Electronic and vibrational properties of doped C₆₀

Author(s):
Wehrli, Samuel

Publication Date:
2004

Permanent Link:
https://doi.org/10.3929/ethz-a-004959774

Rights / License:
In Copyright - Non-Commercial Use Permitted
ELECTRONIC AND VIBRATIONAL PROPERTIES OF DOPED C₆₀

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

for the degree of
DOCTOR OF NATURAL SCIENCES

presented by

SAMUEL WEHRLI

Dipl. Phys. EPFL
born 11.4.1975
Swiss citizen

accepted on the recommendation of

Prof. Dr. M. Sigrist, examiner
Prof. Dr. J. Osterwalder, coexaminer
Dr. E. Koch, coexaminer

2004
Abstract

This thesis deals with various aspects related to the doped C$_{60}$. The first chapter is a brief overview in order to place this thesis in a wider context. Chapter 2 is concerned with field doped C$_{60}$. In the first section we investigate the charge profile which is induced by the electric field. A tight-binding Hamiltonian is used for the kinetic energy and the Coulomb interaction is treated within a mean-field approximation. We find that the charge is confined to the surface layer for doping higher than 0.3 electron per C$_{60}$. This regime is further explored in the second section where the effect of the electric field on the two-dimensional bandstructure of the surface layer is investigated. We use a multipole expansion and group theory to describe the electronic response and the level-splitting of the C$_{60}$ molecules. We find that the Stark effect leads to a substantial splitting of the level such that a gap opens in the density of states for doping higher than 2 electrons per C$_{60}$. The last section deals with the effect of steps in the surface layer of various types of field effect devices. We find that in the high-field regime a charge dipole builds up in the region of the step which leads to a barrier for the transport along the surface. The transmission through the step is exponentially suppressed as function of the applied field and step height.

Chapter 3 considers the $T_{1u} \otimes H_y$ Jahn-Teller effect in C$_{60}^n$ ($n = 1, 2$). In the first section we introduce the Hamiltonian and discuss in detail its accidental SO(3) symmetry. We also show that multiple $H_y$ modes can be replaced by an effective mode which yields an upper bound for the ground state energy. The second section introduces a variational ground state for C$_{60}$. We show that the variational ground state becomes exact in both, the small and strong coupling limit. Furthermore, it yields an excellent estimate of the ground state energy in the intermediate coupling regime. In section three we consider C$_{60}^2$ and discuss the competition between the Jahn-Teller effect and the Hund's rule coupling. In the parameter range of C$_{60}$, the ground state is a spin singlet and SO(3) invariant due to the dynamic Jahn-Teller effect. The low energy excitations are well described by the spectrum of a quantum rotator where only even angular momenta are allowed.

In chapter 4 we explore the ground states of K$_4$C$_{60}$ and Na$_2$C$_{60}$ which are related by particle-hole symmetry. We discuss in the first section that, because of the
strong on-site Coulomb repulsion $U$, the two compounds are described by a lattice of $\text{C}_{60}^{2-}$ ions which interact through virtual hopping which leads to a coupling of the order $\kappa = t^2/U$ ($t$ is the hopping amplitude). In the second section we show that this model can be mapped onto a model of interacting rotators and derive realistic parameters for the effective coupling in K$_4$C$_{60}$ and Na$_2$C$_{60}$. The third section solves the rotator model at finite temperature within the mean-field approximation. We find that K$_4$C$_{60}$ should show a second order phase transition to a staggered phase when applying pressure at $T = 0$. Na$_2$C$_{60}$ is found to be in an ordered phase and should undergo a first order phase transition to a disordered phase at a finite temperature (of the order 30 K). The last section discusses possible experiments which might allow to observe these phase transitions.

Chapter 5 deals with angle-integrated photoemission of K$_n$C$_{60}$. Experimentally, metallic K$_3$C$_{60}$ shows pronounced structure and a sharp Fermi edge in integrated photoemission spectra while the insulating K$_4$C$_{60}$ and K$_6$C$_{60}$ phases display only a broad structureless peak. We find that both types of spectra can be explained by the coupling to the optic vibrations of the K$^+$ ions. This is suppressed in K$_3$C$_{60}$ due to metallic screening but is strong in the insulating phases. In the first section we use the non-crossing approximation to calculate the density of states (DOS) of electrons in K$_3$C$_{60}$ coupled to the intramolecular $H_g$ modes in good agreement with the experiment. For K$_4$C$_{60}$ and K$_6$C$_{60}$ strong coupling to the low energy optic K$^+$ modes (discussed in section two) controls the DOS and yields the broad peaks in the spectra. In the third section a moment expansion is used to calculate the position and width of these peaks which agree well with the experiment.
Kurzfassung

Diese Doktorarbeit beschäftigt sich mit verschiedenen Aspekten von dotiertem C₆₀. Das erste Kapitel ist eine kurze Übersicht, um die vorliegende Arbeit in einen weiteren Kontext zu stellen.


In Kapitel 3 wird das $T_{1u} \otimes H_g$ Jahn-Teller Problem für C₆₀⁻ ($n = 1,2$) behandelt. Im ersten Abschnitt wird der entsprechende Hamiltonoperator definiert und gezeigt, dass dieser SO(3) invariant ist. Des Weiteren wird diskutiert, wie das Problem mehrerer $H_g$ Moden durch eine effektive Mode genähert werden kann, was eine obere Schranke für die Grundzustandsenergie liefert. Im zweiten Abschnitt konstruieren wir einen variationellen Grundzustand von C₆₀⁻. Dieser Zustand wird exakt in den Limites verschwindender, sowie grosser Kopplung und liefert eine gute Nähierung der Grundzustandsenergie bei mittlerer Kopplung. Im letzten Abschnitt wird der Grundzustand von C₆₀⁻ diskutiert, wobei dem Wechselspiel zwischen Jahn-Teller Effekt und Hundschener Regel besondere Aufmerksamkeit geschenkt wird. Im Parameter-Bereich von C₆₀ ist der Grundzustand SO(3) invariant und ein Spin-
Singlet. Die niedrigsten Anregungen entsprechen jenen eines symmetrischen, quantisierten Kreisels, wobei nur gerade Drehimpulszustände erlaubt sind. In Kapitel 4 werden die beiden Systeme $K_4C_{60}$ und $Na_2C_{60}$ behandelt, welche durch die Teilchen-Loch Symmetrie verknüpft sind. Im ersten Abschnitt zeigen wir, dass, bedingt durch die starke Coulombsche Abstossung $U$, die beiden System als ein Gitter von wechselwirkenden $C_6^{2-}$ Ionen beschrieben werden können. Die Wechselwirkung kommt durch virtuelle Hüpfprozesse zustande und ist von der Größenordnung $\kappa = t^2/U$ ($t$ ist die Hüpf-Amplitude). Im zweiten Abschnitt zeigen wir, dass dieses Modell äquivalent ist zu einem Gitter von gekoppelten Kreisen. Die explizite Form der Kopplung für $K_4C_{60}$ sowie für $Na_2C_{60}$ wird ebenfalls hergeleitet. Im letzten Abschnitt lösen wir das Problem der gekoppelten Kreisel mit Hilfe der Molekular-Feld Näherung. In beiden Systemen finden wir einen Phasenübergang von einem unkorrelierten Jahn-Teller Effekt zu einem kooperativen Jahn-Teller Effekt. Dieser Phasenübergang kann beispielsweise durch Druck gesteuert werden. In $K_4C_{60}$ sollte er von zweiter Ordnung sein, wohingegen in $Na_2C_{60}$ ein Erst-Ordnungs-Übergang erwartet wird. Des Weiteren erwarten wir, dass, bei $T = 0$, $Na_2C_{60}$ geordnet ist, $K_4C_{60}$ hingegen nicht.

In Kapitel 5 betrachten wir Photoemission von $K_nC_{60}$. Experimente mit metallischem $K_3C_{60}$ zeigen ein Spektrum mit Feinstrukturen und einer scharfen Fermi-Kante. Dagegen sind die Spektren von den Isolatoren $K_4C_{60}$ und $K_6C_{60}$ Gausskurvenförmig und ohne jede Struktur. Diese Verschiedenheit in den Spektren kann durch die Kopplung der Elektronen an die Schwingungen der $K^+$-Ionen erklärt werden. Diese Kopplung wird durch Abschirmung in metallischem $K_3C_{60}$ unterdrückt, ist aber gross in den isolierenden Systemen. Im ersten Abschnitt dieses Kapitels wird die “Non-Crossing”-Näherung verwendet, um die Zustandsdichte der Elektronen in $K_3C_{60}$ zu berechnen, welche an die intramolekularen $H_g$-Moden koppeln. Das Resultat stimmt gut mit dem Experiment überein. Im zweiten Abschnitt bestimmen wir die Kopplung zu den optischen Schwingungen der $K^+$-Moden welche die Spektren der isolierenden $K_4C_{60}$ und $K_6C_{60}$ Systeme bestimmen. Im letzten Abschnitt wird die Position und Breite der Gausscurven-förmigen Spektren von $K_4C_{60}$ und $K_6C_{60}$ mit Hilfe einer Momenten-Entwicklung hergeleitet. Das Resultat deckt sich wiederum mit dem Experiment.
# Contents

1 About $C_{60}$ 1

2 Field effect with strong electric fields 5
   2.1 Charge profile of field-doped $C_{60}$ 7
      2.1.1 The Hamiltonian 8
      2.1.2 Mean-field approximation 10
      2.1.3 Numerical results 12
      2.1.4 Disorder 14
   2.2 Polarization and Stark splitting in field-doped $C_{60}$ 17
      2.2.1 Multipole expansion 19
      2.2.2 Irreducible response parameters of $C_{60}$ 21
      2.2.3 Level splitting 24
      2.2.4 Molecules in a Layer 29
      2.2.5 Splitting in self-consistent multipole field 32
   2.3 Interface steps in field effect devices 38
      2.3.1 Charge distribution in MISFET and SUFET 38
      2.3.2 Perfect conductor approximation 41
      2.3.3 Transmission across the step 43

3 Variational states for $C_{60}^-$ 48
   3.1 Definition of the $T_{1u} \otimes H_g$ Jahn-Teller problem 50
      3.1.1 Hamiltonian 50
      3.1.2 Angular momentum 51
      3.1.3 The real representation 54
      3.1.4 Parametrization of the $l = 2$ distortions 56
      3.1.5 Effective mode approximation (EMA) 58
      3.1.6 Coulomb interaction 61
   3.2 $C_{60}^-$ 62
      3.2.1 Static distortion 62
      3.2.2 Dynamic distortion 63
      3.2.3 Asymptotic behavior for $g \to 0$ 66
Chapter 1

About C$_{60}$

Today, research related to C$_{60}$ has become very large and even after four years of working in the field it still happens that I discover papers concerned about an aspect of C$_{60}$ I wasn’t aware of. Therefore, I attempt to give a brief review in order to show where my work is located in this wide world of C$_{60}$. The topics of the following chapters are quite diverse. Each chapter contains an introduction itself which reviews the corresponding subtopic of C$_{60}$ in detail and gives an account on the work done. In this sense, the four chapters that follow are self-contained and readers interested in a specific topic can jump to the corresponding chapter.

