a thin layer of material. This effect, now known as the Josephson effect, lead to the development of devices such as SQUIDs.

1.2 High Temperature Superconductors

Conventional superconductors have transition temperatures from 20 K down to less than 1 K. It had been believed that there could be no superconductivity above a temperature 30 K. However in 1986 Georg Bednorz and Klaus Alex Müller discovered superconductivity in a lanthanum-based cuprate material at a temperature of 35 K. It was soon found that if lanthanum was replaced with yttrium to produce yttrium barium copper oxide (YBCO) the critical temperature increased to 92 K. This was important because for the first time superconductivity had been observed above the boiling point of nitrogen (77 K). It is far less costly to liquefy nitrogen than helium which had previously been used to cool superconductors. It is estimated that the cost of using liquid nitrogen is 1000 times less than the cost of using liquid helium [2].

Since the discovery of high temperature superconductivity in YBCO a number of other cuprate materials have been found which also superconduct at high temperatures. These include bismuth lead strontium calcium copper oxide (BSCCO) with $T_c = 105$ K, thallium barium calcium copper oxide (TBCCO) with $T_c = 125$ K, and mercury barium calcium copper oxide with $T_c = 133$ K (HBCCO) [2]. Under extremely high pressure T_c in these materials can be increased.

Cuprates are ceramic materials containing copper oxide planes. The structure is essentially that of a sandwich with the copper oxide plain in the centre, this is where the superconducting current flows. Elements other than copper and oxygen play a secondary role. In YBCO yttrium is only a spacer and a contributer of charge carriers. In fact various other rare earth elements can be substituted for the yttrium without significantly affecting the transition temperature [2].

1.3 Applications of Superconductors

One of the main applications of superconductors is in superconducting magnets which are capable of producing very large magnetic fields. Superconducting magnets are used in technologies such as maglev trains, MRI and NMR machines, and for beam-steering in particle accelerators. They could also be used for magnetic separation where weakly magnetic particles are separated from a background of non-magnetic particles.

Superconductors may also be used in digital circuits and in RF and microwave filters for mobile phone base stations. Superconductors form the basis of Josephson junctions which are the essential components of SQUIDs (superconducting quantum interference device); SQUIDS are the most sensitive magnetometers known.

Future applications of superconductors could include high performance transformers, power storage devices, electric power transmission, electric motors (for vehicle propulsion as in maglev trains) and magnetic levitation devices. However superconductors are sensitive to moving magnetic fields so development of devices that use A/C will be more difficult than those that use D/C.

1.4 Theories of Superconductivity

Following the discovery of conventional superconductivity in 1911 there was no theory which adequately explained the phenomenon for many years.

In 1934 the brothers Fritz and Heinz London proposed the London model which showed that the Meissner effect was a consequence of the minimisation of the electromagnetic free energy carried by the superconducting current. The model also predicted the penetration depth λ ; the characteristic length of penetration of the static magnetic flux into a superconductor [3]. In 1950 the phenomenological Ginzburg-Landau theory was devised by Vitaly Ginzburg and Lev Landau. This theory was successful in explaining the macroscopic properties of superconductors and predicted two classes of superconductors known as type I and type II, both of which have now been discovered. Type I exhibit a purely superconducting phase below T_c and completely expel magnetic flux from the interior. Type II exhibit a mixed state of superconducting and non-superconducting regions between an upper and lower critical temperature, and a pure superconductors admit vortices of magnetic flux which can form an ordered triangular lattice. The superconducting current flows around the vortices while the vortex core regions remain in the non-superconducting state. Type I superconductors can only remain in the superconducting state in very low external magnetic fields while Type II superconductors can sustain superconductivity in fields higher than 10 Tesla due to the mixed phase [3]. All known high temperature superconductors are of type II.

Also in 1950 Maxwell and Reynolds *et al* found that the critical temperature of a superconductor depended on isotopic mass, indicating that the electron-phonon interaction could be a possible origin of superconductivity.

In 1957 a complete microscopic theory of superconductivity was devised by Bardeen, Cooper and Schrieffer and became known as the BCS theory. This was based on a demonstration by Fröhlich that a weak attraction could exist between conduction electrons near the Fermi surface due to their interaction with the vibrating ions in the lattice. The theory demonstrated that in a small interval around the Fermi energy electrons with opposite spins form pairs in momentum space, known as Cooper pairs, which strongly overlap in real space, with perhaps billions of electrons existing between two members of a pair. It was shown that the pairs are only stable due to their quantum interaction with other pairs [4]. This means that if you were to take away all Cooper pairs except for one pair then those two electrons would not be a Cooper pair. The pairs are bound with a certain binding energy. If this binding energy is higher than the energy provided by kicks from the oscillating atoms in the lattice (which is true at low temperatures) then the pair will resist all kicks and move as a pair without resistance.

F.London had suggested in 1938 that the superfluid properties of liquid helium 4, which becomes superfluid below $T_c \cong 2.17$ K were intimately linked to the so called Bose-Einstein condensation of the entire assembly of bosons [4].

Electrons are fermions (defined as having half integer spin) which obey Fermi-Dirac statistics and as such must obey the exclusion principle; this states that no two fermions can be in the same quantum state. However pairs of electrons are bosons (with integer spin) which obey Bose-Einstein statistics and are able to condense into a single quantum state.

A condensed system of bosons becomes superfluid because as soon as one Bose particle in the Bose liquid meets an obstacle to its flow, such as an impurity, the others do not allow their partner to be scattered to leave the condensate [4].

The distribution functions for Bose-Einstein statistics and Fermi-Dirac statistics are respectively

$$n_i = \frac{g_i}{e^{(\epsilon_i - \mu)/k_B T} - 1}$$
(1.1)

$$n_{i} = \frac{g_{i}}{e^{(\epsilon_{i} - \mu)/k_{B}T} + 1}$$
(1.2)

where n_i is the number of particles in state *i*, g_i is the degeneracy of state *i*, ϵ_i is the energy of state *i*, μ is the chemical potential, k_B is Boltzmann's constant, and *T* is absolute temperature.

The expression for the temperature of the onset of Bose-Einstein condensation is

$$T_{BEC} = \frac{\hbar^2 n^{2/3}}{2mk} \times 3.31 \tag{1.3}$$

where \hbar is the reduced planck constant and m is the bosonic mass. Helium 4 consists of two protons, two neutrons and two electrons, and is therefore a boson while the isotope helium 3 is a fermion. Therefore helium 3 should not condense into a single state and should not become superfluid at low temperature. Experiments showed that over a substantial temperature range this was true, although the onset of superfluidity was observed at 0.0026 K, this is due to the formation of pairs of helium 3 atoms [4]. The three orders of magnitude difference between the critical superfluidity temperatures of helium 3 and helium 4 suggest a link between Bose-Einstein condensation and high temperature superconductivity.

In 1946 Richard Ogg proposed that since electrons are fermions high temperature superconductivity might involve pairing of electrons. The idea was developed further by Scafroth and others but was largely forgotten because it could not account for the critical parameters of the low temperature superconductors and did not explain the origin of the attractive force required to bind electrons into pairs. Although the model yields a precise estimate of the critical temperature for helium 4 it leads to a completely unrealistic result for superconductors with $T_c = 10^4$ K [4]. In contrast to the Ogg-Scfroth model the BCS theory proposes electron pairs with large seperations at about 10⁴ times the average electron spacing with the pairs strongly overlapping in real space. Unfortunately the successful BCS theory seemed to indicate that there could be no superconductivity above 30 K despite the predictions of the Ogg-Scafroth model.

In 1986 the belief in the impossibility of high temperature superconductivity was finally disproved with the discovery of superconductivity in a cuprate material at 35 K [4].

1.5 Bipolaronic Theory of High Temperature Superconductivity

The BCS theory is a successful description of the microscopic origin of superconductivity in conventional superconductors (those with transition temperatures below 30 K) and of the thermodynamic and electromagnetic properties of conventional superconductors [5]. However evidence suggests that high temperature superconductivity, which occurs largely in the cuprate superconductors, may not originate from the same mechanism as conventional superconductivity as described by the BCS theory [6].

A new theory is therefore required to explain high temperature superconductivity although no widely accepted theory currently exists. The bipolaronic theory of high temperature superconductivity is one of a number of theories that has been extensively researched and which has produced many research papers. It proposes that as an electron moves through a lattice it distorts the lattice and is effectively 'dressed' by a cloud of phonons. This combination of electron and lattice distortion constitutes a polaron [4, 6–13]. Polarons are able to interact with each other via a long-range attractive force mediated by optical phonons. This interaction, routinely ignored in the Hubbard U and t - J models, is the Fröhlich electron-phonon interaction (EPI) and is significant if the interaction is largely unscreened. Polarons may form pairs (bipolarons) due to the EPI. Essentially pairs can form because two polarons can deform the lattice more effectively together than separately.

Most high- T_c superconductors are doped insulators with highly polarisable ionic lattices. Screening is poor in these materials because the low density of carriers is unable to screen effectively the direct Coulomb electron-ion interactions [13]. The layered structure of the cuprates reduces screening even further. The unscreened Fröhlich EPI allows electrons to form real-space pairs (bipolarons) and together with shorter-range deformation potentials overcomes the Coulomb repulsion at distances of about the lattice constant so that continuous (large) bipolarons become local (small) bipolarons. The onset of superconductivity occurs when a gas of small light bipolarons condense into a Bose-Einstein condensate and thereby exhibit superfluid behaviour. The site-local Holstein model describes the extreme short-range limit where electrons form pairs on single atoms. Holstein bipolarons are not good candidates for high temperature supercurrent carriers because in order for the Coulomb repulsion (Hubbard U) to be overcome by the induced attractive force between the electrons, the EPI must be so large that the polaron and bipolaron masses must be huge, meaning that the transition temperature must be tiny. However using a finite-range EPI, it is possible for electrons to pair between sites without requiring the electron-phonon-induced attraction to be larger than the Hubbard U. In this case the individual polarons are significantly lighter, so the mass of the pair has potential to be orders of magnitude smaller than in the Holstein case [6].

Studies of large bipolarons in the continuous limit have led to the discovery that the large bipolaron is only stable in a very limited sector of the parameter space (Coulomb versus Fröhlich coupling constant). It was found that many traditional Fröhlich materials lie outside and far from this stability sector but several high- T_c superconductors lie very close to and even inside the area of stability in the parameter space [6].

The strongest evidence for bipolaronic carriers in high temperature superconductors is the discovery of a substantial isotope effect on the carrier mass predicted by the polaron theory. Recent high-resolution angle-resolved photoemission spectroscopy (APRES) has also produced evidence for a strong electron-phonon interaction (EPI) in cuprates. These, as well as recent tunneling and neutron scattering experiments clearly show that lattice vibrations play a significant role in high-temperature superconductors [6].

1.6 Resonating Valence Bond Theory

The bipolaronic theory is just one of a number of theories which attempt to explain the mechanism underlying high temperature superconductivity. A rival theory known as the theory of resonating valence bonds was developed by Phillip W Anderson in 1987. Anderson was the first to note the possibility of an unconventional ground state in copper-oxide compounds and that it may be connected to a new mechanism of high T_c superconductivity [14]. He investigated the t - J model which was obtained from the one-band Hubbard model in the strong coupling limit U >> t, where U is the Coulomb repulsion between electrons on the same atom and t is the hopping integral. The t - J model is used to describe highly correlated electron systems where J is a coupling constant. In the absence of holes, the antiferromagnetic exchange usually leads to the Neel ground state which is characterised by a long-range antiferromagnetic order in the spin alignment of the lattice sites [14]. Anderson proposed that a disordered state in the form of a quantum liquid of resonating valence bonds (RVB) occurs instead of the Neel ground state in two-dimensional systems such as the copper-oxide plains in cuprate materials [14–16]. The RVB state is characterised by a system of singlet states (valence bonds) for pairs of electrons. The breaking of the singlet bond leads to the appearance of two Fermi excitations with spin 1/2 which have no charge. These neutral fermions are called 'spinons'. Upon doping a new type of excitation called a 'holon' appears. This is a charged hole which has no spin, i.e. a charged Bose quasiparticle. At first superconductivity in the RVB system was thought to be due to the Bose condensation of holons. Another mechanism was subsequently proposed based on the Josephson tunneling of a pair of electrons between the layers of the superconductor [14]. An RVB superconductor would be a BCS type (with d-wave symmetry) in which there are no preformed pairs [17].

The resonating valence bond model is harder to grasp intuitively than the bipolaronic theory with its simple visual analogy of two electrons sharing a lattice deformation. In a course of online lectures [18] Professor A S Alexandrov describes the model in the following terms: "There are no electrons in the cuprate superconductors, every electron decays into a holon which has charge but no spin, and a spinon which has spin but no charge".

It has recently been claimed that spin singlets resonating between many configurations (hence the name of the theory) explain many unusual properties of the cuprates and that there is good agreement between the RVB theory and experiments on almost all quantities studied, including the specific heat, thermal conductivity and in-plane magnetic penetration depth [19].

Anderson has recently made the additional claim that RVB theory has made accurate predictions above T_c [17]. The hole-doped superconductors have been shown to exhibit an unusual phase in the region of their phase diagram above the superconducting "dome" in temperature. This region has been dubbed the "pseudogap" or "spin gap" region. The existence of such a phase was predicted by RVB theory long before it was observed. It was postulated, a few months after the discovery of the high T_c cuprates, that a quantum liquid of singlet pairs of electrons might exist in a Mott insulating system, from which the high T_c superconductor would develop via doping [17].

In his book [20] Anderson expresses a high degree of confidence in his theory stating that: "From about 1987 the mechanism for superconductivity in the cuprates has been clear". Anderson is critical of rival theories including the bipolaronic theory stating: "Aside from theoretical papers which have some germs of truth in them, there is a larger group which is completely inconsistent with the basic realities of the subject. Many of these belong sociologically in the mode of particle theory, where there is no a priori foundation and speculations about the underlying physical model are acceptable, but many others come from naive or careless thinking in which extraneous independent entities like anyons or spin fluctuations or bipolarons are introduced but not tied down to the actual physical model and/or experimental observations".

Not all workers are convinced by Andersons theory. In [18] Professor A S Alexandrov states that "We should wait for experimental justification for this extreme approach".

Chapter 2

Formalism and motivation

2.1 Bloch Theorem

Bloch theorem states that the eigenstates of electrons propagating in a periodic potential have the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = U_{\mathbf{k}}(\mathbf{r})e^{(i\mathbf{k}\cdot\mathbf{r})} \tag{2.1}$$

where $U_{\mathbf{k}}(\mathbf{r})$ has the period of the lattice with $U_{\mathbf{k}}(\mathbf{r}) = U_{\mathbf{k}}(\mathbf{r} + \mathbf{T})$ [21, 22]. The lattice translation vector \mathbf{T} is defined as $\mathbf{T} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}$ where a, b and c are the primitive lattice vectors and n_1, n_2 and n_3 are integers. The subscript \mathbf{k} indicates that the function $U_{\mathbf{k}}(\mathbf{r})$ depends on the wavevector \mathbf{k} . An eigenstate of the form (2.1) is known as a Bloch function. These solutions are composed of travelling waves and can be assembled into wave packets that represent electrons or dimers propagating freely through the lattice. Bloch theorem implies that the simplest basis for an infinite lattice consists of the states found in a single unit cell times the plane wave $e^{(i\mathbf{k},\mathbf{r})}$.

The following proof comes from [21] and is valid when $\psi_{\mathbf{k}}(\mathbf{r})$ is nondegenerate. We consider N identical points on a ring of length Na. The potential is periodic with U(x) = U(x + sa) where s is an integer. Because of the symmetry of the ring we look

for solutions such that

$$\psi(x+a) = C\psi(x) \tag{2.2}$$

where C is a constant. Then, on going once around the ring,

$$\psi(x + Na) = \psi(x) = C^N \psi(x) \tag{2.3}$$

because $\psi(x)$ must be single-valued. It follows that C is one of the N roots of unity, or

$$C = e^{(i2\pi s/N)}; \quad s = 0, 1, 2, \dots, N-1$$
(2.4)

We see that

$$\psi(x) = U(x)e^{(i2\pi sx/Na)} \tag{2.5}$$

satisfies (2.2) provided always that $U_{\mathbf{k}}(x) = U_{\mathbf{k}}(x+a)$. With $k = 2\pi s/Na$ we have the Bloch result (2.1).

2.2 Tight Binding Approximation

The tight-binding method is probably the simplest approach for calculating band structures and is widely used in the description of insulators [21, 23]. The approach has also been used in chemistry for some time under the name of linear combination of atomic orbitals, or LCAO. It is quite good for describing the inner electrons of atoms but is not always a good description of the conduction electrons themselves. The idea is to begin with free atoms whose wavefunctions and electronic energy levels are known and then assume that when placed in a lattice the wavefunctions of the atoms just overlap. The description of the states of the atoms can then be obtained by correcting the free-atom states. The wavefunction for the system is written as a linear combination of atomic orbitals. The overlap of the wavefunctions allows electrons to hop between neighbouring atoms in the lattice. This has the effect of splitting the energy levels spreading them into bands. The energy of an electron in any particular band then depends on its wavevector \mathbf{k} . The width of the bands is proportional to the overlap of the wavefunctions of neighbouring atoms. In general each band will not have the same energy as any other band over any appreciable range of the wavevector but may have the same energy at certain values of \mathbf{k} in the brillouin zone.