The physics of C$_{60}$ in one paragraph

In this thesis, both, the electronic and phonon degrees of C$_{60}$ are important. Since we are dealing with a molecule both degrees of freedom occur in discrete levels which are given by the icosahedral symmetry $I_h$ of C$_{60}$. The icosahedral symmetry group is the largest three-dimensional point group (with 120 elements when the inversion is included) but it is not compatible with any periodic structure. Therefore most group theory books don’t discuss it, but only mention it as a mathematical curiosity. $I_h$ has 10 irreducible representation (IR) $A_x$, $T_{1x}$, $T_{2x}$, $G_x$, $H_x$ with $x = u, g$ denoting the parity and with degeneracy 1, 3, 3, 4, 5 respectively. The electronic level we mostly deal with is the lowest unoccupied molecular orbital (LUMO) which, in alkali doped fullerites, forms a narrow conduction band ($W = 0.5$ eV). This is illustrated in Fig. 1.1 where those electronic levels are shown which arise from carbon $\pi$-orbitals sticking radially outwards. The LUMO has $T_{1u}$ symmetry, is threefold degenerate and the levels transform as a $p$-orbitals under the symmetry operations of $I_h$. As can be seen from Fig. 1.1, the bandwidth is smaller than the molecular level spacing (the gap is 1.5 eV). The reason is that C$_{60}$ bulk materials are weakly bound Van der Waals crystals where most molecular properties survive in the bulk. This fact is important in the present thesis because a number of considerations start from the
Chapter 1. About C$_{60}$

Figure 1.1: Electron energy levels of the C$_{60}$ molecule which arise from carbon $\pi$-orbitals sticking radially outwards. In the solid, they form narrow bands. The figure reproduced from Ref. [1].

molecular physics (section 2.2 and chapter 4). Since a C$_{60}$ molecule is made out of 60 carbon atoms, there are 174 intramolecular phonon modes (6 degrees of freedom are taken up by overall translations and rotations). These 174 modes are quite high in energy ($30 - 200$ meV) because of the stiff carbon-carbon bonds. They can also be classified according the IR of $I_h$. Important for our purpose are the $A_g$ and $H_g$ modes which are the only modes that couple to the LUMO with $T_{1u}$ symmetry. There are two $A_g$ modes and eight $H_g$ multiplets, each of which is five-fold degenerate. The $H_g$ modes transform as $d$-orbitals and give rise to a non-trivial Jahn-Teller effect (chapter 3).

How this thesis relates to the C$_{60}$ research

There are a couple of reasons why C$_{60}$ research is so large. First of all, C$_{60}$ itself is a fascinating molecule and it is a new form of carbon. Its existence was documented for the first time by Kroto et al. in 1985 [2]. Interestingly, their experiment aimed at understanding the mechanism by which long-chain carbon molecules are formed in interstellar space. Therefore, since the beginning, the field of C$_{60}$ also spreads into astrophysics. By the way, the title of their paper was "C$_{60}$: Buck-
minsterfullerene” where they named the molecule after the inventor and architect R. Buckminster Fuller. In that sense, C₆₀ is even related to architecture.

The real boom in solid state physics started in 1990 when Krätschmer et al. developed techniques to produce and separate fullerenes in sufficient quantity to make solids (fullerites) of a size that allowed traditional solid-state experiments [3]. Soon after that, in 1991, Hebard et al. observed superconductivity in K₃C₆₀ with a transition temperature Tₜ = 18 K [4]. Only three month later, Tanigaki et al. published their work on RbCs₂C₆₀ where they found a superconducting transition at Tₜ = 33 K [5]. Thus, a completely new type of superconductor was found with transition temperatures higher than any conventional superconductor. Naturally, these findings triggered intensive studies in a broad part of the solid state community.

The present thesis is not concerned with superconductivity in C₆₀ but I nevertheless give a overview because superconductivity was and is one of the main motivation for fullerene research. Anyone interested in more details is referred to Gunnarsson’s great review on superconductivity in fullerides [6]. Shortly after the discovery of superconductivity it was proposed that the intramolecular H₉ phonons drive the superconductivity [7, 8, 9]. Estimates of the transition temperature using Eliashberg theory and McMillian’s formula yielded results in agreement with the experiments. This success led to the wide spread opinion that C₆₀ superconductors are rather conventional phonon-driven superconductors. However, in my view, this conclusion is too simple because energy scales (kinetic energy, phonon energies, Coulomb interaction, electron-phonon coupling constant) in C₆₀ are all similar, of the order of 1 eV [6]. As a consequence, Migdal’s theorem is not clearly fulfilled and it is not clear whether Eliashberg theory is valid [6]. Moreover, the Coulomb energy is bigger than the bandwidth which suggest correlated physics. Indeed, some compounds, such as (NH₃)K₃C₆₀ are Mott-Hubbard insulators instead of superconductors [10]. Of course, theory groups working in the field were aware of the difficulties and continued research on superconductivity until today. Their goal was and is to include the different effects on an equal footing and dynamical mean-field theory turned out to be a useful tool [11, 12]. The research on superconductivity in C₆₀ experienced a new push when there were claims that C₆₀ could be doped by field effect and that even hole doping was possible (which never was achieved by chemical means). Regrettably, these claims turned out to be based on dishonest data handling and all papers about field-induced superconductivity in C₆₀ were retracted [13]. Nevertheless, field-doping remains an intriguing technique and it is theoretically investigated in chapter 2 for field-doped C₆₀.

Since energy scales in C₆₀ are all similar, there are a lot of potentially important effects which is the reason why many other disciplines of solid state physics made

---

¹For more information about R. Buckminster Fuller visit the web-page of the Buckminster Fuller Institute: www.bfi.org.
connection to the fullerene research as well. An important field for this thesis is dedicated to the Jahn-Teller effect which is present in a charged C\textsubscript{60} molecule. This is a non-trivial problem due to the interaction between degenerate electron orbitals (T\textsubscript{1u}) and degenerate phonon modes (H\textsubscript{g}). Research on this topic goes back to the sixties where a formally equivalent problem in CaO was investigated [14]. Chapter 3 is concerned with this problem and a detailed overview of the field can be found in its introduction. Most of the work done so far on the T\textsubscript{1u} \otimes H\textsubscript{g} Jahn-Teller problem was numerical (exact diagonalisation) or analytical in either the small or strong coupling limit. An analytical solution over the whole coupling range is not possible. However, I show in chapter 3 that excellent variational solutions can be found which are mostly analytical. The approach allows for example to study carefully the interplay between Jahn-Teller effect and the Hund’s rule coupling in C\textsuperscript{2}\textsubscript{60}.

Chapter 4 uses the variational states for C\textsuperscript{2}\textsubscript{60} introduced in chapter 3 and explores the interaction between them when they are brought together to form a solid. This is a model for K\textsubscript{4}C\textsubscript{60} and Na\textsubscript{2}C\textsubscript{60} which are insulating C\textsubscript{60} compounds although bandstructure calculations predict them to be metals (see introduction to chapter 4). The model presented in chapter 4 displays a phase transition from a phase where the Jahn-Teller distortions are uncorrelated (Jahn-Teller-Mott state) to a phase where they are correlated (cooperative Jahn-Teller effect). On the first view, the two insulating compounds K\textsubscript{4}C\textsubscript{60} and Na\textsubscript{2}C\textsubscript{60} may appear less appealing than the superconducting compounds. However, the low energy physics can be worked out by analytical methods which yields a great insight about the Jahn-Teller physics in C\textsubscript{60} compounds in general. Of course, it would be nice if those findings could be extended to the superconducting compounds where analytical models are rare.

On the experimental side, photoemission is a widely used method to investigate C\textsubscript{60} compounds. Recently, Yang et al. succeeded to measure, for the first time, dispersions in C\textsubscript{60} by angle-resolved photoemission (ARPES) [15]. Experiments show very different angle-integrated spectra for metallic K\textsubscript{3}C\textsubscript{60} and insulating K\textsubscript{4}C\textsubscript{60}/K\textsubscript{6}C\textsubscript{60}. The metallic spectra show a sharp Fermi edge and pronounced structure whereas the spectra from the insulators resemble much more a broad Gaussian. Chapter 5 aims to explain the difference. The finding is that the optic vibrations of the K\textsuperscript{+} ions play a crucial rule. So far, only little attention was paid to these modes because it was argued that they are negligible in the metallic phases due to screening. Hence, it is interesting to find that they are important when it comes to the understanding of photoemission.
Chapter 2

Field effect with strong electric fields

The field effect transistor is a widely used device, both for commercial products as well as in research on correlated electron system (a recent overview is given in Ref. [16]). Traditionally this technique is applied to semiconductors, such as silicon or GaAs, and more recently to high temperature superconductors (see Ref. [16, 17] and references therein) as well as organic materials [18, 19, 20, 21, 22, 23, 24, 25, 26]. The field effect is intriguing because it allows to tune the charge density continuously by changing the applied voltage between gate and source/drain (see Fig. 2.1). However, field effect experiments on the systems mentioned above are difficult, because high electric fields, limited by the electric breakdown of the insulating dielectric, are required in order to achieve substantial changes of the charge distribution. Nevertheless, new gate insulator materials, such as complex oxide dielectrics and ferroelectric oxides, allowed to push surface charge densities to promising values [16]. Thereby operating a FET at high electric fields leads to a strong confinement of the induced surface charge to the dielectric-semiconductor interface.

In this context, the proposal of doping C_{60} crystals in a field-effect device (FET) and the possibility of metallic conduction and even superconductivity in such devices had raised wide-spread interest. While the revelation of dishonest data handling in some cases [13] led to a severe damping of the initial enthusiasm, fundamental aspects of field effect doping remain a timely and interesting problem. For field-effect transistors made with self-assembled monolayers this question was addressed in Ref. [27, 28, 29] and for the reported enhancement of the superconducting transition temperature in C_{60} crystals intercalated with haloform molecules in Refs. [30, 31]. Attempts to observe the field-effect in graphite were reported in Ref. [32].

In this chapter we investigate questions concerned about FET devices which are operated in a regime of high doping, i.e. strong electric field. The present chapter contains three section, each of which is based on a publication [33, 34, 35]. The
C$_{60}$-based FET serves as a model system and the first two sections of this chapter are specific for C$_{60}$. However, the emerging physics should apply to a wider class of organic FET’s. The last section is more general and different types of FET’s are considered. Ref. [34] is a collaboration with E. Koch who performed all DFT calculations. Ref. [35] was done in collaboration with C. Helm.

In section 2.1 the charge profile of a C$_{60}$-FET is studied. A tight-binding model is used to calculate the charge profile and the Coulomb interaction is treated in a mean-field approximation. It is found that at low doping, the charge profile behaves similarly to the case of a continuous space-charge layer [36] and becomes confined to a single interface layer for doping higher than ~ 0.3 electron (or hole) per C$_{60}$ molecule.

Section 2.2 is concerned with the high doping regime of a C$_{60}$ FET where the charge is confined to the top layer. For an accurate description a multipole expansion of the field, the response of the C$_{60}$ molecules, and the Stark splitting of the molecular levels is introduced. The relevant response coefficients and splittings are calculated \textit{ab initio} for several high symmetry orientations. Using a group theoretic analysis we extend these results to arbitrary orientations of the C$_{60}$ molecules with respect to the external field. This approach allows to calculate the Stark splitting in the C$_{60}$ FET and the resulting change in the density of states. In short, the result is that in C$_{60}$ field-effect devices charge is not simply put into otherwise unchanged bands. Rather, the band-structure changes along with the increase of doping which suggests that the physics of C$_{60}$ FET should be quite different from that of the alkali-doped fullerenes.

Finally, section 2.3 is concerned with imperfections in the doped interface of a FET which become important when the confinement becomes strong. In particular, a planar step at the interface causes a potential drop due to the strong electric field of the FET, which in turn is screened by the doped carriers. Section 2.3 analyzes the dipolar electronic structure of a single step in the Thomas-Fermi approximation and it is found that the transmission coefficient through the step is exponentially suppressed by the electric field and the induced carrier density as well as by the step height.
2.1 Charge profile of field-doped C$_{60}$

In this section the charge profile in a FET device is investigated. The general setup of a FET-device is shown in Fig. 2.1. We chose to consider the case of a C$_{60}$-crystal. More precisely, we consider a C$_{60}$ crystal (fcc lattice) with a [001] plane parallel to the gate. Undoped C$_{60}$ is a semiconductor with a 2 eV gap. However, when an electric potential is applied between the gate electrode and the source/drain electrodes, either electrons or holes accumulate on the interface between the C$_{60}$ crystal and the gate dielectric. This leads to a doping of the C$_{60}$ interface planes which allows current to flow parallel to the interface, between the source and the drain. The resistance of this channel can be measured as a function of temperature and doping. The FET can be represented as a planar capacitance with equal and opposite charges on the metal gate and the C$_{60}$ planes near to the interface as shown in Fig. 2.1(b). In the following, we calculate the charge profile as a function of the total charge induced at the interface (or equivalently on the metal gate) rather then in terms of the potential applied to the gate. We limit ourselves to the case of an ideal planar interface with no steps or imperfections. In section 2.1.1, a tight-binding Hamiltonian is introduced to describe the electronic structure of the C$_{60}$ crystal. The effects of Coulomb interactions are treated within a mean-field (or Hartree) approximation in section 2.1.2 and the numerical results are discussed in section 2.1.3. The resulting density profile gives rise to highly structured density of states (DOS). However, we show in section 2.1.4 that the inclusion of merohedral (or orientational) disorder leads to a broadening and suppression of this structure in the DOS.

![Figure 2.1: Left panel: Schematic picture of a FET-device. Right panel: Model of the electronic system in the C$_{60}$-based FET.](image-url)
2.1.1 The Hamiltonian

The C\textsubscript{60} molecule, which has icosahedral symmetry, is almost spherical. Therefore, in the solid, it orders naturally in the close packed fcc structure. In the following we will assume the (hypothetical) unidirectional structure where all C\textsubscript{60} molecules have the same orientation [37]. The space group for this structure is \textit{Fm\overline{3}} and its primitive cell contains one molecule. The actual low-temperature structure with space group \textit{Pn\overline{3}} is more complicated and has a unit cell with 4 molecules. However, in the present work, we are interested in the overall charge filling of the layers, for which details of the band structure are unimportant. The lattice constant of the cubic cell (containing two molecules) is \( a = 14 \) Å for pure C\textsubscript{60} [38]. We introduce here the unit vectors \( \mathbf{e}_x, \mathbf{e}_y \) and \( \mathbf{e}_z \) which span the cubic cell. If one considers only a [001] layer, then the C\textsubscript{60} molecules form a 2D square lattice. In this case the primitive cell has a side length of \( b = \frac{a}{\sqrt{2}} = 10 \) Å which is the distance between two neighboring molecules. The 2D primitive cell is spanned by the unit vectors \( \mathbf{e}_1 = \frac{1}{\sqrt{2}} (\mathbf{e}_x + \mathbf{e}_y) \) and \( \mathbf{e}_2 = \frac{1}{\sqrt{2}} (-\mathbf{e}_x + \mathbf{e}_y) \).

The kinetic energy is well described by a tight-binding Hamiltonian with nearest neighbor (n.n.) hopping [37, 39]:

\[
H_{\text{kin}} = \sum_{\langle \ell n, \ell' n' \rangle} t_{\ell n \ell' n'}(\delta) \, c_{\ell n}^{\dagger}(k) \, c_{\ell' n'}(k) , \tag{2.1}
\]

where \( t_{\ell n \ell' n'}(\delta) \) are the hopping integrals depending on the relative position \( \delta \) of neighboring molecules. The label \( \ell \) denotes the different layers starting with the \( \ell = 1 \) layer closest to the gate. Within a layer \( \ell \), the different sites are labelled by the index \( n \). Finally, the index \( n \) denotes the different orbitals of the C\textsubscript{60} molecule. The brackets \( \langle \rangle \) indicate a summation over n.n. only. Summation over spin degrees of freedom is implicitly assumed. Hamiltonian (2.1) is invariant under translations parallel to the \( z = 0 \) plane and can partly be diagonalized in the 2D \( k \)-space:

\[
H_{\text{kin}} = \sum_{k} \sum_{\ell n} \sum_{\ell' n'} H_{\ell n,\ell' n'}(k) \, c_{\ell n}^{\dagger}(k) \, c_{\ell' n'}(k) , \tag{2.2}
\]

where \( |\ell - \ell'| \leq 1 \) and \( k \) is the two-dimensional wave-vector parallel to the planes. In the case of the conduction band, the structure of the hopping integrals \( t_{\ell n \ell' n'}(\delta) \) are given by the \( T_{1u} \) symmetry of the LUMO (Lowest Unoccupied Molecular Orbital) which is threefold degenerate [39]. The corresponding wave-functions can be chosen such as to transform as \( x, y \) and \( z \) under the icosahedral symmetry group which reduces the number of independent hopping integrals to 4. They are given in Table 2.1. The matrix elements \( H_{\ell n,\ell' n'}(k) \) in (2.2) can be calculated explicitly which yields for intraplanar processes (\( \ell' = \ell \)),

\[
H_{\ell x,\ell x}(k) = 2 t_{xx} [\cos(k_1 b) + \cos(k_2 b)] ,
\]
2.1. Charge profile of field-doped C\textsubscript{60}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\multicolumn{1}{|c|}{\textit{x}} & \multicolumn{1}{|c|}{\textit{y}} & \multicolumn{1}{|c|}{\textit{z}} \\
\hline
\langle x \rangle & t_{xx} = 5.5 & \pm t_{xy} = -27.8 & 0 \\
\langle y \rangle & \pm t_{xy} = -27.8 & t_{yy} = 41.8 & 0 \\
\langle z \rangle & 0 & 0 & t_{zz} = -23.5 \\
\hline
\end{tabular}
\caption{Hopping integrals (in meV) for hopping in the \(\delta = (110)\) direction of the \([e_x e_y e_z]\) coordinate system. The sign of \(t_{xy}\) changes for hopping in the \((110)\) direction. Hopping integrals in other directions follow from rotations around the threefold \((111)\) axes. Numerical values were taken from Ref. [37] where they are given for \(K_3C_{60}\). Since pure \(C_{60}\) has a somewhat smaller lattice constant, the hopping integrals were adjusted by a factor 1.11.}
\end{table}

\[ H_{ly,ly}(k) = 2t_{yy}(\cos(k_1b) + \cos(k_2b)), \]
\[ H_{ly,lz}(k) = 2t_{xy}(\cos(k_1b) - \cos(k_2b)), \]
\[ H_{lz,lz}(k) = 2t_{zz}(\cos(k_1b) + \cos(k_2b)), \]

(2.3)

and for interplanar processes \((l' = l + 1)\),

\[ H_{lx,lz}(k) = 2t_{yy}\cos[(k_1-k_2)b/2] + 2t_{xz}\cos[(k_1+k_2)b/2], \]
\[ H_{ly,lz}(k) = 2t_{xx}\cos[(k_1-k_2)b/2] + 2t_{yy}\cos[(k_1+k_2)b/2], \]
\[ H_{lx,ly}(k) = i2t_{xy}\sin[(k_1-k_2)b/2], \]
\[ H_{lx,lz}(k) = i2t_{xy}\sin[(k_1+k_2)b/2]. \]

(2.4)

The band structure and DOS of a single layer (interplanar processes are turned off) are shown in Fig. 2.2. As a comparison, the 3D DOS is shown as well. The logarithmic van-Hove singularities are clearly apparent in the DOS. Moreover, one observes a symmetric DOS. This is explained by the substitution \(k \rightarrow k + (\frac{\pi}{a}, \frac{\pi}{b})\) which leads to \(H \rightarrow -H\) for the one-layer Hamiltonian (2.3). It implies also that all bands at \((\frac{\pi}{a}, \frac{\pi}{b})\) cross at zero energy. Coupling to neighboring layers breaks this symmetry. The structure of the hopping integrals for the valence band are somewhat more complicated due to the fivefold degeneracy of the HOMO (Highest Occupied Molecular Orbital) with \(h_u\) symmetry. They are described in detail in Ref. [39] and similar matrix elements as in (2.3) and (2.4) were calculated with parameters taken from [39].

The Coulomb interaction can be included by adding the following term to the tight-binding Hamiltonian (2.1),

\[ H_{ee} = \sum_{l} U_{\text{Gate}}(l)n_{ijn} + \frac{1}{2} \sum_{l\neq l', l''} V_{ee}(l, l')n_{ijn}n_{ljn'}, \]

(2.5)
Chapter 2. Field effect with strong electric fields

Figure 2.2: Left panel: C_{60} conduction band of the 2D square lattice. The coordinates of the high-symmetry points in the Brillouin zone are Γ(0,0), P(\frac{\pi}{2},0), Q(\frac{\pi}{2}, \frac{\pi}{2}). Right panel: DOS per C_{60} and for both spins in two (solid line) and three (dashed line) dimensions.

where $n_{ijm}$ is the number operator. The first term is the potential due to the positive charge on the gate. The second term is the electron-electron Coulomb repulsion. Here we follow Antropov et al. [40] by using a renormalized Coulomb interaction for electrons on different sites and an on-site interaction $U_0$ for electrons on the same site,

$$V_{ee}(l_j, l_{j'}) = \begin{cases} U_0 & \text{if } R_{ij} = R_{l_{j'}} \\ \frac{\mu^2}{\varepsilon |R_{ij} - R_{l_{j'}}|} & \text{if } R_{ij} \neq R_{l_{j'}} \end{cases},$$

(2.6)

with $\varepsilon$ being the dielectric constant of C_{60} and $R_{ij}$ denoting the positions of the sites. Note that this interaction does not distinguish between different orbitals. The dielectric constant $\varepsilon$ and the on-site interaction $U_0$ are easily accessible in the literature. We use the experimental estimation of $\varepsilon = 4.4$ by Hebard et al. [41] and the theoretical value of $U_0 = 1$ eV by Antropov et al. [40]. Somewhat different values of $\varepsilon = 3.66$ and $U_0 = 1.27$ eV are proposed from theoretical calculations by Pederson et al. [42].