The following derivation comes from [21]. Suppose that the ground state of an electron moving in the potential $U(\mathbf{r})$ of an isolated atom is an *s* state $\phi(\mathbf{r})$ and that the energy is E_0 . We obtain an approximate wavefunction for one electron in the whole lattice by taking

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{j} C_{kj} \phi(\mathbf{r} - \mathbf{r}_{j})$$
(2.6)

where the sum is over all lattice points. This function is of the bloch form if $C_{kj} = N^{-\frac{1}{2}}e^{i\mathbf{k}\cdot\mathbf{r}_j}$, which gives for a lattice of N atoms

$$\Psi_{\mathbf{k}}(\mathbf{r}) = N^{-\frac{1}{2}} \sum_{j} e^{i\mathbf{k}\cdot\mathbf{r}_{j}} \phi(\mathbf{r} - \mathbf{r}_{j})$$
(2.7)

The electronic Hamiltonian is given by H = T + U where T is kinetic energy and U is the periodic crystal field potential. The first order energy is found by calculating the diagonal matrix elements of the electronic Hamiltonian:

$$\langle \mathbf{k} | H | \mathbf{k} \rangle = N^{-1} \sum_{j} \sum_{m} e^{i\mathbf{k}.(\mathbf{r}_{j} - \mathbf{r}_{m})} \langle \phi_{m} | H | \phi_{j} \rangle$$
(2.8)

where $\phi_m \equiv \phi(\mathbf{r} - \mathbf{r}_m)$. Writing $\mathbf{R}_m = \mathbf{r}_m - \mathbf{r}_j$,

$$\langle \mathbf{k} | H | \mathbf{k} \rangle = \sum_{m} e^{-i\mathbf{k}.\mathbf{R}_{m}} \int dV \phi(\mathbf{r} - \mathbf{R}_{m}) H \phi(\mathbf{r})$$
(2.9)

We now neglect all integrals in (2.9) except those on the same atom and those between nearest neighbours connected by **R**. We obtain

$$\int dV \phi^*(\mathbf{r}) H \phi(\mathbf{r}) = -\alpha \tag{2.10}$$

and

$$\int dV \phi^*(\mathbf{r} - \mathbf{R}) H \phi(\mathbf{r}) = -t \qquad (2.11)$$

We now have the first order energy provided $\langle \mathbf{k} | \mathbf{k} \rangle = 1$.

$$\langle \mathbf{k} | H | \mathbf{k} \rangle = -\alpha - t \sum_{m} e^{-i\mathbf{k}.\mathbf{R}_{m}} = E_{\mathbf{k}}$$
 (2.12)

The hopping integral decreases exponentially with separation and will ordinarily be negative since the potential due to each atom is attractive. For a simple cubic structure the nearest neighbour atoms are at

$$\mathbf{R}_m = (\pm a, 0, 0) \ (0, \pm a, 0) \ (0, 0, \pm a) \tag{2.13}$$

so that (2.12) becomes

$$E(\mathbf{k}) = -\alpha - 2t\left(\cos\left(k_x a\right) + \cos\left(k_y a\right) + \cos\left(k_z a\right)\right) \tag{2.14}$$

Thus the energies are confined to a band of width 12t. The weaker is the overlap the narrower is the energy band. For $ka \ll 1$, $E(\mathbf{k}) \cong -\alpha - 6t + tk^2a^2$ where we have used the expansion

$$cosx = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} \cdots$$
 (2.15)

and ignored terms above the second order. The k dependent term in the energy $-6t + tk^2a^2$ is the contribution which gives rise to interesting band structure effects. The zero of energy is routinely shifted so that the less important term -6t does not appear.

The effective mass m^* of an electron for a given band structure is related to the curvature of the bands by the expression

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\delta^2 E}{\delta k^2}|_{k=0}$$
(2.16)

Electrons will tend to fill the lowest energy states located near the band minima preferentially. The band minima are therefore the regions of interest when making calculations of effective mass. Because the band minima are approximately quadratic in k we can find the effective mass of electrons by fitting the dispersion curve for the free electron (also quadratic in k) to the band minima. For the free electron we have

$$E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m^*}$$
(2.17)

so for the simple cubic structure in the region $ka \ll 1$ we can say that

$$E(\mathbf{k}) = tk^2 a^2 = \frac{\hbar^2 k^2}{2m^*}$$
(2.18)

and the effective mass becomes

$$m^* = \frac{\hbar^2}{2ta^2} \tag{2.19}$$

When the overlap integral t is small, the band is narrow and the effective mass is high. This reflects the fact that if the overlap of the wavefunctions is small the electrons are quite immobile. If the overlap is large then the mass becomes small and the electrons become quite mobile. However as electrons become very mobile the tight-binding approach becomes inaccurate. Thus in simple metals where electrons behave as quite free the tight binding approximation will not be an accurate description of the wavefunctions. However in ionic lattices the overlap of atomic valence states is very small such that the tight-binding approach can be quite accurate [21, 23].

2.3 The Hubbard Model

The Hubbard model is probably the simplest model which can be used to describe the electronic properties of lattices for many electrons. The model stems from the tightbinding approach in which electrons are viewed as occupying the standard orbitals of the constituent atoms and then hopping between atoms during conduction. This is represented as a hopping integral between neighbouring atoms. The Hubbard model builds on the tight-binding approach by including an additional on-site repulsion term to describe the Coulomb repulsion between electrons.

The complexities of atomic physics are ignored so that all that remains is the competition between chemical bonding and Coulomb repulsion; the two dominant forces in determining the behaviour of mobile electrons in condensed matter [24].

The model is usually written in the form

$$H = -t \sum_{\langle ii' \rangle \sigma} c^{\dagger}_{i\sigma} c_{i'\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$
(2.20)

where $c_{i\sigma}^{\dagger}$ and $c_{i'\sigma}$ are creation and annihilation operators respectively, which create or annihilate an electron of spin $\sigma \equiv \uparrow, \downarrow$ on a site i, in terms of which $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$ is an electron number operator and simply counts the number of electrons of spin σ on a site *i*. Attention is normally restricted to hopping between neighbouring atoms, denoted by $\langle ii' \rangle$.

The first term is the hopping term which relates to chemical bonding. This term is a single particle interaction and hops an electron from one atom to a nearest neighbour atom with a hopping matrix element t. This contribution favours itinerant electrons. The second term corresponds to the Coulomb repulsion between two electrons and is therefore a two-particle interaction. The long-range interaction is assumed to be screened and only the interaction when both the electrons are on the same atom is

retained, yielding an additional energy of U when the atom is doubly occupied.

Once the energy scale has been determined, there is only one remaining dimensionless ratio of energies t/U, which determines which of the chemical bonding or Hubbard repulsion forces is stronger. This does not determine which of the two forces is most significant, because the Coulomb repulsion is a two particle interaction and therefore its effect depends on the probability of finding the second particle involved. The model attempts to determine the types of ground states that occur at low temperature and their underlying mechanisms [24].

Ferromagnetism in the Hubbard Model

In some solids, electronic spins spontaneously align with each other to form strong ferromagnetic ordering. For example Fe maintains long range magnetic order up to the Curie temperature at 1043 K [25]. The existence of such strong order is difficult to explain given that the interactions between electrons in a solid are almost spin independent.

Heisenberg showed that if electrons are mostly localised at atomic sites, the Coulomb interaction combined with the Pauli exclusion principle can generate an effective exchange interaction between electron spins [25]. However the sign of this interaction usually leads to antiferromagnetism rather than ferromagnetism.

It was Bloch who proposed that the itinerant nature of electrons might play a fundamental role in ferromagnetism. This has lead to many approximate theories which are all based on the Hartree-Fock approximation and its perturbative corrections [25]. However these approximations have been unable to determine whether the spin-independent Coulomb interaction alone can be the origin of ferromagnetism in an itinerant electron system.

In 1965, the first rigorous example of ferromagnetism in the Hubbard model was given

by Nagoaka and independently by Thouless [25]. Further examples of ferromagnetism in Hubbard models have since been found by Lieb, Mielke and Tasaki. A common feature in the examples of Lieb, Mielke, and Tasaki is that each model has a completely degenerate band in the corresponding single-electron spectrum, and ferromagnetism is proved (in the interacting many electron problem) when the degenerate band is exactly or nearly half filled [25]. A general consensus on whether ferromagnetism appears in systems with a degenerate single-electron band has not been reached.

2.4UV Model

The bipolaronic theory postulates an effective attraction between electrons which can lead to pairing. Such an attraction can be accommodated in the UV model where Vis an effective interaction between electrons on different sites. This interaction can be attractive or repulsive as it can contain both the Coulomb repulsion and an effective EPI. The UV model can be obtained from the Coulomb-Fröhlich model [13, 26] in which electrons interact with lattice distortions on neighbouring sites. The electron together with the distortion forms a new quasiparticle – the polaron. An effective attraction between polarons can exist because two polarons can deform the lattice more effectively together than separately. The Hamiltonian for the Coulomb-Fröhlich model is written as

$$H = -\sum_{ij\sigma} T_{ij}c^{\dagger}_{i\sigma} c_{j\sigma} + U\sum_{i} n_{i\uparrow} n_{i\downarrow} + \frac{1}{2}\sum_{i}\sum_{j\neq i}\sum_{\sigma\sigma'} V^{c}_{ij}c^{\dagger}_{i\sigma}c_{i\sigma}c^{\dagger}_{j\sigma'}c_{j\sigma'} - \sum_{m}\frac{\hbar^{2}}{2M}\frac{\partial^{2}}{\partial\xi_{m}^{2}} + \sum_{m}\frac{M\omega^{2}\xi_{m}^{2}}{2} - \sum_{mi\sigma}f_{mi}c^{\dagger}_{i\sigma}c_{i\sigma}\xi_{m}$$
(2.21)

where $c_{i\sigma}^{\dagger}$ and $c_{j\sigma}$ are electron creation and annihilation operators respectively, T_{ij} is the bare hopping matrix, U is the onsite Coulomb repulsion and V_{ij}^c is the Coulomb interaction between electrons on neighbouring sites i and j. The ion at site m has displacement ξ_m . The phonons are Einstein oscillators with frequency ω and mass M. For two-dimensional electrons interacting with c-axis ionic displacements in a neighbouring plane the force f_{mi} between electrons and ions could be of the screened Fröhlich type [27, 28],

$$f_{mi} = \frac{\kappa}{\left[(\mathbf{r}_m - \mathbf{r}_i)^2 + a^2\right]^{3/2}} \exp\left(-\frac{|\mathbf{r}_m - \mathbf{r}_i|}{R_{sc}}\right)$$
(2.22)

where $\mathbf{r}_{m(i)}$ is the position of the ion (electron), κ is a constant and R_{sc} is the screening length. We require κ large enough for the Coulomb repulsion to be overcome at short range and $R_{sc} \approx a$, where a is the lattice parameter, if next-nearest-neighbour repulsion is required. The electron-phonon term may be written as

$$H_{el-ph} = -\hbar\omega \sum_{im\sigma} g_{mi} c^{\dagger}_{i\sigma} c_{i\sigma} (d^{\dagger}_m + d_m)$$
(2.23)

where d_m^{\dagger} creates a phonon at site m and $g_{mi} = f_{mi}/\sqrt{2m\hbar\omega^3}$ is a dimensionless coupling.

The Lang-Firsov transformation [29] replaces the operators as follows:

$$\tilde{d}_m^{\dagger} = d_m^{\dagger} + \sum_i g_{mi} n_i \tag{2.24}$$

$$\tilde{c}_{i\sigma}^{\dagger} = c_{i\sigma}^{\dagger} \exp\left[\sum_{m} g_{mi} (d_{m}^{\dagger} - d_{m})\right].$$
(2.25)

Taking the expectation value of the hopping term with respect to the phonon vacuum gives the UV model for the polaron effective Hamiltonian, valid for strong coupling [9]:

$$H = -\sum_{ij\sigma} t_{ij}c^{\dagger}_{i\sigma} c_{j\sigma} + U\sum_{i} n_{i\uparrow} n_{i\downarrow} +$$

$$+ \frac{1}{2}\sum_{i}\sum_{j\neq i}\sum_{\sigma\sigma'} V_{ij}c^{\dagger}_{i\sigma}c_{i\sigma}c^{\dagger}_{j\sigma'}c_{j\sigma'} - E_p\sum_{i\sigma} c^{\dagger}_{i\sigma} c_{i\sigma}$$

$$(2.26)$$

where t_{ij} is a renormalized hopping, V_{ij} is the polaron-polaron potential containing the Coulomb repulsion and the (non-retarded) effective attraction due to the Fröhlich EPI, and E_p is the polaron shift (which we assume to be absorbed into the chemical potential). A residual polaron-phonon interaction vanishes to leading order in inverse coupling. For much of this work we take the on-site repulsion U to be infinite so that basis states with two electrons on a single site are suppressed.

2.5 Dimer Lattice Formalism

The following Dimer-lattice and Hilbert space formalism come from [6] and are also made use of in [30]. The Hilbert space of two (for simplicity, distinguishable) particles on on a d-dimensional tight-binding lattice can be represented as a particle on a 2ddimensional lattice. However, if the attraction between the particles is strong enough to bind them into a dimer over the whole Brillouin zone, the low-lying states will have large amplitude only near a d-dimensional subspace where the particles are in close proximity. Accordingly a truncation of the Hilbert space of dimers to a small number of bond lengths will capture the essential physics. We call the truncated Hilbert space of the dimers the *dimer lattice*. Let

$$D_i = \{j : 0 < r_{ij} \le L_{\max}\}$$
(2.27)

be the set of sites j whose distance r_{ij} from a site i is no more than L_{\max} . We shall call D_i the neighbours of i. (In the present work we consider the $U = \infty$ limit, which suppresses on-site dimers.) A dimer will have (spin-independent) diagonal potential V_{ij} . We write V_1 for the nearest-neighbour potential, V_2 for the next-nearest-neighbour potential, and so on. We can now distinguish two types of dimer motion: *crab-like*, in which the constituent electrons retain their spacing, and *crawler*, which requires virtual transitions of energy cost ΔV (see figure 2.1) [6, 7, 13, 31]. The crab-like dimer bandwidth will be O(t), while the crawler bandwidth will be $O(t^2)$, if $t \ll \Delta V$.



Figure 2.1: Two electrons (open circles) form a dimer which can propagate by (a) crawler motion or (b) crab-like motion on the square lattice with nearest- and next-nearest neighbour hopping. Arrows indicate single electron hoppings to nearest-neighbour sites in crawler motion and to next-nearestneighbour sites in crab-like motion. Crawler motion requires virtual transitions to a higher energy state if $V_2 > V_1$.

If a lattice Λ has N sites and the mean number of neighbours $|D_i|$ is ν then the singleelectron Hilbert space is 2N-dimensional, the two-electron Hilbert space is N(2N-1)dimensional and the dimer Hilbert space is $4\frac{\nu}{2}N$ -dimensional. We can further reduce to one singlet and three triplet spaces, each of dimensionality $\nu N/2$. The singlet dimer space is

$$S = \operatorname{span} \left\{ \frac{1}{\sqrt{2}} \left(|i \uparrow j \downarrow\rangle + |j \uparrow i \downarrow\rangle \right) : i \in \Lambda, j \in D_i \right\}$$
(2.28)

and the $S_z = 1, 0, -1$ sectors of the triplet dimer space are

$$\mathcal{T}_1 = \text{span } \{ |i \uparrow j \uparrow \rangle : i \in \Lambda, j \in D_i \}$$

$$(2.29)$$

$$\mathcal{T}_{0} = \operatorname{span} \left\{ \frac{1}{\sqrt{2}} \left(|i \uparrow j \downarrow\rangle - |j \uparrow i \downarrow\rangle \right) : i \in \Lambda, j \in D_{i} \right\}$$
(2.30)

$$\mathcal{T}_{-1} = \operatorname{span} \{ |i \downarrow j \downarrow \rangle : i \in \Lambda, j \in D_i \}$$

$$(2.31)$$

In each case basis states are double-counted in the span. We note that triplets are spatially antisymmetric and singlets are symmetric; if we represent the above dimer basis states as arrows pointing from i to j, then $|i \rightarrow j\rangle = \pm |j \rightarrow i\rangle$ with + for singlets. The above formalism enables us to write the Hamiltonian of the dimers in each sector as a tight-binding Hamiltonian on a dimer lattice constructed by placing a node on the line joining each site i to each point $j \in D_i$. If $j \in D_i$ and $k \in D_i$, and $t_{jk} \neq 0$, then the dimer can hop from ij to ik. A dimer hopping vector is then drawn between the two nodes on the dimer lattice with hopping integral t_{jk} .

In figures it is convenient to represent singlets and triplets as double-headed and single-headed arrows respectively throughout, with the arrows connecting the sites i and j on which the electrons in the dimer are located. This makes singlets and triplets easily distinguishable in diagrams where a distinction is necessary, and reflects the symmetric properties of singlets and triplets.

2.6 Motivation

A growing number of observations suggest that high- T_c superconductors may not be conventional Bardeen-Cooper-Schrieffer superconductors [5] but rather derive from the Bose-Einstein condensation (BEC) of real-space pairs [4, 6–11]. Within the effectivemass approximation, the Bose-Einstein condensation temperature of non-interacting bosons in three dimensions is given by

$$k_{\rm B}T_{\rm BEC} = \frac{2\pi\hbar^2 n^{2/3}}{\zeta(\frac{3}{2})^{\frac{2}{3}} (m_a^* m_b^* m_c^*)^{\frac{1}{3}}},$$
(2.32)

where n is the density of bosons, $m_{a,b,c}^*$ are the eigenvalues of the effective mass tensor and k_B is Boltzmann's constant. Thus pairs (which we refer to as dimers) with a small in-plane effective mass and some inter-plane hopping may form a charged condensate at fairly high temperatures. Such dimers could be bound by a short-range attraction. If a virtual transition to a high-energy radially excited "stretched" dimer is required for hopping to occur, the dimer bandwidth would be of second order in the single-particle hopping t: we call this motion *crawler*. However, if one particle of the dimer can hop without leaving the low energy sector (for example, around a triangular plaquette), the dimer bandwidth can be of *first order* in t and the dimers will have relatively low mass: we call this motion *crab-like*.

A competing process is the formation of larger clusters or stripes [32], which will be much less mobile. This therefore motivates our search for conditions under which the ground state is a condensate of dimers.