2.1.2 Mean-field approximation

The full Hamiltonian including the Coulomb term is a complicated many-body problem. We solve it within the mean-field approximation. From symmetry, solutions should be invariant under translations parallel to the planes. The mean-field charge distribution and the resulting potential are then independent of the in-plane site.
position $j$ and the wave-functions can be decomposed as

$$
\Psi_{\nu k}(jn) = \frac{1}{\sqrt{N_{\square}}} e^{i R_{\square} k} \psi_{\nu k}(ln),
$$

where $\nu$ is a band index and $R_{\square}$ is the inplane component of $R_{ij}$. $N_{\square}$ is the number of sites per layer. For a fixed $k$, the perpendicular part $\psi_{\nu k}(ln)$ of the wavefunction is the solution of a Schrödinger equation with a partly discrete spectrum $\{E_{\nu k}\}$. In the mean-field approximation, every occupied electronic $\nu k$ state contributes $|\psi_{\nu k}(ln)|^2 / N_{\square}$ electrons to each orbital $n$ in layer $l$. The sum over all these contributions leads, at zero temperature, to the electron distribution

$$
\rho(l) = \frac{2}{N_{\square}} \sum_{E_{\nu k} < E_F} \sum_n |\psi_{\nu k}(ln)|^2,
$$

where $\rho(l)$ is the total number of electrons per site in layer $l$. The factor 2 comes from the spin degrees of freedom. Within the mean-field approximation, the Coulomb part (2.5) can be written as $H_{ee}^{MF} = \sum_{ijn} U_{MF}(l)n_{ijn}$ where

$$
U_{MF}(l) = U_{\text{Gate}}(l) + \sum_{l',j',j''} \rho(l') V_{ee}(lj,j'l'j'').
$$

The sum in the second term as well as the potential created by the gate are divergent. However, these divergences cancel when the overall system is neutral. In order to make this more explicit, we add and subtract a hypothetical potential created by uniformly charged layers whose total charge equals the actual charge of the $C_{60}$ layers. The mean-field potential can then be rewritten as a sum of two terms

$$
U_{MF}(l) = U_{\text{Cap}}(l) + U_{\text{Corr}}(l).
$$

The first term, $U_{\text{Cap}}$, is given by the superposition of a series of planar capacitances formed by the negative charge $-\epsilon \rho(l')$ on each layer $l'$ combined with the corresponding positive charge $+\epsilon \rho(l')$ on the gate. Choosing $U_{\text{Cap}}(1) = 0$ yields

$$
U_{\text{Cap}}(l) = \frac{4\pi e^2}{\epsilon \sqrt{2} b} \sum_{l'} \rho(l') [\min(l,l') - 1],
$$

where it has to be distinguished whether the given layer $l$ lies inside or outside the capacitance with charges $\pm \epsilon \rho(l')$. Using $\epsilon = 4.4$ and $b = 10$ Å leads to a prefactor $4\pi e^2 / \epsilon \sqrt{2} b = 2.9$ eV. The second part of the mean-field potential, $U_{\text{Corr}}$, includes the corrections arising from the discreteness of the charge distribution and is given
Chapter 2. Field effect with strong electric fields

\[ \Delta l = |l - l'| \quad \begin{array}{c|c} \hline & V_{\text{Corr}}(\Delta l) \text{ (eV)} \\ \hline 0 & U_0 - 3.90 e^2/\varepsilon b = U_0 - 1.28 = -0.28 \\ 1 & -0.042 e^2/\varepsilon b = -0.014 \\ 2 & -10^{-3} e^2/\varepsilon b = -3 \times 10^{-4} \\ \hline \end{array} \]

Table 2.2: The function $V_{\text{Corr}}(\Delta l)$ as calculated by numerical summation.

by

\[ U_{\text{Corr}}(l) = \sum_{l'} \rho(l') V_{\text{Corr}}(|l - l'|) \quad \text{with (2.12)} \]

\[ V_{\text{Corr}}(|l - l'|) = \sum_{j'} V_{\text{ee}}(l_j, l_j') - \int \frac{d^2 R_e}{b^2 \varepsilon |R_l - R_{l'}|}, \]

where $b^2$ is the area of the two-dimensional unit cell and $R_l$ lies in the plane $l$. In equation (2.12) we expect the largest corrections for $l' = l$ since the difference of the potential created by a uniformly and a discretely charged plane is only sizeable at short distance. $V_{\text{Corr}}$ cannot be expressed analytically since it involves an infinite sum over a two-dimensional lattice. The result from numerical summation is given in Table 2.2. The function $V_{\text{Corr}}(\Delta l = |l - l'|)$ is rapidly decreasing and we will only retain the $\Delta l = 0$ term in the following. The correction term then becomes

\[ U_{\text{Corr}}(l) = -\rho(l) \left( 3.9 \frac{e^2}{\varepsilon b} - U_0 \right). \quad (2.13) \]

In fact, the second part of this correction overestimates the on-site interaction $U_0$. The contribution of this term is proportional to $\rho(l)$ which reflects the fact that an electron feels its own mean-field. This is an artifact of the mean-field approximation. In order to improve our model, we require that the on-site interaction should only be effective when there is more than one electron on the molecule ($\rho(l) > 1$), leading to the correction term

\[ U_{\text{Corr}}(l) = -3.9 \frac{e^2}{\varepsilon b} \rho(l) + U_0 \max[0, \rho(l) - 1]. \quad (2.14) \]

2.1.3 Numerical results

The mean-field Hamiltonian was solved self-consistently at zero temperature by numerical means. The mean-field potential (2.10) was used with the correction term (2.14). The resulting charge profile as a function of total charge is shown in Fig. 2.3. We have done the calculation for both, conduction and valence band,
2.1. Charge profile of field-doped CeO$_2$

Figure 2.3: Relative charging of the first layers as a function of total charge in the system (per area of the 2D unit cell). Both axis are in logarithmic units. Solid line: Conduction band. Dashed line: Valence band.

which led to similar results. In the following we focus on the conduction band. It can be seen that more than 98% of the total charge is confined to the first layer for doping higher than $\rho_{\text{tot}} = 0.3$ (in units of particles per area of the 2D unit cell). Furthermore, the confinement to the interface increases with the total charge. The mean distance of the charge distribution from the interface is defined as $z_0 = \sum_{d \geq 1} l d \rho(l)/\rho_{\text{tot}}$, where $d = 7 \text{Å}$ is the width of one layer. For $\rho_{\text{tot}} < 0.1$, this mean distance is found to follow a power law given by $z_0[\text{Å}] \approx 3.8 \rho_{\text{tot}}^{-1/3}$. This power law behavior with respect to $\rho_{\text{tot}}$ is identical to the case of a standard space-charge layer in a continuous medium [36], which predicts $z_0[\text{Å}] = 3.02 (\rho_{\text{tot}} m_s/\varepsilon)^{-1/3} = 5.08 \rho_{\text{tot}}^{-1/3}$, where the effective mass (perpendicular to the interface) of the bulk conduction band minima (X(1,0,0) points) is estimated to be $m_s = 0.92 m_e$ [37, 39]. However, it is important to notice that our microscopic calculation gives a different prefactor. In addition, $z_0$ tends to saturate for $\rho_{\text{tot}} > 0.1$, a regime that cannot be understood in the continuum model. In order to test the role of the correction term, we repeated the same calculation with $U_{\text{MF}} = U_{\text{Cap}}$, i.e. for uniformly charged planes. This led to a somewhat weaker confinement at high doping (∼10% less charge on the first layer for $\rho_{\text{tot}} = 1$). At low doping the effect of $U_{\text{Corr}}$ vanishes because the charge is distributed over several layers. Knowing the charge profile and hence $U_{\text{MF}}(l)$, the band structure can be calculated. Fig. 2.4 shows the conduction band for $\rho_{\text{tot}} = 0.1$. Few bands lie below the continuous spectrum and only the lowest
Figure 2.4: Solid lines: Conduction bands below the continuous spectrum for $\rho_{tot} = 0.1$. Bold solid line: Onset of the continuous spectrum. Dashed line: Fermi energy.

of the 3 LUMO-bands is occupied in the region of the Q-point. In Fig. 2.5(a) the evolution of the discrete states at Q is shown as a function of doping. One observes that the Fermi level is always below the bottom of the continuous spectrum. This is true in general and reflects the fact that all electrons are bound to the interface since the overall system is neutral. Furthermore, only the lowest band is occupied at low doping which is again consistent with theory of space-charge layers [36]. Of course, at doping higher than $\rho_{tot} \approx 2$ the second LUMO-band has to be filled as well. In addition, we note that the continuous spectrum shifts up sharply as the total charge increases. Therefore, at doping higher than $\rho_{tot} \approx 0.3$, the first layer becomes essentially decoupled from the continuous states of the subsequent layers. The energy levels at Q remain constant and the dispersion is given by the LUMO-bands of a single, isolated layer (Fig. 2.2(a)). The decoupling effect is due to the correction term (2.14) which drastically shifts the energy of the first layer with respect to the second one. If this term is omitted, as shown in Fig. 2.5(b), then the bottom of the continuous spectrum follows roughly the Fermi energy and the decoupling of the first layer is much less effective.

2.1.4 Disorder

In A$_3$C$_{60}$, a scaling of the superconducting $T_c$ with increasing lattice constant and hence with the DOS is observed [6]. Hence, sharp features due to Van Hove-singularities of a 2D DOS might be important in a C$_{60}$-based FET. However, it is also known that A$_3$C$_{60}$ is structurally disordered (also called merohedral disorder) down to lowest temperatures. The effect of this disorder on the DOS is investigated
2.1. Charge profile of field-doped C\textsubscript{60}

Figure 2.5: Left panel: Discrete levels at Q as a function of \( \rho_{\text{tot}} \) (solid lines). The bold solid line indicates the bottom of the continuous spectrum and the dashed line is the Fermi energy. Right panel: As the left panel, but without correction term \( U_{\text{Corr}} \).

| \( \langle \hat{y} \rangle \) | \( \hat{t}_{xy} = 22.9 \) | \( \pm \hat{t}_{yy} = 40.8 \) | 0 |
| \( \langle \hat{x} \rangle \) | \( \pm \hat{t}_{xx} = 19.2 \) | \( \hat{t}_{xy} = 22.9 \) | 0 |
| \( \langle \hat{z} \rangle \) | 0 | 0 | \( \hat{t}_{zz} = -29.4 \) |

Table 2.3: Hopping integrals (in meV) for hopping from an unflipped to a flipped molecule in the (110) direction of a fcc lattice. The new (tilded) wave-functions were ordered according to their parity. Note that the sign of \( \hat{t}_{xx} \) and \( \hat{t}_{yy} \) change for hopping in the (110) direction. Numerical values were taken from [43] and adjusted by a factor 11 as proposed by Gelfand and Lu.

in the following.

The rotational motion of a C\textsubscript{60} molecule in a crystal is described by a potential in the three Euler angle coordinates. This potential has, in addition to an absolute minimum, a local minimum which is only \( \Delta = 11 \) meV higher and corresponds to a non-equivalent orientation of the molecule [44]. Therefore, C\textsubscript{60} molecules can flip into the second orientation causing the so-called merohedral disorder. The ratio between the number of flipped and unflipped molecules is given by a Boltzmann factor \( \exp(-\Delta/kT) \). However, a freezing in is observed at 85 K. Below this temperature the crystal is in a glass phase with 15% of the molecules being flipped. If the problem is considered from a tight-binding point of view, then one expects the hopping integrals to be different for hopping between inequivalently oriented molecules. Hence, one gets a tight-binding model where different hopping integrals
are distributed randomly. This will suppress structure in the DOS, as was calculated by Gelfand and Lu in the case of bulk C$_{60}$ [43]. Here, we consider the effect of merohedral disorder on the DOS of a single electron-doped [001] layer. The two types of inequivalent orientations lead to two sets of LUMO wave-functions. We shall denote the new ones on flipped molecules as $|\bar{x}\rangle$, $|\bar{y}\rangle$ and $|\bar{z}\rangle$. These two sets can be related by a 90-degree rotation around the $z$-axes. The hopping integrals between inequivalently oriented molecules are given in Table 2.3. In order to calculate the DOS of the disordered system we set up a finite, two dimensional system which could be diagonalized exactly (for non-interacting electrons). The resulting DOS is shown in Fig. 2.6. The van-Hove singularities are washed out, but a rather sharp peak remains at the center of the band.

Figure 2.6: DOS for a disordered 50x50 site lattice and a flipping ratio of 15%. The statistical average over 200 disorder configurations was taken.
2.2 Polarization and Stark splitting in field-doped C$_{60}$

In this section we address the question how strongly C$_{60}$ can be doped in an electric field before its electronic structure is substantially changed and how this structure changes in even stronger fields. Again, C$_{60}$ is a model system and the physics discussed below should be relevant for all field-doped devices based on molecular crystals such as pentacene, tetracene or rubrene (see section 2.3.1 for a discussion and references). Generally, the effects of the applied field on the bandstructure are twofold. First, the bands are bent by the field and the surface charge distributes in a selfconsistent fashion. The simplest description of this effect is Thomas-Fermi screening. More rigorously, the carriers have to be treated quantum mechanically rather than classically. An extensive review for continuous models is given in Ref. [36]. A discrete model for the case of C$_{60}$ was discussed in the previous section. The second effect of the applied electric field is the modification of the properties of the atoms or molecules which constitute the crystal in the FET. More precisely, the electric field leads to a Stark effect and therefore to splitting of the atomic or molecular energy levels. Along with the level splitting comes the modification of the wavefunctions which in return may give rise to changes in overlap integrals. Both, level splitting and changes in the overlap lead to a modification of the bandstructure. In order for this effect to be relevant, the level splitting should be comparable to the bandwidth. For a rough estimate, one can assume that the splitting is of the same order as the polarization energy $\Delta E \approx \alpha E^2$, where $\alpha$ is the atomic or molecular polarizability and $E$ is the electric field. To give an example, the highest achievable electric field in silicon is 10 MV/cm due to the electric breakdown of SiO$_2$ [16]. The polarizability of silicon is $\alpha = 5.38 \, \text{Å}^3$ which yields $\Delta E \approx 4 \times 10^{-3} \, \text{eV}$ and which is much smaller than the bandwidth (5 – 10 eV). Similar values are found for other conventional FET's which means that the Stark effect can be neglected in conventional FET's. However, this is different in the case of a molecular crystal such as C$_{60}$ which has a high molecular polarizability $\alpha = 85 \, \text{Å}^3$. This leads to a splitting $\Delta E \approx 0.1 \, \text{eV}$ (for an electric field of 10 MV/cm). On the other hand, C$_{60}$ forms a molecular crystal where the overlap between molecules is small which leads to a narrow band with width 0.5 eV. Consequently, the Stark effect if of the same order as the bandwidth and therefore non-negligible. Note that this complicates the physics of field-doped C$_{60}$ compared to alkali-doped C$_{60}$.

In the following we attempt to calculate the splitting of the molecular orbitals in field-doped C$_{60}$ crystal. This requires the knowledge of the effective field acting on each molecule, which, due to screening, differs from the external field. Solving the problem of screening exactly is a difficult task because the whole bandstructure has to be taken into account. However, since the overlap of wave-functions on different
molecules is small, the polarization is dominated by the molecular polarization which allows to consider the molecules as independent entities. In this case, the quantum mechanical problem of the response of the crystal is reduced to the problem of the response of a single molecule. Using the high symmetry of the C\textsubscript{60} molecule and multipole expansion, the electrostatic behavior of a single molecule can be cast into a few parameters. The way how this is done is described in detail below and parameters are calculated by density functional theory (DFT). If the response of a single molecule is known, then the response of the whole crystal can be calculated by classical electrostatics. Once the effective field acting on a molecule is known, the splitting of the levels can be calculated. Again, the high symmetry of the molecule allows to described the splittings with a few parameters which are also calculated by DFT. Finally, the splitting can be included into a bandstructure calculation. As in the previous section, we use a tight-binding model where we add the splitting which yields the bandstructure and density of states in a mono-layer of a field-doped C\textsubscript{60} crystal.

All calculations reported below have been performed for a neutral molecule which has proper icosahedral symmetry and where a group theoretical approach is particularly elegant. Of course, when electrons are filled in a molecule exposed to an external field, they will occupy only the lowest of the split orbitals. Thereby, the symmetry is broken which would require a different calculation for charged molecules. We are, however, not interested in the splitting per se, but in the effect of the splitting on the band structure of a monolayer. Thus, allowing electrons only in the energetically lowest levels would mean that in the lattice, the electrons are not allowed to hop to energetically higher ones of the split levels. This implies that the original band structure would already be separated into a set of bands originating from occupied, and another set of bands originating from the empty orbitals. Therefore, since we consider the Stark effect as a perturbation of the band-structure, we perform calculations for neutral molecules.

The organization of this section reflects this approach: In section 2.2.1 we present generally the method of multipole expansion. Using group theory, in section 2.2.2, the irreducible parameters for the multipole response are determined. In section 2.2.3 we give an analogous treatment for the Stark splittings. In section 2.2.4 we use these ingredients to self-consistently solve for the screened field seen by a molecule in a charged monolayer. The splitting of the molecular levels in this self-consistent multipole field and the effect of this splitting on the density of states is presented in section 2.2.5.
2.2.1 Multipole expansion

Multipole expansion and linear response

The polarizability $\alpha$ of a molecule describes the linear dependence of the induced dipole moment $\mathbf{p} = \alpha \mathbf{E}$ on the applied electric field $\mathbf{E}$. In the case of a multipole expansion, $\alpha$ becomes a matrix $\alpha_{l_1 m_1 l_2 m_2}$ describing the response to all multipole fields [45]. In the following discussion we follow the notation of Ref. [45]. The solutions of the Laplace equation $\nabla^2 V(r) = 0$ are given by

$$ V(r) = V^e + V^i = \sum_{lm} V_{lm} R_{lm}(r) + Q_{lm} I_{lm}(r), \quad (2.15) $$

where the two terms denote the external potential ($V^e$), and the induced potential ($V^i$) due to a charge distribution $\rho$ located around $r = 0$. Note that both, the Laplace equation as well as the expansion of $V^i(r)$ into multipoles only holds for $r$ which lie outside the charge distribution. We have introduced the regular and irregular spherical harmonics [45]

$$ R_{lm}(r) = r^l \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\Omega), \quad (2.16) $$

$$ I_{lm}(r) = \frac{1}{r^{l+1}} \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\Omega). \quad (2.17) $$

Special cases for the regular spherical harmonics are $R_{00} = 1$ and $R_{10} = z$, hence, the external field, $V_{00} = V_0$ corresponds to a constant shift, and $V_{10} = -E_z$ is the $z$-component of the electric field. For the irregular spherical harmonics we have $I_{00} = 1/r$ and $I_{10} = z/r^3$, thus for the induced potential, $Q_{00} = q$ gives the monopole charge while $Q_{10} = p_z$ is the dipole moment. Generally, the coefficients $Q_{lm}$ are the multipole moments of the charge distribution $\rho$

$$ Q_{lm} = \int d^3r \rho(r) R_{lm}(r). \quad (2.18) $$

Decomposing the charge distribution $\rho = \rho_0 + \Delta \rho$ into the unperturbed charge density and the change in the charge density due to the external potential, we obtain a decomposition of the multipole moments $Q_{lm} = Q_{lm}^0 + \Delta Q_{lm}$. Within linear response, the coefficients $\Delta Q_{lm}$ of the induced multipole moments depend linearly on the coefficients $V_{lm}$ of the external potential, which defines the linear-response matrix $\alpha_{l_1 m_1 l_2 m_2}$:

$$ \Delta Q_{l_1 m_1} = -\sum_{l_2 m_2} \alpha_{l_1 m_1 l_2 m_2} V_{l_2 m_2}, \quad (2.19) $$

where the sign takes into account that the induced fields oppose the external fields. Then $\alpha_{l_1 m_1 l_2 m_2}$ gives the dipolar response tensor, while $\alpha_{0000}$ is the self-capacitance.
The interaction energy of the molecule with the external potential is $E_{\text{ext}} = \int d^3r \rho(r) V^e(r)$, which, using the previous definitions, reduces to

$$E_{\text{ext}} = \sum_{lm} V_{lm} Q_{lm}^*.$$  \hfill (2.20)

Therefore, $V_{lm}$ and $Q_{lm}$ are pairs of conjugate variables and the electrostatic energy of the molecule as a function of the external field is given by

$$E_{\text{mol}} = \frac{1}{2} \sum_{l_1 m_1 l_2 m_2} \alpha_{l_1 m_1 l_2 m_2} V_{l_1 m_1} V_{l_2 m_2}^* + \sum_{lm} V_{lm} (Q_{lm}^0)^*.$$  \hfill (2.21)

Since this is a quadratic form, we see that the matrix $\alpha$ is hermitian. The total energy can also be expressed as function of the variables $\Delta Q_{l_1 m_1}$. Inverting relation (2.19) and substituting into the quadratic term yields

$$E_{\text{mol}} = \frac{1}{2} \sum_{l_1 m_1 l_2 m_2} \alpha_{l_1 m_1 l_2 m_2}^{-1} \Delta Q_{l_1 m_1} \Delta Q_{l_2 m_2}^* + \sum_{lm} V_{lm} (Q_{lm}^0)^*.$$  \hfill (2.22)

Note that all quantities can be made real when real spherical harmonics are used (see appendix B). In this case $\alpha$ becomes real and symmetric.

### Interaction between multipole moments

In the following we want to consider not only one C$_{60}$ molecule, but a lattice of them, each one characterized by a position $r$ and some multipole moments $Q_{rim}$. The molecules are assumed to be only coupled by electrostatic interaction and to be otherwise independent. This is a reasonable assumption for C$_{60}$ bulk systems which are bound by Van der Waals interaction. In order to calculate the electrostatic fields, we need to know the interaction energy between multipole moments $Q_{rim}$ of different molecules ($r \neq r'$). In order to derive this interaction energy we start with the expression for the electrostatic energy of a system with charge distribution $\rho$:

$$E = \frac{1}{2} \int d^3r \int d^3r' \rho(r) \rho(r') \frac{1}{|r-r'|}.$$  \hfill (2.23)

The charge distribution can be written as a sum of charge distributions $\rho(r) = \sum_i \rho_i(r-r_i)$, where the charge distribution $\rho_i$ is localized at positions $r_i$ and corresponds to the charge distribution of the molecule at position $r_i$. The energy of the system becomes $E = \frac{1}{2} \sum_{ij} E_{ij}$. The term $E_{ii}$ is the self energy of the molecule on position $r_i$ and given by the quadratic term of (2.22). The terms $E_{ij}$ are interaction energies between different molecules and given by

$$E_{ij} = \int d^3r \int d^3r' \frac{\rho_i(r) \rho_j(r')}{|r-r'-(r_j-r_i)|}.$$  \hfill (2.24)
2.2. Polarization and Stark splitting in field-doped CeO

We want to rewrite formula (2.24) in terms of the multipole moments \( Q_{\text{rim}} \) which is possible using the complicated formula [45]:

\[
\frac{1}{|a - b - R|} = \sum_{l_1,m_1} \left[ (-1)^{l_2+m_1+m_2} \frac{(2l_1 + 2l_2)!}{(2l_1)!(2l_2)!} C_{l_1,m_1,2l_2} \right] R_{l_1m_1}(a) R_{l_2m_2}(b) I_{l_1+l_2-(m_1+m_2)}(R) \]

\[
= \sum_{l_1,m_1} \left[ \left( \frac{l_1 + l_2 + m_1 + m_2}{l_1 + m_1} \right) \left( \frac{l_1 + l_2 - m_1 - m_2}{l_1 - m_1} \right) \right] \frac{(-1)^{l_2+m_1+m_2}}{(2l_1)!(2l_2)!} I_{l_1+l_2-(m_1+m_2)}(R), \tag{2.26}
\]

which holds for \(|a - b| < R\). \( C_{l_1m_1,2l_2}^{L,M} \) denote the Clebsch-Gordon coefficients. In the second equality the explicit expression for the Clebsch-Gordan coefficients were used [46]. Note that in the case \( b = 0 \), the formula reduces to well know expansion of \( 1/|a - R| \). This formula can also be derived from other sources (see Ref. [46, 47]). The denominator of (2.24) can be expanded using this formula which yields

\[
E_{ij} = \sum_{l_i,m_i,l_j,m_j} \beta_{r_i l_i m_i r_j l_j m_j} Q_{r_i l_i m_i}^* Q_{r_j l_j m_j}, \tag{2.27}
\]

with

\[
\beta_{r_i l_i m_i r_j l_j m_j} = (-1)^{m_j + l_j} \left[ \frac{(2l_1 + 2l_2)!}{(2l_1)!(2l_2)!} \right] \frac{1}{C_{l_1,m_1,2l_2}} R_{l_1m_1}(a) R_{l_2m_2}(b) I_{l_1+l_2-(m_1+m_2)}(r_j - r_i) \tag{2.28}
\]

One verifies, that the matrix \( \beta \) is complex conjugate under the exchange of all indices. The coefficient \( \beta_{r_i l_i m_i r_j l_j m_j} \) can be understood as follows: A multipole moment \( Q_{r_j l_j m_j} \) at position \( r_j \) induces a potential at position \( r_i \) with components \( V_{l_i m_i} = \beta_{r_i l_i m_i r_j l_j m_j} Q_{r_j l_j m_j} \).