There are a number of mechanisms by which local dimers may form [6, 15, 16]. In the bipolaronic model an electron or hole carries with it a distortion in the surrounding lattice, propagating as a new quasiparticle - the polaron. At weak coupling, two polarons can be bound into a large bipolaron by means of the Fröhlich electron-phonon interaction (EPI). At strong coupling, the EPI may overcome the Coulomb repulsion between electrons, so the resulting interaction becomes attractive at a distance of the order of the lattice constant and two small polarons form tightly bound pairs, i.e. small bipolarons. There is experimental and theoretical evidence for this kind of interaction in two-dimensional and three-dimensional lattices. Continuous-time quantum Monte Carlo studies show that such bipolarons can still be sufficiently light to allow a high BEC temperature [6, 7]. Numerical studies using the variational Monte Carlo method have shown that even a relatively weak Fröhlich EPI is sufficient to induce a superconducting state with substantial condensation energy in a doped Mott-Hubbard insulator, and that such a state is stable against clustering [33].

We investigate the existence of a dimer-based ground state in a triangular lattice, a square lattice and a perovskite layer, and show that a condensate of light dimers is possible in the last two of these for suitable values of the interaction. In order to introduce some important concepts we begin by examining the diatomic and triangular molecules in the two following chapters. In each of these finite systems there is a constant intersite potential V_{ij} which for convenience we set equal to zero. In the finite systems we will look at variable U while infinite U will be assumed in extended lattices in later sections.

2.7 Overview of chapters

In the first chapter we introduced the Bipolaronic Theory of High Temperature Superconductivity. In the second chapter we introduced the UV model and other necessary formalism as well as the motivation for this work. The following chapters are organised as follows: Chapters 3-5 look at the diatomic and triangular molecules and the staggered ladder in order to introduce some important concepts. In chapters 6-8 we explore the parameter space for the triangular and square lattices and the perovskite layer, in order to determine whether a condensate of mobile dimers is possible in each case. We note that in the simplest case Dirac points appear for dimers on the triangular lattice. In chapter 9 we investigate Dirac points with particular reference to graphene as this is currently an area of considerable interest. We identify the origin of Dirac points and confirm that two- and three-dimensional Dirac points appear for a number of other lattices under certain circumstances. Chapter 10 is largely devoted to the surprise discovery that triplet dimers can be strictly localised in some lattices. We also show that there are localised singlet and triplet eigenstates of the Hamiltonian for the simple cubic and body centred cubic lattice, under some circumstances. In chapter 11 we look at the dynamics of electrons and dimers on lattices using Green's functions. We show that the probability of finding an initially localised particle at its initial location usually takes the form of a decaying oscillation. We show how this changes if states which are localised for all time contribute to the initially localised state. In chapter 12 we summarise the conclusions we have drawn from previous chapters.

Chapter 3

The Diatomic Molecule

3.1 Finite U

In order to introduce some important concepts we begin by examining the diatomic molecule in this chapter and proceed to the triangular molecule in the next chapter. In each of these finite systems there is a constant intersite potential V_{ij} which for convenience we set equal to zero. In the finite systems we will look at variable U while infinite U will be assumed in extended lattices in later sections.

In the case of a single electron on the diatomic molecule, with spin up or down, there are four basis states

$$|1\uparrow\rangle, |2\uparrow\rangle, |1\downarrow\rangle, |2\downarrow\rangle \tag{3.1}$$

corresponding to the electron being on site 1 or site 2 with spin up or down. Applying the Hamiltonian (2.20) to the states with spin up separately we obtain the hopping matrix

$$\mathbf{H} = \begin{pmatrix} 0 & -t \\ -t & 0 \end{pmatrix} \tag{3.2}$$
An identical hopping matrix is obtained for states with spin down. Diagonalising (3.2) we obtain the eigenvalues $E = \pm t$ corresponding to the eigenfunctions

$$|0\rangle = \frac{|1\uparrow\rangle + |2\uparrow\rangle}{\sqrt{2}} \tag{3.3}$$

$$|1\rangle = \frac{|1\uparrow\rangle - |2\uparrow\rangle}{\sqrt{2}} \tag{3.4}$$

where (3.3) is the ground state of the system with energy E = -t. The eigenstates for spin down are obtained by replacing \uparrow with \downarrow in equations (3.3) and (3.4).

In the case of two electrons on a diatomic molecule there are six basis states:

$$|1\uparrow 2\uparrow\rangle |1\downarrow 2\downarrow\rangle |1\uparrow 2\downarrow\rangle |1\downarrow 2\uparrow\rangle |1\downarrow 1\downarrow\rangle |2\uparrow 2\downarrow\rangle (3.5)$$

and we obtain the hopping matrix

All matrix elements in the first two rows in the hopping matrix are zero reflecting the fact that $|1 \uparrow 2 \uparrow\rangle$ and $|1 \downarrow 2 \downarrow\rangle$ cannot hop to other states due to the exclusion principle. These basis states therefore constitute triplet eigenstates, which have zero energy, corresponding to $S_z = \pm 1$. For the third triplet eigenstate corresponding to $S_z = 0$, which by spin symmetry also has zero energy, we obtain

$$|T_{s_z=0}\rangle = \frac{|1\uparrow 2\downarrow\rangle - |1\downarrow 2\uparrow\rangle}{\sqrt{2}} \tag{3.7}$$

Singlet eigenvalues and eigenstates are summarised in Table 3.1. The eigenvalue E = U in the second row corresponds to a linear combination of doubly occupied sites, hence the energy cost U, where hopping to single-occupancy states has cancelled due to interference. The singlet energies given in table 3.1 are illustrated in figure 3.1 where t is taken to be unity. The ground state energy tends asymptotically to E = 0 as

Energy	$1 \uparrow 2 \uparrow$	$1\downarrow 2\downarrow$	$1\uparrow 2\downarrow$	$1\downarrow 2\uparrow$	$1 \uparrow 1 \downarrow$	$2\uparrow 2\downarrow$
$\boxed{\frac{U - \sqrt{U^2 + 16t^2}}{2}}$	0	0	1	1	$-\frac{U-\sqrt{U^2+16t^2}}{4t}$	$-\frac{U-\sqrt{U^2+16t^2}}{4t}$
U	0	0	0	0	1	-1
$\boxed{\frac{U+\sqrt{U^2+16t^2}}{2}}$	0	0	1	1	$-\frac{U+\sqrt{U^2+16t^2}}{4t}$	$-\frac{U+\sqrt{U^2+16t^2}}{4t}$

Table 3.1: Singlets on a diatomic molecule. Each row shows an energy eigenvalue in the left hand column and then from left to right the coefficients that make up the corresponding eigenstates (unnormalised). The first and third row correspond to the ground state and the state of highest energy respectively.



Figure 3.1: Energies of singlets on a diatomic molecule. Triplets have zero energy due to the exclusion principle.

 $U \to \infty$ and to E = U as $U \to -\infty$. The highest energy tends asymptotically to E = U as $U \to \infty$ and to E = 0 as $U \to -\infty$. The ground state of the system is a singlet state for all U.

The case of three electrons on the diatomic molecule is equivalent to the singleelectron case because we can consider the one unoccupied orbital or 'hole' to behave as if it was an electron. The eigenvalues are the same as in the single-electron case except that there is an energy shift of U due to double occupancy. The eigenvalues for three electrons on the diatomic molecule are therefore

$$E = U - t, \ U - t, \ U + t, \ U + t,$$
 (3.8)

The case of four electrons is equivalent to the case of zero electrons in that there are zero holes. As in the zero electron case there is only one eigenvalue which is E = 2U in this case, corresponding to double occupancy on both sites.

3.2 Small and Large Coupling Expansion

In the case of small or large coupling the solutions $E = \frac{U \pm \sqrt{U^2 + 16t^2}}{2}$, which correspond to the ground state and the state of highest energy for dimers, may be expanded so that the energy of the unperturbed state, and a small perturbation, or exchange interaction, appear as separate terms. The energies can also be obtained in this form, for small or large coupling, using perturbation theory. Applying the binomial expansion in the case $U \gg t$ the solutions become (this is the standard derivation for the exchange interaction)

$$E = 0 - \frac{4t^2}{U} + \frac{16t^4}{U^3} + \dots$$
 (3.9)

and

$$E = U + \frac{4t^2}{U} - \frac{16t^4}{U^3} + \dots$$
 (3.10)

for the ground state and state of highest energy respectively. The first term in (3.9) is the energy of the unperturbed ground state

$$|S_1\rangle = \frac{|1\uparrow 2\downarrow\rangle + |1\downarrow 2\uparrow\rangle}{\sqrt{2}} \tag{3.11}$$

and the first term in (3.10) is the energy of the unperturbed state of highest energy

$$|S_3\rangle = \frac{|1\uparrow 1\downarrow\rangle + |2\uparrow 2\downarrow\rangle}{\sqrt{2}} \tag{3.12}$$

The second term in (3.9) and (3.10) is the spin-dependent exchange interaction or singlet-triplet splitting. We ignore higher order terms. The ground state energy (3.9) corresponds to a singlet rather than a triplet state because the electrons in the singlet can hop in order to reduce its energy whereas electrons in the triplet are forbidden from hopping due to the Pauli exclusion principle. For $U \ll t$ we obtain

$$E = -2t + \frac{U}{2} - \frac{U^2}{16t} + \cdots$$
 (3.13)

and

$$E = 2t + \frac{U}{2} + \frac{U^2}{16t} + \dots$$
 (3.14)

for the ground state and highest energy state respectively. The first term in (3.13) is the energy of the unperturbed ground state

$$|S_1\rangle = \frac{|1\uparrow 2\downarrow\rangle + |1\downarrow 2\uparrow\rangle + |1\uparrow 1\downarrow\rangle + |2\uparrow 2\downarrow\rangle}{2}$$
(3.15)

and the first term in (3.14) is the energy of the unperturbed state (of highest energy)

$$|S_3\rangle = \frac{|1\uparrow 2\downarrow\rangle + |1\downarrow 2\uparrow\rangle - |1\uparrow 1\downarrow\rangle - |2\uparrow 2\downarrow\rangle}{2}$$
(3.16)

The second and third terms in (3.13) and (3.14) are the exchange interaction. The second term reflects the fact that for U = 0 there is a probability of one half that both electrons will be on the same site. Higher order terms are ignored.

3.3 Strong and Weak Coupling Perturbation Theory

We show that equations (3.9) and (3.13), which are the ground state energies for weak and strong coupling respectively, can be obtained by the application of perturbation theory, from which we apply the equation

$$E_{n} = E_{n}^{(0)} + H_{nn}' + \sum_{k \neq n} \frac{\left|H_{kn}'\right|^{2}}{E_{n}^{(0)} - E_{k}^{(0)}} + \cdots$$
(3.17)

Note that the third term in (3.17) must always be negative or zero if $|n\rangle$ is the ground state. The third term contains a sum over states but, since the triplet states have zero energy for all U/t due to the exclusion principle, their contribution is zero in the sum. The triplet states (exact for all U/t) are

$$|T_1\rangle = |1\uparrow 2\uparrow\rangle \tag{3.18}$$

$$|T_2\rangle = \frac{|1\uparrow 2\downarrow\rangle - |1\downarrow 2\uparrow\rangle}{\sqrt{2}} \tag{3.19}$$

$$|T_3\rangle = |1\downarrow 2\downarrow\rangle \tag{3.20}$$

The unperturbed singlet states for $U \gg t$ are

$$|S_1\rangle = \frac{|1\uparrow 2\downarrow\rangle + |1\downarrow 2\uparrow\rangle}{\sqrt{2}} \tag{3.21}$$

$$|S_2\rangle = \frac{|1\uparrow 1\downarrow\rangle - |2\uparrow 2\downarrow\rangle}{\sqrt{2}} \tag{3.22}$$

$$|S_3\rangle = \frac{|1\uparrow 1\downarrow\rangle + |2\uparrow 2\downarrow\rangle}{\sqrt{2}} \tag{3.23}$$

with the energies E = 0, E = U and E = U respectively where (3.21) is the unperturbed ground state and (3.22) is exact for all U/t due to cancellation of hopping. For $U \gg t$ the unperturbed Hamiltonian is

$$H_0 = U \sum_i n_{i\uparrow} n_{i\downarrow} \tag{3.24}$$

and the perturbation in the Hamiltonian is

$$H' = -t \sum_{\langle ii' \rangle \sigma} c^{\dagger}_{i\sigma} c_{i'\sigma}$$
(3.25)

Applying equation (3.17) to the unperturbed ground state for $U \gg t$ (3.21) and using (3.22), (3.23), (3.24) and (3.25) we obtain

$$E = 0 - \frac{4t^2}{U} \cdots \tag{3.26}$$

where the first term is the energy of the unperturbed ground state (3.21) and the second term is the exchange interaction. This is the same result as was obtained using binomial theorem (3.9) except that fewer terms are included.

The unperturbed singlet states for $U \ll t$ are

$$|S_1\rangle = \frac{|1\uparrow 2\downarrow\rangle + |1\downarrow 2\uparrow\rangle + |1\uparrow 1\downarrow\rangle + |2\uparrow 2\downarrow\rangle}{2}$$
(3.27)

$$|S_2\rangle = \frac{|1\uparrow 1\downarrow\rangle - |2\uparrow 2\downarrow\rangle}{\sqrt{2}} \tag{3.28}$$

$$|S_3\rangle = \frac{|1\uparrow 2\downarrow\rangle + |1\downarrow 2\uparrow\rangle - |1\uparrow 1\downarrow\rangle - |2\uparrow 2\downarrow\rangle}{2}$$
(3.29)

with the energies E = -2t, E = 0 and E = 2t respectively where (3.27) is the unperturbed ground state and (3.28) is exact for all U/t due to cancellation of hopping. For $U \ll t$ the unperturbed Hamiltonian is

$$H_0 = -t \sum_{\langle ii'\rangle\sigma} c^{\dagger}_{i\sigma} c_{i'\sigma}$$
(3.30)

and the perturbation in the Hamiltonian is

$$H' = U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$
(3.31)

Applying equation (3.17) to the unperturbed ground state for $U \ll t$ (3.27) and using (3.28), (3.29), (3.30) and (3.31) we obtain

$$E = -2t + \frac{U}{2} - \frac{U^2}{16t} + \cdots$$
 (3.32)

where the first term is the energy of the unperturbed ground state (3.27) and the second and third terms are the exchange interaction. This is the same result as was obtained using binomial theorem (3.13).

Chapter 4

The Triangular Molecule

4.1 Single Electrons

Monte Carlo studies have shown that bipolarons on triangular lattices and staggered ladders are very light over a wide range of parameters [7, 34]. This is due to a crablike motion which is only possible for lattices constructed from edge-sharing triangular plaquettes if hopping is restricted to nearest neighbour hopping. Here we investigate the properties of an isolated triangular plaquette.

For a single electron on a triangular molecule with spin up there are three basis states:

$$|1\uparrow\rangle, |2\uparrow\rangle, |3\uparrow\rangle \tag{4.1}$$

corresponding to an electron located on one of three sites. There are three similar basis states corresponding to spin down. Applying the Hamiltonian (2.20) we obtain the hopping matrix

$$\mathbf{H} = \left(\begin{array}{ccc} 0 & -t & -t \\ -t & 0 & -t \\ -t & -t & 0 \end{array} \right)$$

Diagonalising the matrix we obtain the solutions

$$E = -2t, t, t \tag{4.2}$$

The ground state solution E = -2t corresponds to the eigenstate

$$\Psi = \frac{|1\uparrow\rangle + |2\uparrow\rangle + |3\uparrow\rangle}{\sqrt{3}} \tag{4.3}$$

By applying periodic boundary conditions the three eigenstates corresponding to the energies (4.2) can be thought of as waves propagating around the triangle with wave vector $k = 0, \pm \frac{2\pi}{3a}$.

4.2 Dimers with $U = \infty$

Dimers are able to propagate around a triangular plaquette without making virtual transitions into a higher energy sector; we call this motion crab-like motion. We begin by taking $U = \infty$ and separate the dimer Hilbert space into one singlet space and three triplet spaces. The triplet space corresponding to $S_z = +1$ contains three basis states which may be written:

$$|1\uparrow 2\uparrow\rangle, |2\uparrow 3\uparrow\rangle, |3\uparrow 1\uparrow\rangle \tag{4.4}$$

The triplet basis states corresponding to $S_z = -1$ are obtained by replacing \uparrow with \downarrow in the above basis states. The triplet space corresponding to $S_z = 0$ contains three basis states which may be written:

$$|T_1\rangle = \frac{1}{\sqrt{2}} \left(|2\uparrow 3\downarrow\rangle - |3\uparrow 2\downarrow\rangle \right) \tag{4.5}$$

$$|T_2\rangle = \frac{1}{\sqrt{2}} \left(|1\uparrow 3\downarrow\rangle - |3\uparrow 1\downarrow\rangle\right) \tag{4.6}$$

$$|T_3\rangle = \frac{1}{\sqrt{2}} \left(|1\uparrow 2\downarrow\rangle - |2\uparrow 1\downarrow\rangle\right) \tag{4.7}$$

The singlet space contains three basis states which may be written

$$|S_1\rangle = \frac{1}{\sqrt{2}} \left(|2\uparrow 3\downarrow\rangle + |3\uparrow 2\downarrow\rangle\right) \tag{4.8}$$

$$|S_2\rangle = \frac{1}{\sqrt{2}} \left(|1\uparrow 3\downarrow\rangle + |3\uparrow 1\downarrow\rangle\right) \tag{4.9}$$

$$|S_3\rangle = \frac{1}{\sqrt{2}} \left(|1 \uparrow 2 \downarrow\rangle + |2 \uparrow 1 \downarrow\rangle \right) \tag{4.10}$$

We note that triplets are spatially antisymmetric and singlets are symmetric. We also note that an arrow can be drawn along each bond in the triangular plaquette such that any hop will change the direction of the arrow. Hence there will always be a change in the sign of hopping for the triplet and the band structures will be symmetric, given that $|i \rightarrow j\rangle = \pm |j \rightarrow i\rangle$ with + for singlets. This is also true for extended lattices: Singlet-triplet band structure symmetry appears if an arrow, representing a triplet, can be drawn along each bond in a lattice such that any hop will reverse the direction of the arrow. The singlet and triplet situations will then be symmetric with opposite sign of hopping. The condition is satisfied for the staggered ladder and the triangular lattice, if there is nearest neighbour hopping only, since these lattices are composed of triangular plaquettes. The condition is also satisfied for the square ladder and square lattice if hopping is restricted to next-nearest-neighbour hopping.

For the triplet we obtain the hopping matrix (same for each triplet space)

$$\mathbf{H} = \left(\begin{array}{ccc} 0 & -t & t \\ -t & 0 & -t \\ t & -t & 0 \end{array} \right)$$

and the triplet energies E = 2t, -t, -t. For the singlet we obtain the hopping matrix

$$\mathbf{H} = \left(\begin{array}{rrr} 0 & -t & -t \\ -t & 0 & -t \\ -t & -t & 0 \end{array}\right)$$

and the singlet energies E = -2t, t, t. As expected the singlet energies are as for the triplet but with a change in the sign of hopping. The single electron and the singlet dimer both hop between three states arranged around a triangular plaquette hence the situations are equivalent and the solutions are the same in each case (the triplet solutions are different from the single electron solutions due to the change in the sign of hopping). As in the case of the single electron the singlet ground state comprises three basis states with equal amplitudes:

$$|S_{ground}\rangle = \frac{|S_1\rangle + |S_2\rangle + |S_3\rangle}{\sqrt{3}} \tag{4.11}$$

and the three dimer eigenstates can be thought of as travelling waves on the triangular plaquette with wave vector $k = 0, \pm \frac{2\pi}{3a}$.

4.3 Dimers with Finite U

For finite U three additional basis states appear in the singlet space,

$$|S_4\rangle = |1\uparrow 1\downarrow\rangle \tag{4.12}$$

$$|S_5\rangle = |2\uparrow 2\downarrow\rangle \tag{4.13}$$

$$|S_6\rangle = |3\uparrow 3\downarrow\rangle \tag{4.14}$$

implying that three additional singlet eigenstates appear (additional basis states do not appear in the triplet spaces due to the exclusion principle hence the triplet states are unaffected by U). Diagonalising the singlet hopping matrix with finite U we obtain the eigenvalues

$$E = -t + \frac{U \pm \sqrt{36t^2 + 4Ut + U^2}}{2} \tag{4.15}$$

$$E = \frac{t + U \pm \sqrt{9t^2 - 2Ut + U^2}}{2} \tag{4.16}$$

where (4.16) is doubly degenerate. In the limit U = 0 the energies (4.15) and (4.16) become E = -4t, -t, -t, 2t, 2t, 2t. Each of the energies for the two-electron states with U = 0 is a sum of two single-electron energies. Recall that the single-electron solutions were E = -2t, t, t. The energy eigenvalues obtained for dimers on the triangular molecule are illustrated in figure 4.1 where we take t = 1. The triplet energies are constant with the values E = 2t, -t, -t. The remaining four curves correspond to the six singlet energies with two of the solutions (dashed) being doubly degenerate.



Figure 4.1: Energies of dimers on a triangular molecule with finite U and t = 1. Triplet energies are constant. Dashed curves indicate energies of degenerate singlet states.

4.4 Small Coupling Expansion

In the case of small or large coupling the solutions (4.15), which correspond to the state of highest energy (for U > 0) and the ground state, may be expanded so that the energy of the unperturbed state, and a small perturbation, or exchange interaction, appear as separate terms. Applying the binomial expansion in the case $U \gg t$ the solutions become

$$E = 0 - t - \frac{9t^2}{U} + \dots$$
 (4.17)

and

$$E = U - t + \frac{9t^2}{U} + \dots$$
 (4.18)

for the ground state and state of highest energy (for U > 0) respectively. The first term in (4.17) is zero and is the energy of the unperturbed ground state

$$|S_{ground}\rangle = \frac{|S_1\rangle + |S_2\rangle + |S_3\rangle}{\sqrt{3}} \tag{4.19}$$

and the first term in (4.18) is the energy of the unperturbed state (of highest energy for U > 0)

$$|S_{highest}\rangle = \frac{|S_4\rangle + |S_5\rangle + |S_6\rangle}{\sqrt{3}} \tag{4.20}$$

The second and third terms in (4.17) and (4.18) are the spin-dependent exchange interaction. We ignore higher order terms.

Chapter 5

The Staggered Ladder

5.1 Staggered Ladder Electrons

Monte Carlo studies have shown that bipolarons on triangular lattices and staggered ladders constructed from triangular plaquettes are very light over a wide range of parameters [7, 34]. Here we demonstrate this analytically for nearest-neighbour dimers on a staggered ladder with nearest neighbour hopping only.

We define the hopping integrals t and t' which correspond to hopping between nearest neighbours on opposite legs and on the same leg respectively. For a single electron on a staggered ladder this is equivalent to an electron on an infinite chain where t and t' are the nearest and next nearest neighbour hopping integrals respectively. An electron on an infinite chain can be described by just one basis state which we call $|A\rangle$ (see figure 5.1). Applying the Hamiltonian (2.26) we obtain the band structure (see figure 5.2)

$$E(\mathbf{k}) = -2t\cos\left(ka\right) - 2t'\cos\left(2ka\right) \tag{5.1}$$

In the limit t' = 0 (5.1) becomes



Figure 5.1: An electron on a staggered ladder is equivalent to an electron on an infinite chain (shown as a dashed line embedded within the staggered ladder).

$$E(\mathbf{k}) = -2t\cos\left(ka\right) \tag{5.2}$$

corresponding to nearest neighbour hopping on the infinite chain. On the staggered ladder this corresponds to an electron hopping from one leg to the other with each hop with no direct hopping along either leg. In the limit t = 0 (5.1) becomes

$$E(\mathbf{k}) = -2t'\cos\left(2ka\right) \tag{5.3}$$

corresponding to next nearest neighbour hopping on the infinite chain. On the staggered ladder this corresponds to an electron propagating along one leg or the other with no hopping between legs.

5.2 Staggered Ladder Dimers

We assume a deep minimum in the potential at the nearest neighbour separation so that dimers will be of fixed length L = a where a is the separation between nearest neighbours on the same leg and on opposite legs of the ladder. For convenience we set the nearest neighbour interaction $V_1 = 0$. We separate the dimer Hilbert space into one



Figure 5.2: Band structure for electron on an infinite chain (equivalent to electron on a staggered ladder) with t = t' = 1.

singlet and three triplet spaces. The singlet dimer space is

$$S = \operatorname{span} \left\{ \frac{1}{\sqrt{2}} \left(|i \uparrow j \downarrow \rangle + |j \uparrow i \downarrow \rangle \right) \right\}$$
(5.4)

and the $S_z = 1, 0, -1$ sectors of the triplet dimer space are

$$\mathcal{T}_1 = \text{span } \{ |i \uparrow j \uparrow \rangle \}$$
(5.5)

$$\mathcal{T}_{0} = \operatorname{span} \left\{ \frac{1}{\sqrt{2}} \left(|i \uparrow j \downarrow \rangle - |j \uparrow i \downarrow \rangle \right) \right\}$$
(5.6)

$$\mathcal{T}_{-1} = \operatorname{span} \{ |i \downarrow j \downarrow \rangle \}$$
(5.7)

In each sector of the Hilbert space we define two basis states, $|A\rangle$ and $|B\rangle$, corresponding to dimers with end-points *i* and *j* on opposite legs and on the same leg of the ladder respectively (see figure 5.3(a)). The dimer lattice of the staggered ladder is equivalent to a sawtooth chain as indicated in figure 5.3(b). For the singlet we obtain the hopping matrix

$$\mathbf{H} = \begin{pmatrix} -t'e^{-ika} - t'e^{ika} & -t - te^{ika} \\ -t - te^{-ika} & 0 \end{pmatrix}$$
(5.8)

The triplet hopping matrix is as for the singlet but with a change in the sign of hopping. We obtain the singlet solutions

$$E_{s}(\mathbf{k}) = -t' \cos(ka) \pm \sqrt{t'^{2} \cos^{2}(ka) + 4t^{2} \cos^{2}\left(\frac{ka}{2}\right)}$$
(5.9)

and the triplet solutions

$$E_t(\mathbf{k}) = t' \cos(ka) \pm \sqrt{t'^2 \cos^2(ka) + 4t^2 \cos^2\left(\frac{ka}{2}\right)}$$
(5.10)

as illustrated in figure 5.4. The singlet and triplet band structures are related by $E_s(\mathbf{k}) = -E_t(\mathbf{k})$. The singlet-triplet symmetry is expected since the symmetry condition is satisfied: an arrow, representing a triplet, can be drawn on each bond in the staggered ladder such that any hop will change the direction of the arrow. In the limit t' = 0 (no hopping along legs) exchange paths vanish so that the singlet and triplet band structures coincide. The solutions become

$$E_t(\mathbf{k}) = E_s(\mathbf{k}) = \pm 2t \cos\left(\frac{ka}{2}\right)$$
 (5.11)

This corresponds to the dimer hopping from $|A\rangle$ to $|B\rangle$ to $|A\rangle e^{ika}$ and so on, so that each hop along the ladder involves an electron hopping from one leg to the other (see figure 5.3(a)). In the limit t = 0 (no hopping across legs) the singlet solutions become

$$E_s(\mathbf{k}) = -2t'\cos\left(ka\right) \tag{5.12}$$

and



Figure 5.3: (a) Triplet dimers on a staggered ladder. (b) The dimer lattice of the staggered ladder is a sawtooth chain. A flat band appears for $t' = t/\sqrt{2}$. The amplitudes of the corresponding localised eigenstate are indicated in brackets.

$$E_s = 0 \tag{5.13}$$

and the triplet solutions become

$$E_t(\mathbf{k}) = 2t'\cos\left(ka\right) \tag{5.14}$$

and

$$E_t = 0 \tag{5.15}$$



Figure 5.4: Band structure of singlet (solid line) and triplet dimers (dashed) on a staggered ladder with t = t' = 1. Triplet dimer band structure is as for singlets but with a change in the sign of hopping.

In this limit exchange paths have again vanished so that the singlet and triplet band structures are related by $E_s(\mathbf{k}) = E_t(\mathbf{k} + \frac{\pi}{a})$. Solutions (5.12) and (5.14) correspond to $|A\rangle$ in which the dimer can propagate by means of crab-like motion. Solutions (5.13) and (5.15) correspond to $|B\rangle$ in which electrons are on the same leg so that the dimer cannot propagate without one of the electrons hopping to the opposite leg.

For $t' = t/\sqrt{2}$ the singlet solutions become

$$E_s(\mathbf{k}) = -\sqrt{2}t\left(\cos\left(ka\right) + 1\right) \tag{5.16}$$

and

$$E_s = \sqrt{2}t \tag{5.17}$$

and the triplet solutions become

$$E_t(\mathbf{k}) = \sqrt{2t} \left(\cos\left(ka\right) + 1 \right) \tag{5.18}$$

$$E_t = -\sqrt{2}t \tag{5.19}$$

Note that at this ratio t/t' the upper band is flat for singlets while the lower band is flat for triplets. The corresponding localised eigenstate (indicated in figure 5.3(b)) is a superposition of two basis states lying along the edges of the ladder, $|B\rangle$ and $|Be^{-i\frac{k}{2}}\rangle$, with a third, $|A\rangle$, which has its endpoints on opposite legs the ladder. The state $|A\rangle$ cannot hop to $|Ae^{i\frac{k}{2}}\rangle$ or $|Ae^{-i\frac{k}{2}}\rangle$ because in each case the hopping cancels with that of $|B\rangle$ or $|Be^{-i\frac{k}{2}}\rangle$.

5.3 Effective Mass

For an electron on a staggered ladder with t = 0 (no hopping between sites on opposite legs) we obtain the effective mass

$$m_e^* = \frac{\hbar^2}{8t'a^2}$$
(5.20)

For an electron on a staggered ladder with t' = 0 (no hopping between sites on the same leg) we obtain the effective mass

$$m_e^* = \frac{\hbar^2}{2ta^2} \tag{5.21}$$

In each of the limits t = 0 and t' = 0 the dimer effective mass is $m_d^* = 4m_e^*$ (singlet and triplet effective masses are the same since exchange paths vanish in each of these limits). In each case the effective mass of the dimer is larger than that of the single electron because it takes twice as many hops for the dimer to travel the same distance as the single electron. For an electron on a staggered ladder with t' = t we obtain the

47

and

effective mass

$$m_e^* = \frac{\hbar^2}{10ta^2} \tag{5.22}$$

With t' = t we obtain $m_s^* \approx 5m_e^*$ for singlet dimers and $m_t^* = 10m_e^*$ for triplet dimers. With t' = t the effective mass of the triplet is twice as large as that of the singlet because the lower band for triplets is less dispersive than that for singlets (see figure 5.4).

Chapter 6

The Triangular Lattice

6.1 Objectives and Method

We have seen that dimers on a staggered ladder have low effective mass due to crab-like motion. This motion is possible, with hopping restricted to nearest neighbour hopping, because the staggered ladder is composed of edge-sharing triangular plaquettes. We therefore expect that dimers on the triangular lattice, with hopping restricted to nearest neighbour hopping, will be comparably light. Crab-like motion is also possible in the square lattice if next nearest neighbour hopping is allowed so in this case dimers should also have low effective mass. In this chapter and the following two chapters we verify that dimers have low effective mass in the triangular and square lattices and the perovskite layer. We also investigate the feasibility of a dimer-based ground state in each case and aim to determine whether a condensate of light dimers is possible for suitable values of the interaction. The procedure is to calculate the band structures for single fermions, dimers, trimers and larger clusters for each lattice, assuming a suitably parametrised effective interaction between the fermions, and then to identify any regions of the parameter space in which dimers are favoured. We also determine the effective mass of dimers in regions where they are favoured.

6.2 Nearest-Neighbour Dimers

We begin our investigation of two-dimensional lattices with the triangular lattice. We assume a repulsive next-nearest-neighbour potential V_2 . This allows us to truncate the Hilbert space by restricting D_i to nearest-neighbour sites. We assume nearestneighbour hopping only. From (2.26) we obtain the band structure for a single electron with nearest neighbour hopping only

$$E_e(\mathbf{k}) = -2t\cos(k_x a) - 2t\cos\left(k_x \frac{a}{2} - \sqrt{3}k_y \frac{a}{2}\right) - 2t\cos\left(k_x \frac{a}{2} + \sqrt{3}k_y \frac{a}{2}\right)$$
(6.1)

where t is the nearest-neighbour hopping integral and a is the lattice parameter. This corresponds to a band edge at -6t and an effective mass

$$m_e^* = \frac{\hbar^2}{3ta^2}.\tag{6.2}$$

For nearest-neighbour dimers with nearest neighbour hopping only, the dimer lattice of the triangular lattice is the kagome lattice. In this case we obtain the singlet hopping matrix

$$\mathbf{H} = \begin{pmatrix} V_1 & -t - te^{-ik_x a} & -t - te^{-ik_x \frac{a}{2} - i\sqrt{3}k_y \frac{a}{2}} \\ -t - te^{ik_x a} & V_1 & -t - te^{ik_x \frac{a}{2} - i\sqrt{3}k_y \frac{a}{2}} \\ -t - te^{ik_x \frac{a}{2} + i\sqrt{3}k_y \frac{a}{2}} & -t - te^{-ik_x \frac{a}{2} + i\sqrt{3}k_y \frac{a}{2}} & V_1 \end{pmatrix}$$

and the singlet dimer band structure (see figure 6.1)

$$E_{s1,2}(\mathbf{k}) = V_1 - t \pm t \sqrt{3t^2 - tE_e(\mathbf{k})}$$
(6.3)

$$E_{s3}(\mathbf{k}) = V_1 + 2t \tag{6.4}$$

The two lower bands are dispersive, meeting at Dirac points, while the upper band is



Figure 6.1: Band structure of the kagome lattice and hence band structure of singlet nearestneighbour dimers on the triangular lattice with t = a = 1 and $V_1 = 0$. Note that the flat band has the highest energy for singlets.

flat. The lowest band has a lower band edge at $V_1 - 4t$ and an effective mass

$$m_s^* = \frac{2\hbar^2}{ta^2} = 6m_e^*. \tag{6.5}$$

The band structure for triplets is as for singlets (6.3–6.4) but with a change of sign of hopping [6]. The singlet-triplet symmetry is expected since an arrow, representing a triplet, can be drawn on each bond in the triangular lattice such that any hop will change the direction of the arrow. The singlet-triplet symmetry only holds for dimers of fixed length L = a with hopping restricted to nearest-neighbour hopping. The triplets have an infinitely degenerate ground state at $V_1 - 2t$ and have infinite effective mass. Singlet dimers form the ground state, but triplets have the lowest energy in parts of the Brillouin zone as is also borne out by Monte Carlo calculations on the full electronphonon system [6].

The localised eigenstates corresponding to the singlet and triplet flat bands consist

of dimers confined within a hexagonal plaquette (see figure 6.2). Hopping to dimers that lie along the edges of the plaquettes cancels, hence there are no hopping paths into neighbouring plaquettes. In each case one electron is localised at the center while the other is delocalised around the edge of the plaquette. The localised singlet and triplet



Figure 6.2: Localised eigenstates for (a) triplet and (b) singlet nearest-neighbour dimers in the triangular lattice with nearest neighbour hopping t only.

eigenstates have energy $E = V_1 + 2t$ and $E = V_1 - 2t$ respectively. In each case the non-zero kinetic energy is due to dimers within the plaquette hopping to each other.