### 2.2.2 Irreducible response parameters of C_{60}

The structure of the response matrix \( \alpha \) depends on the symmetry of the molecule. For a metallic sphere of radius \( R \) the response is isotropic, i.e., \( \alpha \) is diagonal in the basis of the spherical harmonics: \( \alpha_{l_1m_1 l_2m_2} = \delta_{l_1 l_2} \delta_{m_1 m_2} R^{2l_1+1} \). Lowering the symmetry to icosahedral, \( I_h \), introduces some anisotropy. To understand the response matrix of a neutral C_{60} molecule we have to consider how the irreducible representations (IR) of the rotation group \( SO(3) \) split into IRs of the \( I_h \) (see Tab. 2.4). An
Chapter 2. Field effect with strong electric fields

<table>
<thead>
<tr>
<th>$l$</th>
<th>$I_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$A_g$</td>
</tr>
<tr>
<td>1</td>
<td>$T_{1u}$</td>
</tr>
<tr>
<td>2</td>
<td>$H_g$</td>
</tr>
<tr>
<td>3</td>
<td>$G_u \oplus T_{2u}$</td>
</tr>
<tr>
<td>4</td>
<td>$G_g \oplus H_g$</td>
</tr>
<tr>
<td>5</td>
<td>$T_{1u} \oplus T_{2u} \oplus H_u$</td>
</tr>
<tr>
<td>6</td>
<td>$A_g \oplus T_{1g} \oplus G_g \oplus H_g$</td>
</tr>
</tbody>
</table>

Table 2.4: Decomposition of the irreducible representations (IR) of the rotation group $SO(3)$ into the IR of the icosahedral group $I_h \subset SO(3)$.

A external multipole field of angular momentum $l$ can only give rise to a response with angular momentum $l'$, if both IRs of the $SO(3)$ contain a common IR of the $I_h$. In particular, because of parity, fields with even (odd) $l$ can only give rise to responses with even (odd) $l'$. Furthermore, as the irreducible representations with $l \leq 2$ are also irreducible with respect to the $I_h$, for $l \leq 2$ we have $\alpha_{lm,l'm'} = \alpha_{l} \delta_{mm'}$. Thus, restricting the multipole expansion to $l \leq 2$, the response of $C_{60}$ is isotropic.

For $l > 2$ the space spanned by the spherical harmonics $Y_{lm}$ is no longer irreducible with respect to the $I_h$. Thus we need to find linear combinations of the spherical harmonics that span the irreducible representations of the icosahedral group. We call them $Y_{lkx}$, where $l$ and $x$ denote the IR of the $SO(3)$ and $I_h$, respectively, while the index $k$ labels the functions within an irreducible representation of the $I_h$. If in the decomposition an IR $x$ should occur several times, we would have to introduce an additional multiplicity label. However, as can be seen from Tab. 2.4, up to $l = 6$ each IR appears at most once. We therefore suppress the multiplicity label here. Explicit expressions for the basis functions $Y_{lkx}$, can, e.g., be found in Ref. [48], chapter 16, or Ref. [49], Tab. 4.2. In the new basis, the matrix $\alpha$ is built of blocks of diagonal matrices

$$
\alpha_{ll'k_1k_2} = \alpha_{l_1l_2}(x_1) \delta_{x_1x_2} \delta_{k_1k_2},
$$

where $\alpha_{l_1l_2}(x_1)$ constitute the minimal set of parameters, and, $\alpha$ being real symmetric, $\alpha_{l_1l_2}(x_1) = \alpha_{l_2l_1}(x_1)$. The matrix elements of $\alpha$ were calculated up to $l = 6$ using the results from DFT calculations done by E. Koch. Details are given Ref. [34]. The parameters $\alpha_{l_1l_2}(x_1)$ are listed in Tab. 2.5. We find that the linear response of a $C_{60}$ molecule is very similar to that of a metallic sphere of radius 4.4 Å. This effective sphere radius shows a slight increase with $l$. In addition there are weak off-diagonal terms. From this minimal set of independent parameters we can determine the response for arbitrary orientations of the $C_{60}$ molecule relative to the external multipole field. An example
2.2. Polarization and Stark splitting in field-doped C_60

| α_{00}(A_g)  | 1.019 | α_{55}(T_{1u})  | 1.707(9) | α_{06}(A_g)  | 1.598(5) |
| α_{11}(T_{1u}) | 0.990(0) | α_{55}(T_{2u})  | 1.430(4) | α_{06}(H_g)  | 1.209(21) |
| α_{22}(H_g) | 1.154(0) | α_{55}(H_u)  | 2.031(13) | α_{06}(G_g)  | 1.964(2) |
| α_{33}(G_u) | 1.268(1) | α_{15}(T_{1u})  | -0.077(5) | α_{66}(T_{1g})  | 2.503 |
| α_{33}(T_{2u}) | 1.376(3) | α_{35}(T_{2u})  | 0.039(6) | α_{26}(H_g)  | -0.023(13) |
| α_{44}(H_g) | 1.542(6) | | | α_{46}(H_g)  | 0.195(12) |
| α_{44}(G_g) | 1.477(9) | | | α_{46}(G_g)  | -0.337(13) |
| α_{24}(H_g) | 0.074(6) | | | | |

Table 2.5: Linear response coefficients of a neutral C_60 molecule derived from the results of our density functional calculations. The matrix elements α_{i,j}(x) are normalized with R_0 = 8.25 bohr. By comparing matrix elements determined from the response to potentials applied along the 2-, 3-, and 5-fold axis, we have determined, wherever possible, the uncertainties in the values of the matrix elements. The value of α_{00}(A_g) is given by the quadratic term of the change of the ground state energy upon charging of the molecule.

<table>
<thead>
<tr>
<th>IR of I_h</th>
<th>5-fold axis</th>
<th>3-fold axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>G_u</td>
<td>-</td>
<td>(\frac{2\sqrt{2}}{3}Y_{30} - \frac{1}{3}Y_{3c3})</td>
</tr>
<tr>
<td>T_{2u}</td>
<td>-Y_{30}</td>
<td>-(\frac{1}{3}Y_{30} - \frac{2\sqrt{2}}{3}Y_{3c3})</td>
</tr>
</tbody>
</table>

Table 2.6: Transformed l = 3 spherical harmonics, which are partner functions for the IR of I_h and which contain Y_{30}. The second (third) column is for the case where the 3-fold (5-fold) axis of the molecule is parallel to the z-axis. The real spherical harmonic is Y_{3c3} = \(\sqrt{2}\text{Re}(Y_{33})\).

of how to do this is given below. The practical advantage of this procedure is clear: We only need to perform density functional calculations for a number of highly symmetric configurations, for which the numerical effort is much reduced. Using group theory the response for arbitrary configurations can then be determined from these special cases.

Response for general orientation: an example

To illustrate the use of the response coefficients given in Tab. 2.5, we show, how to calculate the response for a multipole potential with (lm) = (30) for different orientations of the z-axis with respect to the C_60 molecule. This is the first non-trivial case, as the response for multipoles with l ≤ 2 is isotropic. To start with, we need the basis functions Y_{lxk} spanning the irreducible representation of the I_h,
that were introduced in section 2.2.2. For specific orientations, these can be found, e.g., in the Ref. [48], chapter 16, or Ref. [49], Tab. 4.2. For arbitrary orientations, they have to be derived by explicitly finding the basis functions that span the irreducible representations of the icosahedral group. For the sake of the example, we consider the response for \( z \) along the 5-fold and the 3-fold axis of the \( \text{C}_{60} \) molecule. The corresponding basis functions are then both found in Ref. [48]. Since we are interested in the response to an external multipole with \((lm) = (30)\), we have to identify those basis functions that contain \( Y_{30} \). They are shown in Tab. 2.6. It turns out that for \( z \) parallel to the 5-fold axis the \((lm) = (30)\) potential corresponds to a pure \( T_{2u} \) potential. Thus the response is given by \( \Delta Q_{30} = \alpha_{33}(T_{2u}) V_{30} \). For \( z \) along the 3-fold axis the situation is more complicated, as the potential is now a mixture of partner functions of \( G_u \) and \( T_{2u} \): As can be seen from Tab. 2.6, it mixes with the \( Y_{3c3} = \sqrt{2} \text{Re}(Y_{33}) \) component. By construction, the response matrix \( \alpha \) in the subspace spanned by \{\( Y_{30}, Y_{3c3} \}\) is diagonal, with diagonal elements \( \alpha_{33}(H_u) \) and \( \alpha_{33}(T_{2u}) \), when written in the basis functions listed in Tab. 2.6. However, to obtain the multipole response we have to use the basis \( \{Y_{30}, Y_{3c3}\}\), for which there are off-diagonal elements:

\[
\alpha = \frac{1}{9} \begin{pmatrix}
8 \alpha_{33}(H_u) + \alpha_{33}(T_{2u}) & \sqrt{8} \left[\alpha_{33}(T_{2u}) - \alpha_{33}(H_u)\right] \\
\sqrt{8} \left[\alpha_{33}(T_{2u}) - \alpha_{33}(H_u)\right] & \alpha_{33}(H_u) + 8 \alpha_{33}(T_{2u})
\end{pmatrix}.
\]

(2.30)

We thus find

\[
\Delta Q_{30} = \frac{1}{9} [8 \alpha_{33}(H_u) + \alpha_{33}(T_{2u})] V_{30},
\]

\[
\Delta Q_{3c3} = \frac{\sqrt{8}}{9} \left[\alpha_{33}(T_{2u}) - \alpha_{33}(H_u)\right] V_{30}.
\]

2.2.3 Level splitting

In this section, a minimal set of parameters describing the Stark effect in a neutral molecule is deduced using the Wigner-Eckart theorem for the icosahedral symmetry [48]. This is achieved in the framework of density-functional perturbation theory [50] where an external perturbation \( V \) induces a change in the effective potential (self-consistent field) \( V^{\text{eff}} \) which couples the degenerate energy levels. In linear order the change is given by

\[
\Delta V^{\text{eff}}(r) = V(r) + \Delta V^l(r) + \frac{d\nu_{\text{xc}}}{dn} \Delta n(r),
\]

(2.31)

where \( \Delta V^l(r) = e^2 \int dr' \Delta n(r') |r - r'|^{-1} \) is the change in the induced potential due to the linear change \( \Delta n(r) \) in the electron distribution. The last term is the exchange-correlation potential. Within linear response, the change in the charge distribution
2.2. Polarization and Stark splitting in field-doped $C_{60}$

Figure 2.7: Splitting of the $H_u$ and $T_{1u}$ levels of a $C_{60}$-molecule in an external multipole field $V(r) = V_{lm}R_m^2(r)$ with $z$ along a 2-fold axis. Due to parity, for small external fields, the splitting for $(lm) = (10)$ is quadratic in the external field, while for $(lm) = (20)$ it is linear. The $V_{lm}$ are given in atomic units and $R_g = 7$ bohr. $(lm) = (10)$ corresponds to a homogeneous field with $E_z = -V_{10}$, thus $V_{10}R_g^2 = 1$ in atomic units corresponds to a homogeneous field of about 1 V/Å.