6.3 Feasibility of a Nearest-Neighbour-Dimer Ground State

We address the question of whether the ground state of electrons on a triangular lattice can consist of the above mobile singlet dimers in some region of the parameter space. We begin with the above case of nearest-neighbour hopping t and restriction of D_i to nearest-neighbour sites. In this case dimers propagate by crab-like motion, while trimers are immobile. Extension of D_i to next-nearest neighbours would allow crawler motion of trimers. From equations (6.1) and (6.3) we know that the single electron ground state energy is $E_e = -6t$ and that the singlet dimer ground state energy is $E_s = V_1 - 4t$. The trimer energy is $E_3 = 3V_1$. Figure 6.3 shows a plot of the energy per electron of electrons, dimers and trimers in their ground states, with t = 1. We see that there are no values of V_1 for which dimers form the ground state. With repulsive V_1 single electrons form the ground state as expected. With attractive $V_1 < -6t$ trimers form the ground state. This is because, with attractive V_1 , two electrons can lower their energy by occupying nearest neighbour sites, but a third electron can always be added to a site which is a nearest neighbour of the first two, thereby lowering the total energy even further. With attractive $V_1 > -6t$ single electrons are favoured because of the larger kinetic energy. Our results appear to rule out a ground state consisting of dimers in the low density limit on the triangular lattice with nearest-neighbour hopping only and bonds of fixed length L = a.



Figure 6.3: Energy per electron of electrons, dimers and trimers in their ground states on the triangular lattice with t = 1. We see that there are no values of V_1 for which dimers form the ground state.

6.4 Stretching Dimers and Trimers

We now consider the case in which a repulsive third-neighbour potential V_3 is assumed. This allows us to truncate the Hilbert space by restricting D_i to nearest and nextnearest-neighbour sites. We assume nearest-neighbour hopping only. In this case dimers propagate by crablike motion and crawler motion, trimers propagate by crawler motion and tetramers are immobile. The stretching dimer lattice looks the same as the kagome lattice. However each lattice point now represents an unstretched dimer and a stretched dimer which are at right angles to each other and share the same mid-point. The unit cell of the dimer lattice now contains six basis states. At the point $\mathbf{k} = 0$ we obtain the ground state energy for dimers

$$E_d(\mathbf{k}=0) = -2t + \frac{V_1 + V_2}{2} + \frac{1}{2}\sqrt{80t^2 - 8tV_1 + 8tV_2 + V_1^2 + V_2^2 - 2V_1V_2}$$
(6.6)

With D_i extended to next-nearest neighbours trimers propagate by crawler motion. The additional restriction that one bond at a time is allowed to stretch simplifies the trimer lattice to that shown in figure 6.4 and reduces the problem to that of an 8x8 hopping matrix. In this case the unit cell of the trimer lattice is a parallelogram containing eight basis states.

With $V_1 = V_2 = 0$ we obtain four dispersive solutions and four flat band solutions (see figure 6.5). The flat band energies are E = -t and E = +t with the former solution being triply degenerate. The dispersive band solutions are

$$E_{t1}(\mathbf{k}) = \frac{1}{2}t\left(1 - \sqrt{25 + 8\sqrt{3 + 2\cos(\alpha) + 2\cos(\beta) + 2\cos(k_x)}}\right)$$
$$E_{t2}(\mathbf{k}) = \frac{1}{2}t\left(1 + \sqrt{25 + 8\sqrt{3 + 2\cos(\alpha) + 2\cos(\beta) + 2\cos(k_x)}}\right)$$
$$E_{t3}(\mathbf{k}) = \frac{1}{2}t\left(1 - \sqrt{25 - 8\sqrt{3 + 2\cos(\alpha) + 2\cos(\beta) + 2\cos(k_x)}}\right)$$
$$E_{t4}(\mathbf{k}) = \frac{1}{2}t\left(1 + \sqrt{25 - 8\sqrt{3 + 2\cos(\alpha) + 2\cos(\beta) + 2\cos(k_x)}}\right)$$



Figure 6.4: The triangular lattice and its trimer lattice (overlaid) where D_i includes nearest and next-nearest neighbours with the additional restriction that only one bond at a time can be stretched. The unit cell of the trimer lattice (dashed) contains eight basis states, each of which is either an unstretched trimer (bold) or a stretched trimer (bold). Points in the trimer lattice are placed at the centre of the trimer configurations they represent.

where
$$\alpha = \left(\frac{k_x a}{2} + \frac{\sqrt{3}k_y a}{2}\right)$$
 and $\beta = \left(\frac{k_x a}{2} - \frac{\sqrt{3}k_y a}{2}\right)$.

The four flat bands are due to several 'hopping pairs' in the unit cell of the trimer lattice (see figure 6.4) where the members of a pair hop to each other but all other hopping cancels. At the point $\mathbf{k} = 0$ we obtain the ground state energy for trimers

$$E_t(\mathbf{k}=0) = \frac{1}{2}V_2 + \frac{5}{2}V_1 + \frac{1}{2}t - \frac{1}{2}\sqrt{V_1^2 + V_2^2 - 2tV_1 + 2tV_2 - 2V_1V_2 + 49t^2}$$
(6.8)

6.5 Feasibility of a Stretching-Dimer Ground State

Figure 6.6 shows the phase diagram of the triangular lattice with nearest-neighbour hopping t = 1 and D_i restricted to nearest and next-nearest neighbour sites. With repulsive V_1 and V_2 single electrons form the ground state as expected and with attractive V_1 and V_2 tetramers are largely favoured as expected. Trimers, consisting largely



Figure 6.5: Band structure of trimers on a triangular lattice, with t = a = 1 and $V_1 = V_2 = 0$, where D_i includes nearest and next-nearest neighbours and one bond at a time can be stretched. There are four flat bands, three of which are degenerate at E = -t, and four dispersive bands.

of bonds of length L = a with energy V_1 , are favoured in the top left corner with attractive V_1 and repulsive V_2 . Trimers are also favoured in the bottom right corner, with repulsive V_1 and attractive V_2 , and here consist largely of bonds of length $L = \sqrt{3}a$ and energy V_2 . Trimers propagate by crawler motion in both regions. (The trimer configurations in the bottom right corner with all three bonds stretched at the same time should strictly have been included in the band structure calculations but were omitted for simplicity; they have been added to the phase diagram with energy $E = 3V_2$ so that the diagram is consistent with D_i including nearest and next-nearest neighbours. It is expected that their proper inclusion in the calculations would not change the phase diagram appreciably.) The reason that dimers do not appear in the diagram is the same as in the previous case: if, with small t, the energy of two electrons is minimised



Figure 6.6: Phase diagram of the triangular lattice with nearest neighbour hopping t = 1 and D_i restricted to nearest and next nearest neighbours such that the maximum bond length is $L = \sqrt{3}a$. Diagram shows regions in which electrons, trimers and tetramers form the ground state. Dimers do not appear in the diagram.

at some separation d, a third electron can always be added at a distance d from each of the first two electrons, thereby lowering the total energy even further. This argument fails for larger t but in that case single electrons are favoured. We have also considered the same cases but with the inclusion of next-nearest-neighbour hopping, and again found no parameter regions in which dimers form a ground state. Other variations on the cases we have looked at can be considered. However our study suggests that at low density the geometry of the triangular lattice always favours trimers or larger clusters over dimers, where an effective attraction exists, unless t is sufficiently large for electrons to be favoured.

Despite this finding it might be possible to obtain a mixture of dimers and single polarons away from the low-density limit when many-body effects are taken into account [35–37]. If the number of states below the Fermi level in the polaron band is less than the

number of electrons, bipolarons remain stable mobile quasi-particles because the Pauli exclusion principle prevents their decay into single polarons. A comprehensive analysis by Kornilovitch of a two-body problem on the square lattice with nearest-neighbour attraction strongly supports such a model of overdoped cuprates [37].

Chapter 7

The Square Lattice

7.1 Square Lattice Dimers

Dimers on a square lattice can propagate by crab-like motion if next-nearest-neighbour hopping t' is allowed and by crawler motion if nearest-neighbour hopping t and virtual transitions into a higher energy sector are allowed. We assume a sufficiently large third-nearest-neighbour repulsion V_3 such that dimers and larger clusters with bond lengths $L > \sqrt{2}a$ have large energy. This allows us to truncate the dimer Hilbert space, restricting D_i to nearest and next-nearest-neighbour sites. The maximum bond length is then $L_{\max} = \sqrt{2}a$ and there are four dimer configurations, $|A\rangle$, $|B\rangle$, $|C\rangle$ and $|D\rangle$, per unit cell of the square lattice, in each of the four Hilbert spaces (2.28–2.31) (see figure 7.1(a))[13]. The dimer lattice is equivalent to a plane of corner-sharing octahedra, the unit cell of which is shown in figure 7.1(b). The path $|A\rangle \rightarrow |C\rangle \rightarrow \pm |A\rangle$ induces a sign change for triplets only. Unlike the case of a triangular lattice, the band structures of singlets and triplets on the square lattice are not related by symmetry (see figure 7.2).

Figure 7.2 shows singlet and triplet band structures for various t' with $V_1 = V_2$, where V_1 and V_2 are nearest- and next-nearest-neighbour potentials respectively. Figure 7.2(c)



Figure 7.1: (a) The dimer configurations $|A\rangle$, $|B\rangle$, $|C\rangle$ and $|D\rangle$ in the square lattice. Single-headed arrows indicate triplets. (b) Unit cell of the dimer lattice of the square lattice. Solid lines represent nearest-neighbour hopping t and dotted lines represent next-nearest-neighbour hopping t'. Where $\pm t$ and $\pm t'$ appear the sign is positive for singlets and negative for triplets.

shows that at $t' = t/\sqrt{2}$ the highest and lowest triplet bands are flat (so that for those parameters triplets would be immobile). Figure 7.2(e) shows that in the singlet case with t' = 0 there are two flat bands with energy E = 0; one of these bands corresponds to the localised state $(|B\rangle - |D\rangle)/\sqrt{2}$ and remains flat for non-zero t'.

For specific t/t' and V_1/V_2 there are two triplet flat bands. If $V_1 = V_2$ the triplet flat bands appear for $t' = t/\sqrt{2}$ with energy $E = -2\sqrt{2}t$ and $E = 2\sqrt{2}t$, where we have taken $V_1 = V_2 = 0$ for convenience (see figure 7.2(c)). The corresponding localised eigenstates each consist of dimers confined within a square plaquette (see figure 7.3). Hopping to dimers that lie along the edges of the plaquette cancels so that there are no hopping paths into neighbouring plaquettes. The state in figure 7.3(a) consists of one localised electron while the other is delocalised around the edge of the plaquette. Both electrons are delocalised in the state in figure 7.3(b).



Figure 7.2: Band structure of triplet dimers on the square lattice for $V_1 = V_2$, with (a) t' = 0, (b) t' = t/4, (c) $t' = t/\sqrt{2}$ and (d) t' = t, and of singlet dimers with (e) t' = 0 and (f) t' = t.

7.2 Feasibility of a Dimer-Based Ground State

We seek to identify regions in parameter space, with arbitrary V_1 and V_2 , in which dimers are favoured over single electrons and larger clusters. The dimer ground state is always a singlet, of energy

$$E_{s,1} = \frac{V_1 + V_2}{2} - 2t' - \frac{\sqrt{(V_2 - V_1 + 4t')^2 + 64t^2}}{2},$$
(7.1)

so we only consider singlet dimers in the following. The ground state energy of a single electron is $E_e(\mathbf{0}) = -4t - 4t'$. The trimer, which has kinetic energy but is confined to the square unit cell, has ground state energy $E = 2V_1 + V_2 - 2t - t'$. The tetramer is immobile and has energy $E = 4V_1 + 2V_2$. A large repulsive third-neighbour potential V_3 is assumed to prevent larger clusters from forming. The phase diagram in figure 7.4 indicates the regions in parameter space in which each entity is favoured in the case



Figure 7.3: Localised triplet eigenstates in the square lattice for $t' = t/\sqrt{2}$ and $V_1 = V_2$ where dimensions have maximum length $L = \sqrt{2}a$. The states have energy (a) $E = -2\sqrt{2}t$ and (b) $E = 2\sqrt{2}t$ where we have taken $V_1 = V_2 = 0$.

t' = t. With both potentials repulsive single electrons are favoured while with both potentials attractive tetramers are favoured. Singlet dimers are favoured with attractive V_1 and repulsive V_2 in the top left corner of the diagram. Dimers are also favoured in the bottom right corner with repulsive V_1 and attractive V_2 , however these dimers have a larger weight on next-nearest-neighbour sites and will propagate by crawler motion and therefore have a large effective mass. Trimers do not appear in the diagram. Figure 7.5 shows how the energy per electron varies with V_2 for electrons, singlet dimers, trimers and tetramers in their ground states on the square lattice with t' = t = 1 and $V_1 = -12$. The ground state consists of dimers with $V_2 \ge 7$.

Figure 7.6 shows the singlet dimer band structure for the parameter values t' = t, $V_1 = -12$ and $V_2 = 7$ corresponding to the upper triple point in figure 7.4. The two lower bands (centered around V_1 in energy) are highly dispersive around the ground state point k = 0 because dimers consisting of electrons on nearest-neighbour sites can propagate by crab-like motion with next-nearest-neighbour hopping without virtual transitions into higher energy sectors. The large dispersion disappears moving away



Figure 7.4: Phase diagram of the square lattice with nearest-neighbour and next-nearest-neighbour potentials V_1 and V_2 respectively with t' = t = 1. We assume large next-next-nearest neighbour repulsion V_3 so that larger clusters do not form. Diagram indicates regions in which the ground state consists of single electrons, singlet dimers and tetramers. Trimers and triplet dimers do not appear in the phase diagram.

from k = 0 (see figure 7.6) because next-nearest-neighbour hopping cancels along the Brillouin zone edges. The small dispersion along the edges is due to crawler motion only. The two upper bands (centered around V_2 in energy) are almost flat and completely flat respectively as they are dominated by the diagonal dimer configurations, which can only propagate by crawler motion. In contrast, the dimer region with $V_2 < V_1$ in the bottom right of figure 7.4 corresponds to diagonal dimers of large mass.

7.3 Effective Mass

From the electron dispersion we obtain the single electron effective mass

$$m_e^* = \frac{\hbar^2}{2ta^2 + 4t'a^2} \tag{7.2}$$


Figure 7.5: Energy per electron as a function of V_2 for electrons, singlet dimers, trimers and tetramers in their respective ground states on the square lattice, taking t' = t = 1 and $V_1 = -12$.

so that for t' = t

$$m_e^* = \frac{\hbar^2}{6ta^2} \tag{7.3}$$

For singlet dimers with t' = t, $V_1 = -12t$ and $V_2 = 7t$, we find a mass $m_s^* = 5.2 \times m_e^*$ in the lowest band. With $V_2 = \infty$ crawler motion is disabled so that the band structure becomes

$$E_s(\mathbf{k}) = \pm 4t' \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \tag{7.4}$$

and $m_s^* = \left(\frac{2t}{t'} + 4\right) m_e^*$ so that for t' = t we obtain $m_s^* = 6m_e^*$, indicating that crawler motion results in a small perturbative reduction in m_s^* if $|V_1 - V_2| \gg t$. As $t' \to 0$ the effective mass of the single electron remains low, due to nearest neighbour hopping, while the dimer-effective mass becomes large, due to vanishing crab-like motion.



Figure 7.6: Band structure of singlet dimers on the square lattice with $V_1 = -12$, $V_2 = 7$ and t' = t = 1 where $\Gamma = (0,0)$, $X = (\pi,0)$ and $M = (\pi,\pi)$.

Chapter 8

The Perovskite Layer

8.1 Introduction

We consider the perovskite layer with nearest and next-nearest-neighbour hopping tand t' respectively, nearest-neighbour in-plane and out-of plane interactions V_1 and V_2 respectively and next-nearest-neighbour interaction V_3 (see figure 8.1). We assume that



Figure 8.1: Perovskite layer with nearest and next-nearest-neighbour hopping t and t' respectively.

 $a_{in} = a_{out} = a$ where a_{in} and a_{out} are the in-plane and out-of-plane lattice parameters

respectively. We take the onsite Hubbard $U = \infty$. We assume a large repulsive V_3 and truncate the Hilbert space accordingly to include nearest-neighbour bonds only. Dimers then have fixed length L = a and propagate by in-plane and out-of-plane crab-like motion and additionally hop between in-plane and out-of-plane bonds; this is crawler motion if $V_1 \neq V_2$, otherwise it also crab-like motion. Trimers have sides of fixed length L = a and also hop by crab-like motion but are confined within a unit cell. Trimer exchange paths vanish so that the band structure for the spin S = 1/2 trimer is as for the S = 3/2 trimer. The trimer problem is then reduced from that of a 48×48 matrix to that of a 4×4 matrix. Energies obtained for the truncated Hilbert space should be a good approximation to those for smaller V_3 and a less restricted Hilbert space, since further crawler motion only perturbs the band structure slightly as seen previously.

8.2 Feasibility of a Dimer-Based Ground State

For single electrons with k = 0 we obtain the ground state energy

$$E_e = -4t' - 2t - 2\sqrt{5}t \tag{8.1}$$

Solving a 12×12 matrix and taking k = 0 we obtain the dimer ground-state energy

$$E_{d} = -t - 3t' + \frac{1}{2}V_{1} + \frac{1}{2}V_{2} - \frac{1}{2}\sqrt{4(tV_{1} - tV_{2} - t'V_{1} + t'V_{2}) + 36t^{2} + 4t'^{2} - 8tt' + V_{1}^{2} + V_{2}^{2} - 2V_{1}V_{2}}$$

$$(8.2)$$

The ground state for dimers is a singlet state. For trimers we obtain the ground state energy

$$E_t = -2t' + V_1 + 2V_2 \tag{8.3}$$

Using eqns (8.1), (8.2) and (8.3) we obtain the phase diagram in figure 8.2 where we have taken t' = t/2 = 1/2. The diagrams are qualitatively the same for all t/t'.



Figure 8.2: Phase diagram indicating regions in which electrons, dimers and trimers form a ground state on the perovskite layer where we have taken t' = t/2 = 1/2.

With repulsive V_1 and V_2 single electrons form the ground state as expected and with attractive V_1 and V_2 trimers are largely favoured as expected. Dimers, consisting largely of in-plane bonds with energy V_1 , are favoured in the top left corner with attractive V_1 and repulsive V_2 . Dimers consisting largely of out-of-plane bonds with energy V_2 are favoured in the bottom right corner, with repulsive V_1 and attractive V_2 .

8.3 Effective Mass

Since dimers are weighted mostly in-plane or out-of-plane in regions where they are favoured we can obtain an approximate effective mass for each region by neglecting the in-plane or out-of-plane (whichever is the minor) component in each case. In this approximation the mostly-in-plane-dimer problem is reduced to that of dimers of fixed length L = a on a square lattice with next-nearest-neighbour hopping (i.e. crab-like motion only). In this case there are just two dimer configurations per unit cell. We obtain the band structure

$$E_d(\mathbf{k}) = \pm 4t' \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \tag{8.4}$$

and the effective mass

$$m_d^* = \frac{\hbar^2}{t'a^2} \tag{8.5}$$

The mostly-out-of-plane-dimer problem is reduced to that of dimers which hop between the out-of-plane bonds on a plane of corner-sharing pyramids by crab-like motion. In this case there are four dimer configurations $|A\rangle$, $|B\rangle$, $|C\rangle$ and $|D\rangle$ per unit cell (see figure 8.3). Taking t' = t and $V_1 = 0$ we obtain the band structure (see figure ??)



Figure 8.3: Basis states for out-of-plane dimers on a plane of corner-sharing pyramids.

$$E_1(\mathbf{k}) = 2t \tag{8.6}$$

$$E_2(\mathbf{k}) = 0 \tag{8.7}$$

$$E_3(\mathbf{k}) = -t + t\sqrt{5 + 2\cos(k_x a) + 2\cos(k_y a)}$$
(8.8)

$$E_4(\mathbf{k}) = -t - t\sqrt{5 + 2\cos(k_x a)} + 2\cos(k_y a)$$
(8.9)



Figure 8.4: Band structure for dimers on a plane of corner-sharing pyramids with t' = t = a = 1and $V_1 = 0$.

and the effective mass

$$m_d^* = \frac{3\hbar^2}{2ta^2}$$
(8.10)

As $t' \to 0$ dimers become confined to a unit cell and $m_d^* \to \infty$. We conclude that dimers are favoured on the perovskite layer for $V_2 >> V_1$ (weighted mostly in-plane) and for $V_1 >> V_2$ (weighted mostly out-of-plane) and in each case effective mass is low if $t' \gg 0$.

8.4 Summary

We have investigated the possibility of a ground state consisting of mobile dimers on square and triangular lattices and the perovskite layer. Such a ground state would require an effective attraction between electrons and an effective repulsion between dimers. Various mechanisms could lead to an effective attraction which, in combination with the Coulomb repulsion, could lead to pairing without forming larger clusters. We applied the UV model, which is not specific to the pairing mechanism but can be obtained from the strong-coupling Fröhlich-Coulomb model. We obtained ground state energies for single electrons, dimers, trimers and larger clusters for each lattice in Hilbert spaces truncated to the low-energy sector. Comparing these energies over the parameter space we found no parameter regions in which dimers form a ground state on the triangular lattice. This is because in the low-density limit the geometry of the triangular lattice always favours trimers over dimers where an effective attraction exists, unless t is relatively large in which case electrons will be favoured. Despite this finding it might be possible to obtain a mixture of dimers and single polarons away from the low-density limit on the triangular lattice when many-body effects are taken into account [35, 36]. If the number of states below the Fermi level in the polaron band is less than the number of electrons, bipolarons remain stable mobile quasi-particles because the Pauli exclusion principle prevents their decay into single polarons.

For the square lattice with nearest and next nearest neighbour hopping we found a substantial region in which dimers form a ground state, with nearest-neighbour attraction and next-nearest-neighbour repulsion. These dimers can be very light due to a crab-like propagation. With t' = t the dimer-effective mass is no more than six times the single-electron mass in the same lattice.

For the perovskite layer, with nearest and next-nearest-neighbour hopping we found a substantial region in which dimers, weighted mostly in-plane or mostly out-of-plane, form a ground state. The mostly in-plane dimers can be approximated by dimers confined to a square lattice while the mostly-out-of-plane dimers can be approximated by dimers which hop between the out-of-plane bonds on a plane of corner-sharing pyramids. In each case the dimers can be light due to crab-like motion. The results indicate that stable small mobile bipolarons are very sensitive to the lattice structure.

Chapter 9

Graphene and Dirac points

9.1 Electronic Properties of Graphene

Graphene consists of a one-atom-thick sheet of carbon atoms arranged in a honeycomb lattice. There is currently considerable interest in Graphene due to its novel electronic properties [38–43]. In particular its band structure, assuming nearest neighbour hopping t only, consists of two dispersive bands which meet at Dirac points - these are points where the tips of cones formed in each band meet (see figure 9.1). At zero temperature the lower band is filled with electrons while the upper band is empty. The Fermi surface is the horizontal plane containing the Dirac points and separates the two bands. When the temperature increases some of the electrons obtain additional energy and move into the upper band, leaving holes under the Fermi surface. The band structure of graphene has a width of about 20 eV corresponding to a temperature of 200,000 K [42]. Room temperature, at around 300 K, is comparatively small. Consequently the electrons and holes (low energy excitations) remain close to the Fermi surface. The dispersion of electrons



Figure 9.1: Band structure of graphene with t = a = 1. Dirac points appear at the Brillouin zone corners.

and holes is linear in these regions. The Hamiltonian is given by a 2×2 matrix

$$\mathbf{H} = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} = \hbar v_F \sigma. \mathbf{k}$$
(9.1)

where σ is the 2D Pauli matrix and V_F is the Fermi velocity (the single constant characterising electrons in graphene), whose value is about 300 times smaller than that of light [42]. The Dirac points, and hence electronic properties of graphene are a direct consequence of graphene's crystal symmetry. Its honeycomb lattice is bipartite, being made up of two equivalent sublattices A and B (see figure 9.2). Cosine-like energy bands associated with the sublattices intersect at the Fermi energy near the edges of the Brillouin zone, giving rise to conical sections of the energy spectrum for |E| < 1eV[43]. It is easy to see how this happens by considering the simple one-dimensional bipartite lattice in figure 9.3, where the integer n is the index of the unit cell and we allow nearest-neighbour hopping t only. If all points in the lattice were equivalent we would obtain the single band of energy $E(\mathbf{k}) = -2t \cos{(ka)}$. However by artificially making the lattice bipartite, as shown in figure 9.3, we obtain the band structure $E(\mathbf{k}) = \pm 2t \cos{(ka)}$ (see figure 9.4). We see that the energy is split into two cosine-like bands which cross with linear dispersion close to the crossing points. The graphene



Figure 9.2: The graphene lattice consists of two sublattices A and B, represented by open and filled circles respectively. The unit cell (dashed) contains two basis states, $|A\rangle$ and $|B\rangle$.



Figure 9.3: Simple one-dimensional bipartite lattice.



Figure 9.4: Band structure of the one-dimensional bipartite lattice shown in figure 9.3.

wave function has a two-component structure (spinor)

$$\psi(\mathbf{r}, \mathbf{t}) = \begin{pmatrix} A(\mathbf{r}, t) \\ B(\mathbf{r}, t) \end{pmatrix}$$
(9.2)

where $|A\rangle$ and $|B\rangle$ represent the electronic wave function in the two equivalent sublattices of the honeycomb lattice. For single electrons on the graphene lattice we obtain the hopping matrix

$$\mathbf{H} = \begin{pmatrix} 0 & -t\left(1 + e^{i(-X+Y)} + e^{i(-X-Y)}\right) \\ -t\left(1 + e^{i(X-Y)} + e^{i(X+Y)}\right) & 0 \end{pmatrix}$$
(9.3)

where $X = \frac{3}{2}k_x a$ and $Y = \frac{\sqrt{3}}{2}k_y a$ and a is the lattice parameter. From (9.3) we obtain the band structure

$$E(\mathbf{k}) = \pm t \sqrt{3 + \cos\left(\frac{3k_x a}{2} + \frac{\sqrt{3}k_y a}{2}\right) + \cos\left(\frac{3k_x a}{2} - \frac{\sqrt{3}k_y a}{2}\right) + \cos\left(\sqrt{3}k_y a\right)} \quad (9.4)$$

9.2 Dimer Lattice of Graphene

We note that dimers of fixed length L = a can propagate on the graphene lattice if next nearest neighbour hopping is allowed. In this case the dimer lattice of graphene is the kagome lattice, which is also the dimer lattice of the triangular lattice (for dimers of fixed length L = a with nearest neighbour hopping). The triangular and graphene lattices share the same dimer lattice for the following reason: If we fix the position of one of the electrons in a triangular-lattice dimer, the mid-point of the dimer is confined to a hexagonal plaquette which has the fixed electron at its centre. If we then fix the position of the second electron and allow the first electron to hop to other sites the mid-point of the dimer is confined to another hexagonal plaquette. These neighbouring hexagonal plaquettes form a kagome lattice. If we fix the position of an electron in a graphene-lattice dimer, the mid-point of the dimer is confined to a triangular plaquette rather than a hexagonal plaquette. Since the kagome lattice can be assembled from triangular or hexagonal plaquettes, the dimer lattice of graphene is also a kagome lattice.

9.3 Graphene Bilayer

An important property of the graphene bilayer is that only points in one of the sublattices of the upper layer has nearest neighbours in the lower layer (see figure 9.5) [42]. The Hamiltonian for each layer in isolation is the 2×2 matrix of equation 9.3. The Hamiltonian for the bilayer is obtained by coupling the two matrices with interlayer



Figure 9.5: Graphene bilayer; lower layer is indicated in grey. Upper layer shows sublattices A (open circles) and B (filled circles).

terms so that we obtain a 4×4 matrix. We take the nearest neighbour interlayer hopping equal to the nearest neighbour in-plane hopping t. Diagonalising the matrix we obtain the band structure

$$E(\mathbf{k}) = \frac{\pm t \pm t\sqrt{13 + 8\cos(X) + 8\cos(Y) + 8\cos(Z)}}{2}$$
(9.5)

where $X = \left(\frac{3k_xa}{2} + \frac{\sqrt{3}k_ya}{2}\right)$, $Y = \left(\frac{3k_xa}{2} - \frac{\sqrt{3}k_ya}{2}\right)$ and $Z = \left(\sqrt{3}k_ya\right)$. In this case two

of the bands form touching paraboloids rather than Dirac points (see figure 9.6)[42]. We conclude that Dirac points, and hence the novel electronic properties of graphene do not persist for the graphene bilayer. However Dirac points can occur in multilayer graphene if the number of layers is odd depending on the stacking order [38].

9.4 Origin of Dirac Points

The electronic properties of graphene are due to the intersection of cosine-like bands associated with its sublattices. The Dirac points observed for the kagome lattice can



Figure 9.6: (a) Band structure of the graphene bilayer with t = a = 1. (b) Two of the bands form touching paraboloids.

also be explained in this way. However in this case there are three sublattices, with all hopping being from one sublattice to another, hence the kagome lattice is a tripartite lattice. The above observations suggest that Dirac points may be found for other bipartite (or tripartate) lattices. For each of the bipartite lattices that follow, Dirac points are observed. We therefore speculate that a bipartite (or tripartate) lattice is a necessary condition for the appearance of Dirac points. Each of the following bipartite lattices is constructed by taking a simple lattice, such as the square or triangular lattice, and then inserting an additional lattice point midway between nearest-neighbour points in the original lattice. We then restrict hopping to nearest-neighbour hopping t in the new lattice.

9.5 Square Lattice Singlets

Figure 9.7(a) shows the unit cell of a square lattice which has been modified, as described above, to form a bipartite lattice (the resulting lattice is equivalent to the singlet dimer lattice of the square lattice for dimers of maximum length L = a, nearest neighbour hopping integral t and U = V where U is the on-site interaction and V is the nearestneighbour interaction). Taking U = V = 0 we obtain the hopping matrix



Figure 9.7: (a) Unit cell of the dimer lattice for singlets on a square lattice. Open and filled circles, representing onsite dimers and nearest-neighbour dimers respectively, serve to differentiate the sublattices. (b) Localised eigenstate corresponding to the flat band with energy E = 0.

$$\mathbf{H} = \begin{pmatrix} 0 & -t\left(1 + e^{-ik_{x}a}\right) & -t\left(1 + e^{-ik_{y}a}\right) \\ -t\left(1 + e^{ik_{x}a}\right) & 0 & 0 \\ -t\left(1 + e^{ik_{y}a}\right) & 0 & 0 \end{pmatrix}$$
(9.6)

and the band structure

$$E(\mathbf{k}) = \pm t \sqrt{4 + 2\cos(k_x a) + 2\cos(k_y a)}$$
(9.7)

$$E = 0 \tag{9.8}$$

The localised eigenstate corresponding to the flat band (9.8) is indicated in figure 9.7(b) and the band structure is indicated in figure 9.8. Note the appearance of Dirac points as predicted.



Figure 9.8: Band structure for singlets on a square lattice with t = a = 1 and U = V = 0.

9.6 Cubic Lattice Singlets

The above dimer lattice can be extended to three dimensions, i.e. singlets on a cubic lattice with U = V, maximum dimer length L = a and nearest neighbour hopping integral t (the unit cell is the three-dimensional analogue of figure 9.7(a)). In this case the band structure contains three-dimensional Dirac points. Taking U = V = 0 we obtain the hopping matrix

$$\mathbf{H} = \begin{pmatrix} 0 & -t\left(1+e^{-ik_{x}a}\right) & -t\left(1+e^{-ik_{y}a}\right) & -t\left(1+e^{-ik_{z}a}\right) \\ -t\left(1+e^{ik_{x}a}\right) & 0 & 0 & 0 \\ -t\left(1+e^{ik_{y}a}\right) & 0 & 0 & 0 \\ -t\left(1+e^{ik_{z}a}\right) & 0 & 0 & 0 \end{pmatrix}$$
(9.9)

and the band structure

$$E(\mathbf{k}) = \pm t \sqrt{6 + 2\cos(k_x a) + 2\cos(k_y a) + 2\cos(k_z a)}$$
(9.10)

$$E = 0 \tag{9.11}$$

where the flat-band solution (9.11) is doubly degenerate. A cross-section of the band structure with $k_z = \pm \pi/a$ is exactly the band structure of the two-dimensional lattice (see figure 9.8). Equivalent cross-sections are obtained for $k_x = \pm \pi/a$ and $k_y = \pm \pi/a$. The Dirac point coordinates are $\mathbf{k} = (\pm \pi/a, \pm \pi/a, \pm \pi/a)$.

9.7 Modified Triangular Lattice

We also find Dirac points for the modified triangular lattice whose unit cell is shown in figure 9.9(a). We obtain the hopping matrix

$$\mathbf{H} = \begin{pmatrix} 0 & -t\alpha & -t\beta & -t\gamma \\ -t\alpha^* & 0 & 0 & 0 \\ -t\beta^* & 0 & 0 & 0 \\ -t\gamma^* & 0 & 0 & 0 \end{pmatrix}$$
(9.12)

where

$$\alpha = \left(1 + e^{-ik_x a}\right)$$

$$\beta = \left(1 + e^{-i\left(\frac{k_x a}{2} + \frac{\sqrt{3}k_y a}{2}\right)}\right)$$
$$\gamma = \left(e^{-ik_x a} + e^{-i\left(\frac{k_x a}{2} - \frac{\sqrt{3}k_y a}{2}\right)}\right)$$

From (9.12) we obtain the band structure

$$E(\mathbf{k}) = \pm t \sqrt{6 + 2\cos(k_x a) + 4\cos\left(\frac{k_x a}{2} + \frac{\sqrt{3}k_y a}{2}\right)}$$
(9.13)

$$E = 0 \tag{9.14}$$

where solution (9.14) is doubly degenerate and the corresponding localised eigenstates are indicated in figures 9.9(b) and 9.9(c). The band structure is shown in figure (9.10).



Figure 9.9: (a) Unit cell of the modified triangular lattice. (b) and (c) Localised eigenstates in the modified triangular lattice.

9.8 Conclusions

We conclude that the electronic properties of graphene are a direct consequence of graphene's crystal symmetry. Its honeycomb lattice is bipartite and cosine-like energy bands associated with the sublattices intersect at the Fermi energy, giving rise to Dirac



Figure 9.10: Band structure of the modified triangular lattice in figure 9.9(a) with t = a = 1.

points. It is easy to see how this happens by considering a one dimensional bipartite lattice. The band structure of the kagome lattice also exhibits Dirac points which are similarly explained in terms of its three sub-lattices. From these observations we have speculated that a bipartite (or tripartite) lattice is necessary for the appearance of Dirac points. We have investigated several other bipartite lattices and found Dirac points in each case thereby supporting our hypothesis. Our investigation has also revealed that three-dimensional Dirac points appear for the singlet dimer lattice of the cubic lattice under certain circumstances. For the graphene bilayer we find that two of the bands form touching paraboloids; from this we conclude that the novel effects in graphene do not persist for bilayer graphene. However Dirac points do occur in multilayer graphene depending on whether the number of layers is even or odd, and what the stacking order is [38].