$\Delta n$ as well as the induced potential $\Delta V^i$ have the same symmetry (with respect to $I_h$) as the external perturbation $V^e$. Furthermore, if $n(r)$ is the unperturbed charge distribution, then the factor $\frac{dx}{dn}|_{n=n(r)}$ in the last term of (2.31) has $A_g$ symmetry and does not change the symmetry of $\Delta n$. Consequently, $\Delta V^{\text{eff}}$ has the same symmetry as $V^e$ and, using the notation of the previous section, can be written
Figure 2.8: Energy levels of the $C_{60}$ molecule as calculated by density functional theory. The Fermi energy for the undoped molecule is indicated.

Table 2.7: Coupling constants $t_\lambda(x_1 x_2; l)$ as defined by equation (2.33) (indices $n_1$, $n_2$, $l$ are dropped) among the energy levels near the Fermi energy. The coupling constants are given in units of eV (7 bohr)$^{l+1} e^{-1}$ where $l = 1$ for $x = T_{1u}$ and $l = 2$ for $x = H_g$. The negative sign of the coefficients is due to the negative charge of the electrons. Note that the coupling constants $t(H_u H_g; T_{1u})$ and $t(H_u G_g; T_{1u})$ are equal up to the third digit which is due to fact that the $H_g$ and $G_g$ levels have almost the same radial dependence because of the their closeness in energy (see Fig 2.8).

\[
\Delta V^\text{eff}(r) = \sum_{l\alpha k} V_{l\alpha k} f_{z\lambda}^2(r) + O[V_{l\alpha k}^2],
\]

where $f_{z\lambda}^2(r)$ are partner functions of the IR $x$ of $I_h$. Note that $f_{z\lambda}^2$ contains spherical harmonics $Y_{l'\alpha k}$ with all $l'$ allowed by Tab. 2.4. The coupling of the degenerate levels is given by the matrix elements of $\Delta V^\text{eff}$ with respect to the eigenstates of the unperturbed molecule which are denoted by $|n\alpha xk\rangle$, where $n$ is the quantum number differentiating between orbitals with the same IR $x$. In this context, the functions $f_{z\lambda}^2$ play the role of tensor operators of $I_h$ and the Wigner-Eckart theorem can be
used to write the matrix elements as

$$\langle n_2 x_2 k_2 | \Delta V^{\text{eff}} | n_1 x_1 k_1 \rangle = \sum_{i z k} V_{i z k} \sum_\lambda t_\lambda(n_1 x_1 n_2 x_2; l x) C^k_{k2k1}(\lambda; x_2 x_1; x).$$

(2.33)

The coefficients $C^k_{k2k1}(\lambda; x_2 x_1; x)$ denote the $3jm$ symbols (or Clebsch-Gordan coefficients) of $I_h$ and are entirely determined by the icosahedral symmetry. They are discussed in detail in appendix A. In order for $C^k_{k2k1}(\lambda; x_2 x_1; x)$ to be non-zero, the IR $x$ needs to be present in the decomposition of $x_1 \otimes x_2$. If $x$ occurs more than once in $x_1 \otimes x_2$ then the multiplicity index $\lambda$ is required. From this selection rule follows again that even potentials couple linearly whereas odd potentials couple only in second order (quadratic Stark effect). Finally, the factors $t_\lambda(n_1 x_1 n_2 x_2; l x)$ are the coupling constants which constitute the minimal set of parameters describing the level splitting.

We analyze in more detail the level splitting of the LUMO ($x = T_{1u}$) and HOMO ($x = H_u$) for $l = 1$ and $l = 2$ external potentials which correspond to an electric field and a quadrupole potential. We will see in Section 2.2.4 that these two multipoles are dominant in the case of a charged $C_{60}$ layer exposed to an electric field. Within the icosahedral symmetry $I_h$, the two potentials form partners for the IR $T_{1u}$ and $H_u$ respectively (see Tab. 2.4). Details of the calculation are given in appendix A. Since the $l = 1$ external potential is odd, it cannot couple within a single molecular orbital which leads to a quadratic Stark effect. However, $l = 2$ is even which leads to a linear splitting. This is shown in Fig. 2.7 where the energy levels as a function of the strength of an applied $l = 1$ or $l = 2$ external potential were calculated by DFT (see Ref. [34] for details). Using DFT results as shown Fig. 2.7, coupling constants can be derived and are given in Tab. 2.7. In the case of the odd $l = 1$ potential, only second-order coupling to closest-by orbitals was considered ($T_{1g}$ for the LUMO, $H_g$ and $G_g$ for the HOMO, see Fig. 2.8), which, however, as shown below, gives very satisfactory results. For the splitting of the HOMO under the $l = 2$ ($x = H_g$) potential, there are two coupling constants because $H_g$ occurs twice in the product $H_u \otimes H_u = A_2 \oplus T_{1g} \oplus T_{2g} \oplus 2G_g \oplus 2H_g$. In appendix A the coupling matrix $H'_{T_{1u}} (H'_{H_u})$ describing the level splitting of the LUMO (HOMO), due to an applied $(lm) = (10)$ and $(lm) = (20)$ potential along an arbitrary direction of the molecule, is calculated using perturbation theory. To a very good approximation, the result can be cast into the form

$$H'_{T_{1u}}(\theta) = \left( V_{10}^2 c_1 + V_{20} c_2 \right) C_{T_{1u}}(\theta),$$

(2.34)

$$H'_{H_u}(\theta) = \left( V_{10}^2 d_1 + V_{20} d_2 \right) C_{H_u}(\theta),$$

(2.35)

where $c_1$, $c_2$, $d_1$ and $d_2$ are constants depending on the coupling constants of Tab. 2.7 and the energies given in Fig. 2.8. $C_{T_{1u}}(\theta)$ and $C_{H_u}(\theta)$ are matrices within the
Figure 2.9: Splitting of the LUMO for an \((\ell m) = (10)\) and \((\ell m) = (20)\) potential as the molecule is rotated by \(\pi/2\). For the angles \(\tan \theta = 0\), \(\tan \theta = (3 - \sqrt{5})/2\) and \(\tan \theta = (1 + \sqrt{5})/2\) the potentials point along the 2-, 3- and 5-fold axis respectively. The splitting calculated with DFT at these high symmetry orientations are indicated by the filled symbols. The lines give the result of perturbation theory, fitted to the calculation for the 3-fold axis. **Upper panel:** \((\ell m) = (10)\) potential with \(V_{10} = 0.143 \, e \, (7 \, \text{bohr})^{-2}\). The lower level is twofold degenerate. **Lower panel:** \((\ell m) = (20)\) potential with \(V_{20} = 0.180 \, e \, (7 \, \text{bohr})^{-3}\). The upper level is twofold degenerate.

LUMO and HOMO subspace respectively and depend on the angle \(\theta\) between the \(z\)-direction of the \((\ell m) = (10), (20)\) potentials and the 5-fold axis of the molecule. (for more details see appendix A). In Fig. 2.9 and Fig. 2.10 the splitting of the LUMO and HOMO is shown using the previous relations along with the points calculated by DFT. The group-theoretical fit is very satisfactory. Note that the splitting of the LUMO is independent of the orientation of the molecule when only coupling among the LUMO or to the \(T_{19}\) is considered (see appendix A). Furthermore, relations (2.34) and (2.35) are quite remarkable, as they imply that the contributions of the \(l = 1\) and \(l = 2\) potential lift the degeneracy of the molecular levels in the same way, and thus the total splitting is given by the sum of the \(l = 1\) and \(l = 2\) splittings.
2.2. Molecules in a Layer

In this section a simple model of a C\textsubscript{60} FET is considered. As mentioned above a FET can be understood as capacitance where one plate is the gate and the other plate is the material (here C\textsubscript{60}) which is investigated. An analysis of this device, in particular the calculation of the charge distribution, was done in the previous section. It was found, that the charge concentrates on the first layer in the high doping regime. In what follows, we take this as a motivation to consider a single layer of C\textsubscript{60} molecules which acts as a plate of a capacitance. We use the response of a neutral molecule (Tab. 2.5) to describe the electrostatic behavior of the molecules in the layer. The doped charge is taken care of by adding a monopole on every site. The molecules are then exposed to the electric field arising from the gate as well as the monopole fields of the neighboring molecules. In order to simplify the calculation, we assume a perfect lattice, either square, for the (001), or triangular, for the (111) plane of the fcc lattice formed by the C\textsubscript{60} molecules in the bulk. In order for the sites to be equivalent we neglect the non-spherically symmetric part of the electric field.
Table 2.8: Components of the bare and screened potential for the square and triangular lattice with $a/\sqrt{2} = 10 \text{ Å}$. The coefficients are in units of $q/(7 \text{ bohr})^{l+1}$, where $q$ is the charge per $C_{60}$ molecule. Note that $7 \text{ bohr} \approx 3.7 \text{ Å}$ is about the radius of the $C_{60}$ molecule.

<table>
<thead>
<tr>
<th>$lm$</th>
<th>$v^{\text{bare}}_{lm}$</th>
<th>$v^{\text{scr}}_{lm}$</th>
<th>$v^{\text{bare}}_{lm}$</th>
<th>$v^{\text{scr}}_{lm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.862</td>
<td>0.499</td>
<td>0.996</td>
<td>0.530</td>
</tr>
<tr>
<td>20</td>
<td>-0.230</td>
<td>-0.189</td>
<td>-0.280</td>
<td>-0.219</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td>0.039</td>
<td>0</td>
<td>0.053</td>
</tr>
<tr>
<td>40</td>
<td>0.0133</td>
<td>0.0030</td>
<td>0.0177</td>
<td>0.0015</td>
</tr>
<tr>
<td>4c4</td>
<td>0.0174</td>
<td>0.0097</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The response of the $C_{60}$-molecule and use the averaged response given by

$$a_{l_1m_1l_2m_2}^{\text{spher.-sym.}} = \delta_{l_1l_2} \delta_{m_1m_2} \sum_{x_k} \frac{a_{l_1xk,l_2xk}}{2l_1 + 1},$$  \hfill (2.36)

where the sum is taken over all components of the $l_1$ subspace. Since the response of $C_{60}$ for multipoles $l \leq 2$ is isotropic (cf. section 2.2.2), this averaging is exact for $l = 1, 2$.

Because of translational invariance, the total potential is given by

$$V_{\text{tot}}(r) = V^e(r) + \sum_{R_i} V^i(r - R_i),$$  \hfill (2.37)

where the sum is taken over all lattice sites $R_i$. $V^i(r - R_i)$ is potential induced by the molecule on position $R_i$. For $r$ close to the origin and $R_i \neq 0$ this induced potential can be expressed by the multipole moments $Q_{lm}$ (they are the same on all sites due to translational symmetry) and the coefficients $\beta$ given in (2.28):

$$V^i(r - R_i) = \sum_{l_1m_1l_2m_2} \beta_{R_i=0,l_1m_1} R^{l_2m_2}_i Q_{l_1m_1} r^{l_2m_2}_i (r).$$  \hfill (2.38)

At a given site, say $R_i = 0$, the total potential can also be decomposed as $V_{\text{tot}}(r) = V^\text{scr}(r) + V^i(r)$ where the screened potential $V^\text{scr}(r) = V^e(r) + \sum_{R_i \neq 0} V^i(r - R_i)$ contains the external potential $V^e(r)$ as well as the sum of all induced potentials of the other molecules. Relation (2.38) implies that the coefficients of $V^\text{scr}$ can be written as

$$V^{\text{scr}}_{l_1m_1} = V_{l_1m_1} + \sum_{l_2m_2} \chi_{l_1m_1l_2m_2} Q_{l_2m_2}, \quad \chi_{l_1m_1l_2m_2} = \sum_{R_i \neq 0} \beta_{R_i=0,l_1m_1} R_i l_2m_2.$$  \hfill (2.39)
2.2. Polarization and Stark splitting in field-doped $\text{C}_{60}$

Figure 2.11: Screened potential $V^{\text{scr}}$ across the layer with the parameters from Tab 2.8 for the square and triangular lattice. The gate is assumed to be on the left. The lower lines correspond to a cut through the center of the molecule whereas the upper lines are along half-circles with the radius of the molecule ($7 \text{ bohr} \approx 3.7 \text{ Å}$).