Chapter 10

Strictly Localised Triplet Dimers

10.1 Introduction

The effective mass of electrons and dimers is related to the dispersion of the bands in the associated band structure. As bands become flatter effective mass becomes larger. For bands which are flat effective mass is infinite, implying that the electron, or dimer, is localised. Localisation can occur because virtual transitions are required for hopping. For example nearest-neighbour dimers on the square lattice (with nearest neighbour hopping only) are immobile, and hence localised, unless they can adjust their lengths. Localisation can also be due to interference, as is the case for the singlet and triplet flat bands that occur for nearest-neighbour dimers in the triangular lattice when nearest neighbour hopping only is allowed (see figure 6.2 for localised eigenstates). Flat bands also occur for square lattice dimers of maximum length $L = \sqrt{2}a$, with nearest and next-nearest neighbour hopping t and t' respectively, and nearest and next-nearest neighbour interactions V_1 and V_2 respectively. In this case two triplet flat bands appear for specific t/t' and V_1/V_2 (see figure 7.3 for localised eigenstates). A singlet flat band also appears for arbitrary t/t' and a second for t' = 0 if $V_1 = V_2$ in each case.

10.2 The Square Ladder

In this chapter we show that triplet band structures can be obtained in which all bands are flat for one- and two-dimensional lattices for specific t/t', implying that in these cases triplets are strictly localised [44]. This was an unexpected finding which does not help with our search for highly mobile dimers, but is sufficiently surprising to warrant further investigation. We begin with the square ladder with the Hilbert space truncated to include bonds of length L = a and $L = \sqrt{2}a$ and set the nearest- and next-nearest-neighbour interactions $V_1 = V_2 = 0$. The simplest basis that describes this situation consists of five basis states, as indicated in figure 10.1, where n is the index of the unit cell. Triplets acquire a sign change when hopping along the paths $|A, n\rangle \rightarrow |C, n\rangle \rightarrow - |A, n + 1\rangle$ and $|A, n\rangle \rightarrow |E, n\rangle \rightarrow - |A, n + 1\rangle$ (direction of arrow reversed). Applying the Hamiltonian (2.26) we obtain the triplet hopping matrix



Figure 10.1: Triplet basis states in the square ladder where dimers are restricted to length L = aand $L = \sqrt{2a}$. Singlet basis states are as for triplets except that the arrows are double-headed.

$$\mathbf{H} = \begin{pmatrix} 0 & -t - te^{-ika} & -t' + t'e^{-ika} & t + te^{-ika} & -t' + t'e^{-ika} \\ -t - te^{ika} & 0 & -t & 0 & t \\ -t' + t'e^{ika} & -t & 0 & -t & 0 \\ t + te^{ika} & 0 & -t & 0 & t \\ -t' + t'e^{ika} & t & 0 & t & 0 \end{pmatrix}$$
(10.1)

and the triplet solutions

$$E = \pm 2t \tag{10.2}$$

$$E = 0 \tag{10.3}$$

$$E(\mathbf{k}) = \pm \sqrt{8t^2 \cos^2\left(\frac{ka}{2}\right) + 8t'^2 \sin^2\left(\frac{ka}{2}\right)}$$
(10.4)

Note that in general there are three flat bands and two dispersive bands for triplets. For t' = t all triplet bands are flat with the energies $E = 0, \pm 2t, \pm 2\sqrt{2}$ implying that for t' = t all triplet eigenstates of the square ladder are strictly localised. To see why this happens consider a simplified case in which we include only the states $|A, n\rangle$, $|B, n\rangle$ and $|C, n\rangle$, as indicated in figure 10.2(a). The points $|A, n\rangle$ in the dimer lattice are bottlenecks (see figure 10.2(b)), meaning that a dimer propagating along the ladder must repeatedly pass through these points. Any path from $|A, n\rangle$ to a neighbouring bottleneck $|A, n \pm 1\rangle$ can be replaced by a path of opposite sign (and equal magnitude if t' = t) by replacing $|B, n\rangle$ with $|C, n\rangle$ and $|C, n\rangle \rightarrow -|A, n + 1\rangle$. Since each path can be replaced by another path of opposite sign, and equal magnitude if t' = t, the paths cancel each other for t' = t and triplet dimers become strictly localised. The same argument can be extended to include the states $|D, n\rangle$ and $|E, n\rangle$. In this case replacing $|B, n\rangle$ with $|C, n\rangle$, $|C, n\rangle$ with $|B, n\rangle$, $|D, n\rangle$ with $|E, n\rangle$ and $|E, n\rangle$ with $|D, n\rangle$ transforms each path that goes from $|A, n\rangle$ to $|A, n \pm 1\rangle$ into a path



Figure 10.2: (a) Unit cell of the square ladder where only the triplet states $|A, n\rangle$, $|B, n\rangle$ and $|C, n\rangle$ are included and (b) the unit cell of the corresponding triplet dimer lattice.

of opposite sign, and of the same magnitude if t' = t. Figure 10.3 shows the unit cell of the dimer lattice for triplets on the square ladder shown in figure 10.1. Adjacent cells are connected by the points $|A, n\rangle$ which form bottlenecks. This structure is also the basic unit of other triplet dimer lattices which have a dispersionless band structure with t' = t, as we will see. Figure 10.4 shows the localised eigenstates corresponding to each of the five triplet flat bands.

For singlets on the square ladder there are two bands which are flat for all t/t' and an additional flat band in each of the limits t = 0, t' = 0 and t' = t. The corresponding localised eigenstates are indicated in figure 10.5. The flat band for t = 0 in figure 10.5(c) is trivial as this consists of diagonal states which are immobile in the absence of nearest neighbour hopping. Each of the other eigenstates are localised due to cancellation effects.



Figure 10.3: Unit cell of the dimer lattice for triplets on a square ladder, as shown in figure 10.1(a). Adjacent cells are connected by the points $|A, n\rangle$ which form bottlenecks.

10.3 The Square Bilayer

Dispersionless triplet band structures can also be obtained in two-dimensional lattices if they contain bottlenecks, which cannot be circumvented, and each path between neighbouring bottlenecks can be replaced by a path of equal magnitude and opposite sign. This is the case in square and honeycomb bilayers if the following restrictions apply: Dimers have maximum length $L_{max} = \sqrt{a^2 + b^2}$, where a and b are the in-plane and out-of-plane lattice parameters respectively. L_{max} is less than the next-nearestneighbour in-plane separation (hence b < a for the square bilayer). Nearest and nextnearest-neighbour inter-plane hopping t and t' are allowed while in-plane hopping is restricted to nearest neighbour hopping t. With these restrictions the inter-plane states of length L = b form bottlenecks (vertical arrows in figure 10.6 for the square bilayer



Figure 10.4: Localised triplet eigenstates in the restricted Hilbert space of the square ladder with energies (a) E = 2t, (b) E = -2t, (c) E = 0, (d) $E = -2\sqrt{2}t$ and (e) $E = 2\sqrt{2}t$. States (a), (b) and (c) are exact eigenstates of the Hamiltonian for all t/t' while (d) and (e) are eigenstates for t' = t.

and figure 10.9 for the honeycomb bilayer). For t' = t each path between neighbouring bottlenecks can be replaced by a path of opposite sign as in figure 10.2(b), hence the triplet band structures will be dispersionless. In bilayers which contain in-plane triangular plaquettes, such as the triangular bilayer, dimers can still propagate in-plane without adjusting their lengths so that bottlenecks do not appear and a dispersionless triplet band structure is not possible. The triplet basis states for the square bilayer are indicated in figure 10.6. The basic unit of the triplet dimer lattice is as for the square ladder (see figure 10.3) but with four of this unit meeting at each point $|A, n\rangle$. With arbitrary t/t' we obtain the triplet flat-band solutions E = -2t, -2t, 2t, 2t, 0, 0, 0 and the dispersive triplet solutions

$$E(\mathbf{k}) = \pm 2\sqrt{2(t^2 + t'^2) + (t^2 - t'^2)(\cos(k_x a) + \cos(k_y a))}$$
(10.5)



Figure 10.5: Localised singlet eigenstates in the restricted Hilbert space of the square ladder. States (a) and (b) are exact eigenstates of the Hamiltonian for all t/t'. Further localised eigenstates appear in the limits (c) t = 0 (trivial as states immobilised), (d) t' = 0 and (e) t' = t. All eigenstates have zero energy except (e) which has energy E = 2t.

For t' = t the solutions (10.5) are also flat-band solutions with energy $E = \pm 4t$. Figure 10.7 indicates the localised triplet eigenstates for the square bilayer. The eigenstates with energy $\pm 4t$ ((e) and (f)) appear for t' = t while all other eigenstates are exact for all t/t'. The amplitudes of the in-plane basis states in (g), (h) and (i) vary as a function of t/t' to ensure cancellation with the diagonal basis states.

For singlets on the square bilayer we find that there are six flat bands for all t/t' with the energies E = -2t, 2t, 0, 0, 0, 0 and an additional flat band in each of the limits t' = t, t' = 0 and t = 0 with the respective energies E = 2t, 0, 0 (see figure 10.8 for localised eigenstates).



Figure 10.6: Triplet basis for the square bilayer with nearest and next nearest neighbour hopping t and t' respectively. With maximum dimer length $L = \sqrt{a^2 + b^2}$, b < a and in-plane hopping restricted to nearest neighbour hopping, the interplane states of length L = b (vertical arrows) form bottlenecks.

10.4 The Honeycomb Bilayer

We distinguish between the differing structures of the honeycomb and graphene bilayers. A dispersionless triplet band structure is not possible for the graphene bilayer as equivalent points in the upper and lower layer are displaced horizontally with respect to each other. Applying the same restrictions as in the square bilayer there are fourteen triplet basis states per unit cell of the honeycomb bilayer (see figure 10.9). The basic unit of the triplet dimer lattice is as for the square ladder and square bilayer (see figure 10.3), but with three of this unit meeting at each point $|A, n\rangle$. With t' = t the triplet band structure is dispersionless and we obtain the degenerate triplet energies E = 0 (×4), E = -2t (×3), E = 2t (×3), $E = -2\sqrt{3}t$ (×2) and $E = 2\sqrt{3}t$ (×2). In each bilayer the bands which are flat for all t/t' each have energy E = 0 or $E = \pm 2t$. This similarity reflects the fact that the structure of the bilayers, with the applied restrictions, is essentially the same. Each is composed of bottlenecks connected by square ladder sections, but with a differing number of square ladder sections meeting at each



Figure 10.7: Localised triplet eigenstates in the square bilayer with energies (a) E = -2t, (b) E = 2t, (c) E = -2t, (d) E = 2t, (e) E = -4t, (f) E = 4t, (g) E = 0, (h) E = 0 and (i) E = 0. Eigenstates are exact for all t/t' except (e) and (f) which appear when t' = t.

bottleneck. The result is that the localised eigenstates in the bilayers are essentially the same (even though the number of localised eigenstates is different). However the two highest and two lowest bands are dispersive for $t' \neq t$ in the honeycomb bilayer, whereas only the highest and lowest bands are dispersive for $t' \neq t$ in the square bilayer (see figure 10.10). This is because two sets of localised eigenstates analogous to those in figure 10.7(e) and 10.7(f) for the square bilayer, which only exist for t' = t, appear in the honeycomb bilayer due to the large unit cell (see figure 10.11).



Figure 10.8: Localised singlet eigenstates in the square bilayer. States (a) to (f) are exact eigenstates of the Hamiltonian for all t/t' with respective energies E = 0, 0, 0, 0, -2t, 2t. Additional localised eigenstates (g), (h) and (i) appear in the respective limits t = 0 (trivial as diagonal states immobilised), t' = 0 and t' = t with respective energies E = 0, 0, 2t.

10.5 Three-Dimensional Structures

We have shown that a dispersionless triplet band structure is also possible for a threedimensional lattice constructed in the following way: begin with a plane of parallel square ladders (with rungs at right angles to the plane) and then stack identical planes to produce a three-dimensional array of parallel square ladders. Then connect square ladders in neighbouring planes using sloping square ladder sections. Dimers can then propagate in three dimensions. As before, a number of hopping and bond-length restrictions must apply so that dimers cannot propagate without passing through bottlenecks in the ladders. With t' = t all triplet bands are flat and with $t' \neq t$ four of the triplet



Figure 10.9: Triplet basis for the honeycomb bilayer with maximum dimer length $L_{max} = \sqrt{a^2 + b^2}$ where L_{max} is less than the in-plane next-nearest-neighbour separation. With in-plane hopping restricted to nearest neighbour hopping the inter-plane states of length L = b (vertical arrows) form bottlenecks.

bands are dispersive.

10.6 The Simple Cubic Lattice

We also note the existence of localised eigenstates in three-dimensional lattices beginning with the simple cubic lattice. In this case we consider dimers with respective nearest and next nearest neighbour hopping integrals t and t' and truncate the Hilbert space to include bonds of length L = a and $L = \sqrt{2}a$. We set the nearest and next nearest neighbour interactions $V_1 = V_2 = 0$. For triplets we find that there are three flat bands with zero energy for all t/t'. The corresponding eigenstates are indicated in figure 10.12. By symmetry each of these states implies the existence of the other two, hence the number of degenerate flat bands is three. An additional flat band appears for t' = t/2 with energy E = -4t. The corresponding eigenstate, indicated in figure 10.13, consists of one localised electron and another delocalised around a cube. For singlets on the simple cubic lattice we again find that there are three flat bands with



Figure 10.10: Triplet band structure with t = a = 1 and t' = 1/2 for (a) the square bilayer and (b) the honeycomb bilayer. The band structures are similar due to the the bilayer structures being essentially the same, but with a differing number of square ladder sections meeting at the ends of each section.

zero energy. The corresponding eigenstates look similar to the triplet states in figure 10.12 (see figure 10.14) and again, by symmetry, each state implies the existence of the other two.

10.7 The Body Centred Cubic Lattice

We now consider the body centred cubic lattice, with nearest and next-nearest-neighbour hopping t and t' respectively with dimer lengths restricted to L = a (corner to corner of cubic cell) and $L = \frac{\sqrt{3}a}{2}$ (corner to centre of cell) where a is the lattice parameter. We set the nearest and next nearest neighbour interactions $V_1 = V_2 = 0$. For arbitrary t/t'there is one triplet flat band with energy E = -3t'. The localised eigenstate consists of one localised electron while the other is delocalised around a cube (see figure 10.15). The delocalised electron hops between next-nearest-neighbour sites, hence the energy E = -3t'. With t' = 0 there are five flat bands with energy E = 0 for singlets and



Figure 10.11: Localised triplet eigenstates in the honeycomb bilayer with energies (a)-(d) E = 0, (e)-(f) $E = -2\sqrt{3}t$ and (g)-(h) $E = 2\sqrt{3}t$. States (a)-(d) are exact eigenstates of the Hamiltonian for all t/t' while (e)-(h) are eigenstates for t' = t. All localised eigenstates correspond to analogous eigenstates in the square bilayer. Eigenstates with energy $E = \pm 2t$ are omitted as they are essentially the same as for the square bilayer (see figure 10.7 (a)-(d)).

triplets. Next-nearest-neighbour hopping enables crab-like motion and stretching enables crawler motion, so with t' = 0 and dimers restricted to length $L = \frac{\sqrt{3}a}{2}$ all bands are flat with energy E = 0.

10.8 Conclusions

We conclude that triplets are less mobile than singlets on a square ladder and that for t' = t and V' = V, if dimer-lengths are restricted, triplets become strictly localised. This is also true for the square and honeycomb bilayer. A three-dimensional lattice is also possible in which triplet dimers are strictly localised under some circumstances.

We also found that localised eigenstates exist in the simple cubic and body centred cubic lattices under some circumstances. In the simple cubic lattice we found three



Figure 10.12: Localised triplet eigenstates for the simple cubic lattice (states wrap around the cubic cell in each case). States have zero energy and remain eigenstates for all hopping ratios t/t'.

localised singlet and triplet eigenstates for all t/t' (see figures 10.12 and 10.14) and an additional localised triplet eigenstate for t' = t/2 (see figure 10.13). For the body centred cubic lattice we found one localised triplet eigenstate for all t/t' (see figure 10.15).



Figure 10.13: Additional localised triplet eigenstate for the cubic lattice for t' = t/2. One electron is localised while the other is delocalised around a cube.



Figure 10.14: Localised singlet eigenstates for the simple cubic lattice. States have zero energy and remain eigenstates for all hopping ratios $t/t^{'}$.



Figure 10.15: Localised triplet eigenstate for the body centred cubic lattice. One electron is localised while the other, delocalised around a cube, hops between next-nearest-neighbour sites, hence the energy E = -3t'.
Chapter 11

Time Evolution of Wavefunctions

11.1 Introduction

We take the nearest neighbour hopping integral t = 1 in all figures in this section. We begin by introducing the matrix element of the time-dependent Greens function

$$G_{m,n}(\tau) = \langle m | e^{-iH\tau} | n \rangle \tag{11.1}$$

where H is the Hamiltonian of the system, τ is time and m and n are site indices. In general the wave function of a particle initially localised at a site n will spread out with time so that for $\tau > 0$ the wave function will overlap other sites. The square of the overlap of the wave function at site m at time τ , given by $|G_{m,n}(\tau)|^2$, gives the probability of finding the particle on site m at time τ . An initially localised state is obtained by superimposing wave vectors and bands (if there is more than one band). We therefore sum over the Brillouin zone and the band index where we have introduced the band index μ . The matrix element (11.1) becomes

$$G(\tau)_{m,n} = \frac{1}{N} \sum_{k,k',\mu} \langle m|k\rangle \left\langle k|e^{-i\hat{H}\tau}|k'\rangle \left\langle k'|n\rangle\right.$$
(11.2)

where N is the number of sites. Since k takes on a continuum of values we replace the sum in (11.2) with an integral and, assuming a one-dimensional Brillouin zone of length $L = 2\pi$, we replace the prefactor $\frac{1}{N}$ with $\frac{1}{2\pi}$.

$$G(\tau)_{m,n} = \frac{1}{2\pi} \sum_{\mu} \int_{-\pi}^{+\pi} dk \cdot e^{ik(n-m) - iE_{\mu}(k)\tau}$$
(11.3)

In the following calculations we would expect a particle moving randomly on a onedimensional lattice to come back to its starting point infinitely often with a probability equal to one. A particle moving randomly on a two-dimensional lattice is expected to come back to its starting point rarely with probability equal to one. However a particle moving in three dimensions is expected to come back to its starting point with probability less than one.

11.2 Infinite Chain

In the following we look at the case of a single electron on an infinite chain with nearest and next nearest neighbour hopping integrals t and t' respectively. This situation is equivalent to an electron on a staggered ladder where next nearest neighbour hopping on the infinite chain corresponds to nearest neighbour hopping along the legs of the ladder, as discussed in chapter 5 (see figure 5.1). We obtain the band structure

$$E(\mathbf{k}) = -2t\cos\left(ka\right) - 2t'\cos\left(2ka\right) \tag{11.4}$$

where a is the lattice parameter. We begin by looking at the probability of finding an initially localised electron on the initial site n = 0 at time τ . In the case t' = 0 the function $G(\tau)$ is a Bessel function of the first kind. Figure 11.1 shows a comparison of the probability $P(\tau) = |G(\tau)|^2$ of finding the electron on the initial site, as a function of time, for t' = 0, t' = t/2 and t' = t. Each function takes the form of a decaying oscillation. The probability for t' = 0 drops rapidly to zero and then repeatedly comes back to zero. This is because the imaginary part of the integral in equation (11.3) is zero with t' = 0 for all τ , meaning that whenever the real part of the integral is zero the modulus is also zero. The probability for t' = t/2 oscillates more rapidly, and never reaches zero, since the real and imaginary parts of the integral in equation (11.3) are in general not zero and are never equal to zero at the same time. The probability for t' = t shows a more complicated decaying oscillation because, with t and t' on an equal footing, interference between the hopping terms appears. In the case t' = t/2 interference was not apparent because the function was dominated by one hopping term. In each case the power law for long-time asymptotes is $P(\tau) = 1/\tau$.

Figure 11.2 shows a comparison of the probability $P(\tau)$ of finding an electron initially localised on the site n = 0 on the neighbouring site m = 1 at time τ for t' = 0, t' = t/2and t' = t. Each function is equal to zero at $\tau = 0$ and again each function shows a decaying oscillation with $P(\tau)$ oscillating more rapidly for t' = t/2 than for t' = 0. As before $P(\tau)$ repeatedly comes back to zero for t' = 0 but never reaches zero for t' = t/2. Again $P(\tau)$ is not a simple decaying oscillation for t' = t because with t and t' on an equal footing interference effects appear. In the case t' = t/2 interference was not apparent as the function was dominated by one hopping term.



Figure 11.1: Probability $P(\tau)$ of finding an electron on the initial site on an infinite chain as a function of time for different ratios t/t'.

11.3 Staggered Ladder Dimers

We now consider dimers on a staggered ladder with hopping integrals t and t' corresponding to nearest neighbour hopping across legs and along legs respectively. The simplest basis that describes this situation contains two basis states, which we call $|A\rangle$ and $|B\rangle$, corresponding to the electrons in the dimer being on opposite legs and on the same leg of the ladder respectively (see figure 5.3(a)). We obtain the singlet hopping matrix

$$\mathbf{H} = \begin{pmatrix} -t'e^{-ika} - t'e^{ika} & -t - te^{ika} \\ -t - te^{-ika} & 0 \end{pmatrix}$$
(11.5)

which leads to the singlet solutions

$$E_0(\mathbf{k}) = -t' \cos(ka) - \sqrt{t'^2 \cos^2(ka) + 4t^2 \cos^2\left(\frac{ka}{2}\right)}$$
(11.6)



Figure 11.2: Probability $P(\tau)$ of finding an electron on a site m = 1, neighbouring the initial site, on an infinite chain.

and

$$E_1(\mathbf{k}) = -t' \cos(ka) + \sqrt{t'^2 \cos^2(ka) + 4t^2 \cos^2\left(\frac{ka}{2}\right)}$$
(11.7)

where the subscripts 0 and 1 indicate the lower and upper bands respectively. Solving the secular equations obtained from (11.5) we obtain for the lower band

$$\frac{A_0}{B_0} = \frac{-t \left[\cos \left(ka\right) - i \sin \left(ka\right) + 1\right]}{t' \cos \left(ka\right) - \sqrt{t'^2 \cos^2 \left(ka\right) + 4t^2 \cos^2 \left(\frac{ka}{2}\right)}}$$
(11.8)

and for the upper band

$$\frac{A_1}{B_1} = \frac{-t \left[\cos \left(ka\right) - i \sin \left(ka\right) + 1\right]}{t' \cos \left(ka\right) + \sqrt{t'^2 \cos^2 \left(ka\right) + 4t^2 \cos^2 \left(\frac{ka}{2}\right)}}$$
(11.9)

Equation (11.9) differs from equation (11.8) only in the sign of the square root term in the denominator. The bands can now be superimposed such that either $A = A_0 + A_1 = 0$ or $B = B_0 + B_1 = 0$ in the superposition state corresponding to a localised dimer having its electrons both on the same leg or on opposite legs of the staggered ladder respectively. Taking n = m = 0 the matrix element of the Green's function becomes

$$G(\tau)_{(0,0)} = \frac{1}{2\pi} \int_0^{2\pi} dk \left(\frac{1}{A_0 + A_1} A_0 e^{iE_0(k)\tau} + \frac{1}{A_0 + A_1} A_1 e^{iE_1(k)\tau} \right)$$
(11.10)

where we have superimposed the bands such that B = 0 (electrons on opposite legs of the ladder). We have included the factor $\frac{1}{A_0+A_1}$ in order to normalise the Green's function. Figure 11.3 shows a comparison of the probability $P(\tau)$ of finding an initially localised dimer with its electrons on their initial sites for initial sites on opposite legs and on the same leg of the staggered ladder respectively. The plots both show decaying



Figure 11.3: Probability $P(\tau)$ of finding an initially localised dimer with its electrons on their initial sites at time τ for initial sites on the same leg and on opposite legs of the staggered ladder respectively, where we have taken t' = t.

oscillations but with a different interference pattern in each plot. Two distinct frequencies can be seen in the plot for electrons on opposite legs. The interference patterns are different because the proportions of ground state and excited state that go into the initially localised state for electrons on the same leg are reversed for electrons on opposite legs. Also the lower band of energy (11.6) has larger bandwidth than the upper band (11.7) and larger bandwidth leads to faster oscillations. Therefore the ground state contribution shows faster oscillations and since it can be the larger or the smaller contribution there are differing interference patterns for each case.

11.4 Including a Flat Band

We saw in chapter 5 that the upper band for singlets on a staggered ladder is flat when $t' = t/\sqrt{2}$ (the localised eigenstate is indicated in figure 5.3(b)). Figure 11.4 shows a plot of the probability $P(\tau)$ to find a dimer with its electrons on their initial sites for initial sites on the same leg and on opposite legs of the ladder with $t = t'/\sqrt{2}$. We see a decaying oscillation in $P(\tau)$ for both cases but they appear to converge on



Figure 11.4: Probability $P(\tau)$ of finding an initially localised dimer with its electrons on their initial sites at time τ , for initial sites on the same leg and on opposite legs of the ladder, where we have taken $t' = \sqrt{2}t$ so that the upper singlet band is flat.

finite values rather than decaying to zero. This is because the dispersive component of

the initially localised state decays to zero as expected, while the flat-band component remains localised for all time, although it does give rise to a non-decaying component of the oscillation due to the electrons in the dimer hopping to other sites and back again inside the localised eigenstate. We see that $P(\tau)$ converges on a greater value for initial sites on opposite legs than on the same leg. Both plots show interference between the decaying and non-decaying oscillations associated with the dispersive and flat band components respectively.

11.5 Dispersionless Band Structure

We saw in chapter 10 that a dispersionless triplet band structure is obtained for the square ladder with t' = t where t and t' are the nearest and next nearest neighbour hopping integrals respectively. By subtracting the localised eigenstate in figure 10.4(e) from that in 10.4(d) we obtain a state localised on a single point on the dimer lattice (only the vertical arrow has non-zero amplitude). Figure 11.5 shows a plot of the probability $P(\tau)$ to find a dimer on the initial site with t' = t. Since the band structure is dispersionless for t' = t both components of the initially localised state are localised for all time. There is therefore no overall decay in $P(\tau)$ for the initial site. However $P(\tau)$ does oscillate between zero and one due to the dimer hopping to the other sites and back again within the localised eigenstates that went into the superposition state. By repeating the calculation for a site neighbouring the initial site we confirm that $P(\tau) = 0$ for sites outside the localised eigenstate for all time.



Figure 11.5: Probability $P(\tau)$ of finding an initially localised dimer on the initial site on a square ladder dimer lattice at time τ with t' = t, so that all bands are flat.

11.6 Triangular Lattice

In the case of an electron on a triangular lattice there is one band of energy which is given by

$$E(\mathbf{k}) = -2t\cos(k_x a) - 2t\cos\left(k_x \frac{a}{2} - \sqrt{3}k_y \frac{a}{2}\right) - 2t\cos\left(k_x \frac{a}{2} + \sqrt{3}k_y \frac{a}{2}\right)$$
(11.11)

Figure 11.6 shows a plot of the probability $P(\tau)$ of finding an electron initially localised on a triangular lattice on the initial site at time τ . The plot shows as expected that $P(\tau)$ falls more rapidly for the two-dimensional lattice than for a one-dimensional lattice such as the staggered ladder or the infinite chain. The asymptotic power law is $P(\tau) \cong 1/\tau^2$. There are no interference effects since there is only one band, and we have allowed only one hopping integral.



Figure 11.6: Probability of finding an electron, initially localised on a triangular lattice, on the initial site at time τ .

11.7 Modified Graphene Lattice

We have seen that in some lattices such as the kagome lattice and graphene Dirac points appear in the band structures. In the case of graphene there are just two bands. In this case it is straight forward to obtain the ground and excited states which can be superimposed to obtain an initially localised state. Graphene is therefore an ideal choice if we wish investigate the effect of Dirac points on the propagation of particles (which are single electrons in this case). Since we are only interested in the effect of the Dirac points we are free to distort the lattice to make the calculation simpler, so long as Dirac points still appear. We distort the graphene lattice so that its unit cell and its Brillouin zone are rectangular (see figure 11.7), meaning that we can integrate over the Brillouin zone in a single integral. For the modified graphene lattice we obtain the solutions

$$E(\mathbf{k}) = \pm t \sqrt{3 + 2\cos(k_y a) + 2\cos\left(k_x a + \frac{k_y a}{2}\right) + 2\cos\left(k_x a - \frac{k_y a}{2}\right)}$$
(11.12)



Figure 11.7: Modified graphene lattice with a rectangular unit cell and Brillouin zone. Greens function calculation is simplified because we can integrate over the Brillouin zone in a single integral.

Dirac points appear at $\mathbf{k} = (\pm \pi/a, \pm 2\pi/3a)$ (see figure 11.8). Figure 11.9 shows a plot of the probability $P(\tau)$ of finding an electron initially localised on the modified graphene lattice on the initial site at time τ . Comparing figures 11.9 and 11.6 we see that the plots for the triangular and modified graphene lattices are not qualitatively different suggesting that $P(\tau)$ is not affected by the presence of Dirac points. This is because the asymptotic decay rate of $P(\tau)$ for large τ is dominated by the Van Hove singularities in the density of states, which are the band edges in graphene rather than the Dirac points. As in the case of the triangular lattice the asymptotic power law for graphene is $P(\tau) \cong 1/\tau^2$.

11.8 Conclusions

The probability $P(\tau)$ of finding an initially localised electron or dimer at its initial location at later times usually takes the form of a decaying oscillation. In such cases $P(\tau)$ decays according to the power law $P(\tau) \cong 1/\tau$ in one dimension and $P(\tau) \cong 1/\tau^2$



Figure 11.8: Band structure for the modified graphene lattice with t = a = 1. Dirac points appear at $\underline{k} = (\pm \pi, \pm 2\pi/3)$

in two dimensions. Interference effects can appear if more than one band contribute to the initial state or if there is more than one hopping integral. If an initially localised state contains flat-band and dispersive-band components $P(\tau)$ will converge on a finite value since there is a component of the initial state that remains localised for all time. If an initially localised state consists entirely of flat-band components the state remains localised for all time. In this case $P(\tau)$ takes the form of a sine wave, as was seen for a localised triplet dimer on the square ladder. The probability $P(\tau)$ oscillates between zero and one as the dimer hops around inside the localised eigenstate, but there is no decay in the oscillation. We found that Dirac points have no obvious effect on $P(\tau)$ because the asymptotic decay rate of $P(\tau)$ for large τ is dominated by the Van Hove singularities in the density of states, which are band edges rather than Dirac points.



Figure 11.9: Probability of finding an electron, initially localised on the modified graphene lattice, on the initial site at time τ .

Chapter 12

Summary and Conclusions

12.1 Feasibility of a Ground State Consisting of Mobile Dimers

We have investigated the possibility of a ground state consisting of mobile dimers on square and triangular lattices and the perovskite layer. Such a ground state would require an effective attraction between electrons and an effective repulsion between dimers. Various mechanisms could lead to an effective attraction which, in combination with the Coulomb repulsion, could lead to pairing without forming larger clusters. We applied the UV model, which is not specific to the pairing mechanism but can be obtained from the strong-coupling Fröhlich-Coulomb model. We obtained ground state energies for single electrons, dimers, trimers and larger clusters for each lattice in Hilbert spaces truncated to the low-energy sector. Comparing these energies over the parameter space we found no parameter regions in which dimers form a ground state on the triangular lattice. This is because in the low-density limit the geometry of the triangular lattice always favours trimers over dimers where an effective attraction

exists, unless t is relatively large in which case electrons will be favoured. Despite this finding it might be possible to obtain a mixture of dimers and single polarons away from the low-density limit on the triangular lattice when many-body effects are taken into account [35, 36]. If the number of states below the Fermi level in the polaron band is less than the number of electrons, bipolarons remain stable mobile quasi-particles because the Pauli exclusion principle prevents their decay into single polarons.

For the square lattice with nearest and next nearest neighbour hopping we found a substantial region in which dimers form a ground state, with nearest-neighbour attraction and next-nearest-neighbour repulsion. These dimers can be very light due to a crab-like propagation. For some values of the parameters the dimer-effective mass is no more than six times the single-electron mass in the same lattice. Our results show that while effective mass can be low due to crab-like motion, crawler motion results in a small pertubative reduction in effective mass if there is large local variation in inter-site potentials. This is a general result allowing us to simplify effective-mass calculations elsewhere by ignoring crawler motion.

For the perovskite layer, with nearest and next-nearest-neighbour hopping we found a substantial region in which dimers, weighted mostly in-plane or mostly out-of-plane, form a ground state. The mostly in-plane dimers can be approximated by dimers confined to a square lattice while the mostly-out-of-plane dimers can be approximated by dimers which hop between the out-of-plane bonds on a plane of corner-sharing pyramids. In each case the dimers can be light due to crab-like motion. The contrast in the results indicates that stable small mobile bipolarons are very sensitive to the lattice structure.

12.2 Graphene and Dirac Points

We found that the electronic properties of graphene are a direct consequence of graphene's crystal symmetry. Its honeycomb lattice is bipartite and cosine-like energy bands associated with the sublattices intersect at the Fermi energy, giving rise to Dirac points. It is easy to see how this happens by considering a one dimensional bipartite lattice. The band structure of the kagome lattice also exhibits Dirac points which are similarly explained in terms of its three sub-lattices. From these observations we have speculated that a bipartite (or tripartite) lattice is necessary for the appearance of Dirac points. We have investigated several other bipartite lattices and found Dirac points in each case thereby supporting our hypothesis. Our investigation has also revealed that three-dimensional Dirac points appear for the singlet dimer lattice of the cubic lattice under certain circumstances. For the graphene bilayer we find that two of the bands form touching paraboloids; from this we conclude that the novel effects in graphene do not persist for bilayer graphene. However Dirac points do occur in multilayer graphene depending on whether the number of layers is even or odd, and what the stacking order is [38].

12.3 Strictly Localised Triplet Dimers

We found that triplets are less mobile than singlets on a square ladder and that for t' = t and V' = V, if dimer-lengths are restricted, triplets become strictly localised. This is also true for the square and honeycomb bilayer. A three-dimensional lattice is also possible in which triplet dimers are strictly localised under some circumstances.

We also found that localised eigenstates exist in the simple cubic and body centred cubic lattices under some circumstances. In the simple cubic lattice we found three localised singlet and triplet eigenstates for all t/t' (see figures 10.12 and 10.14) and an additional localised triplet eigenstate for t' = t/2 (see figure 10.13). For the body centred cubic lattice we found one localised triplet eigenstate for all t/t' (see figure 10.15).

12.4 Time Evolution of Wavefunctions

We found that the probability $P(\tau)$ of finding an initially localised electron or dimer at its initial location on a lattice at later times usually takes the form of a decaying oscillation. In such cases $P(\tau)$ decays according to the power law $P(\tau) \cong 1/\tau$ in one dimension and $P(\tau) \cong 1/\tau^2$ in two dimensions. Interference effects can appear if more than one band contribute to the initial state or if there is more than one hopping integral. If an initially localised state contains flat-band and dispersive-band components $P(\tau)$ will converge on a finite value since there is a component of the initial state that remains localised for all time. If an initially localised state consists entirely of flat-band components the state remains localised for all time. In this case $P(\tau)$ takes the form of a sine wave, as was seen for a localised triplet dimer on the square ladder. The probability $P(\tau)$ oscillates between zero and one as the dimer hops around inside the localised eigenstate, but there is no decay in the oscillation. We found that Dirac points have no obvious effect on $P(\tau)$ because the asymptotic decay rate of $P(\tau)$ for large τ is dominated by the Van Hove singularities in the density of states, which are band edges rather than Dirac points.

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