Note that the matrix $\chi$ is entirely given by geometry. The screened potential $V^{\text{scr}}$ induces a potential $\Delta V^i$ as given in equation (2.19). Therefore the total induced potential is $V^i = V^{i,0} + \Delta V^i$ with components

$$Q_{l_1m_1} = Q_{l_1m_1}^0 - \sum_{l_2m_2} \alpha_{l_1m_1l_2m_2} V^{\text{scr}}_{l_2m_2}.$$  \hfill (2.40)

Equations (2.39) and (2.40) can be combined by eliminating the coefficients $Q_{l_1m_1}$ which yields

$$V^{\text{scr}}_{l_1m_1} = \sum_{l_2m_2} \left[ 1 + \chi l_1m_1l_2m_2 \right]^{-1} \chi_{l_1m_1l_2m_2} V_{l_2m_2}^{\text{bare}},$$  \hfill (2.41)

$$V_{l_1m_1}^{\text{bare}} = V_{l_1m_1}^{\text{bare}} + \sum_{l_2m_2} \chi_{l_1m_1l_2m_2} Q_{l_2m_2}^0,$$  \hfill (2.42)

where the $V_{l_1m_1}^{\text{bare}}$ describes the bare potential arising from the external potential (the electric field of the gate) and intrinsic moments of the molecules (the induced charge, i.e. monopoles). The square (triangular) lattice in the presence of the electric field has the rotational symmetry $C_{4v}$ ($C_{6v}$). As a consequence, only components with these symmetries are non-zero and therefore they are given by $\text{Re}(Y_{lm})$ with $m$ a multiple of 4 (6). Using relation (2.41) and (2.42) the screened potential can
be calculated. The non-zero components entering (2.42) are the monopole charge \( q_0 = q \) and electric field \( V_{10} = -E_{\text{Gate}} \). As the FET is overall neutral \( E_{\text{Gate}} = -2\pi q/A_{\text{MOL}} \) with \( A_{(001)} = a^2/2 \) for the square lattice and \( A_{(111)} = \sqrt{3}a^2/4 \) for the triangular lattice. The results are given in Tab. 2.8 and graphically depicted in Fig. 2.11. The components \((lm) = (10), (20)\) are most dominant and higher ones are at least one order of magnitude smaller. This justifies a posteriori the assumption of spherical symmetry because (2.36) is exact for \((lm) = (10), (20)\). From Fig. 2.11 it can be seen that the electric field is efficiently screened within the layer. Note that decrease of the electric field yields negative sign of \( v_{20} \) in Tab. 2.8. We also have checked the influence of adjacent layers of \( C_{60} \) and of a close-by dielectric (with a dielectric constant \( \varepsilon = 10 \)). The effects on the parameters in Tab. 2.8 were less than 2%. The reason is that the field inhomogeneities induced by a 2D lattice of multipoles decay exponentially outside the lattice.

### 2.2.5 Splitting in self-consistent multipole field

We are now in the position to estimate the effect of the external field on the electronic structure of the \( C_{60} \) molecules in the monolayer which is charged by the carriers. To do so we have performed density functional calculations for a molecule in the self-consistent multipole fields as determined in the previous section (cf. Tab. 2.8). Fig. 2.12 shows the splitting of the molecular levels in the self-consistent field for a (001) monolayer, where the molecule is oriented with one of its two-fold axes pointing in the direction of the external field. The maximum energy difference between split states is given in Tab. 2.9 and compared to the result from the perturbative formula (2.34) and (2.35), which is in good agreement for \(|q| \leq 2\). As Fig. 2.13 demonstrates, similar results are obtained for other geometries. As mentioned above,
Figure 2.12: Splitting of the molecular levels of a C\textsubscript{60} molecule in the self-consistent multipole potential (l \leq 2) for a (001) monolayer (square lattice) in a homogeneous external field as a function of the induced charge. The molecule is oriented such that one of its two-fold axis points in the direction of the external field (perpendicular to the monolayer). The top panel shows the positions of the split (from bottom to top) $H_{g}$, $G_{g}$, $H_{u}$, $T_{1u}$, and $T_{1g}$ levels. The bottom gives the splitting of the $H_{u}$ (HOMO) and $T_{1u}$ (LUMO) levels relative to their respective center of gravity.

Equations (2.34) and (2.35) imply that the splittings caused by $(lm) = (10), (20)$ potentials are essentially additive. Changing from electron to hole doping, the sign of $V_{20}$ in (2.34) and (2.35) changes whereas the sign of $V_{10}^{2}$ is, obviously, always positive. Thus, we expect the two contributions to the level splitting to add up for one type of doping, while they should compensate for the other. In fact, for electron doping, the splittings of the HOMO seem to almost perfectly cancel, while upon hole doping the splitting of the HOMO is essentially doubled compared to the splitting...
caused by the screened homogeneous field alone. Thus for the HOMO, the splittings happen to add up for an external field that induces hole carriers into that orbital — a situation that is particularly unfavorable for hole doping. For the LUMO the situation is similar: For an external field that induces electrons in the LUMO the splitting is enhanced. So it turns out that the contributions of the higher multipoles conspire to enhance the splitting of the orbital that carries the induced charge. For both, HOMO and LUMO, the splitting becomes comparable to the respective band width for a field that corresponds to about two charge carriers per molecule.
To estimate the effect of the Stark splitting on the density of states (DOS), we have performed tight-binding calculations for the (001) monolayer (square lattice), assuming the unidirectional structure (two-fold axis of the molecules pointing in the direction of the external field). The basis for the tight-binding Hamiltonian and the hopping matrix elements were taken from the parametrization given in Ref. [37]. The splittings shown in Fig. 2.12 were then used to derive an on-site coupling between the different orbitals. In the case of the LUMO, the on-site coupling is diagonal and reduces to orbital dependent on-site energies. The DOS for the LUMO (T₁u) and the HOMO (H_u) bands calculated with this model for different charging are shown in Fig. 2.14 and 2.15, respectively. We find that already for an induced charge of one carrier per molecule the change with respect to the unperturbed DOS is sizable. For q = −2 one of the T₁u-bands is already completely separated from the other two. Also, the HOMO DOS for q = 2 is quite modified and develops a gap for q = 3. We thus conclude that beyond filling |q| = 2 the electronic structure is distorted so much that the picture, where electrons or hole are filled into rigid bands, breaks
The calculation of the density of states in a minimal tight-binding basis involves, of course, approximations: First, in the lattice, not only hopping between LUMO (HOMO) levels is allowed, but also hopping via energetically close-by levels. An orbital at $\Delta \varepsilon$ away will give a contribution to the hopping of about $t^2/\Delta \varepsilon$, where $t$ is the hopping matrix element from the orbital, that we consider explicitly, to the orbital at $\Delta \varepsilon$. The influence of this effect on the hopping between molecules was studied in Ref. [37] and changes of the order of 5% were found. More importantly, due to the deformation of the molecular orbitals in the field, the hopping matrix elements between the HOMO or LUMO orbitals will change. For a simple estimate, we have performed tight-binding calculations of a $C_{60}$ molecule in an external ho-
mogeneous field and determined the average hopping matrix element between the $t_{1u}$-orbitals following the approach of Ref. [51]. We find that the change in the hopping matrix elements depends strongly on the orientation of the molecules. Typical changes are on the order of 10–20%.

**Discussion**

We have analyzed the changes in the electronic structure of a $C_{60}$ monolayer in which charge carriers are induced by the application of an external homogeneous electric field. We find that the effective field seen by each molecule in the monolayer is strongly screened, but that there are additional higher multipole potentials. Although these components are considerably weaker than the screened homogeneous field, for even $l$, they give a significant contribution to the level splitting as they are of first order. In addition the $l = 1$ (homogeneous field) and $l = 2$ potentials split the HOMO and LUMO in almost the same way, so the splittings they produce add up or counteract, depending on the sign of the external field. For both, the HOMO and the LUMO, the signs turn out to be such, that the splitting is enhanced when the charge is induced in the respective level. Thus the level that carries the field-induced charge is strongly changed by the effective field — a particularly unfavorable situation if one wants to achieve doping, i.e., filling of a level without substantially changing its electronic structure.

To summarize, it seems safe to conclude that the physics of field-effect devices based on $C_{60}$ as active material should be quite different from that of the alkali-doped fullerenes, at least at doping levels beyond two carriers per molecule.
2.3 Interface steps in field effect devices

In this section the effect of interface steps in FET devices is considered. Steps occur as imperfections when growing crystals \([19, 20]\), or can be created artificially. Naturally, one expects that steps act as barriers in the transport channel confined to the surface. Below we show under what circumstances this effect should be important, and that the transmission through the step depends exponentially on the electric field and the step height. Therefore, at high enough doping, a step cuts the transport channel and may present a severe problem. This may be particularly important in organic FETs where the step height is given by the molecular size and therefore is quite big. However, in superconducting FETs the step-barrier can act as a weak link and give rise to a Josephson junction where the critical current depends exponentially on the applied field. This might be an interesting way to design a dissipation-free switch in a superconductor \([52]\).

2.3.1 Charge distribution in MISFET and SUFET

We distinguish two types of field effect transistors. The term metal-insulator-semiconductor FET (MISFET) is used for a whole class of devices where the intrinsic carrier density of the semiconductor is negligible \((N_i \approx 0)\) in the absence of the electric field. The electric field serves to induce a conducting space-charge layer on the surface (see Fig. 2.16). In contrast to this, in the superconducting FET (SUFET), the semiconductor is replaced by a superconductor or metal (above \(T_c\)) which has a finite carrier density \(N_i\). In this case the electric field alters the density which, for example, may change the superconducting \(T_c\). In both cases the electric field induces a surface charge which screens the field. However, the extension \(z_0\) of the surface charge perpendicular to the interface differs for MISFET and SUFET due to the difference in \(N_i\). As a surface step of height \(h\) is expected to be important for \(h \gtrsim z_0\), we first give a rough estimate of \(z_0\) for both cases.

In section 2.1 the charge profile of a \(C_{60}\)-based FET was studied in detail. In

![Figure 2.16: Schematic picture of field effect transistor (FET).](image)
the present section, we restrict our considerations to FET devices in general and therefore need an estimate of the charge profile which can be easily applied to FET devices based on arbitrary materials. The appropriate choice is given in Ref. [36] where the space-charge layer in a continuous medium is treated. This approach is fairly general as it involves only a few material parameters which usually are known. In addition, as discussed in section 2.1, the results are in agreement with our discrete model for C60 in the range of low and moderate doping. Below we follow Ref. [36] and refer to this work for more details. In the case of a perfectly flat and infinite interface, the wavefunction of the carriers can be separated into a plane-wave part parallel to the interface and a transverse part \( \zeta(z) \), where the \( z \)-direction is perpendicular to the interface. The charge profile is then given by \( n(z) \propto \zeta(z)^2 \). The transverse function \( \zeta \) is best calculated using a trial wavefunction for the lowest subband, such as the Fang-Howard trial wavefunction \( \zeta(z) \propto z \exp(-bz/2) \), where \( b \) is the variational parameter. We use this ansatz which is sufficient for our purpose, although more accurate trial functions exist [53].

Minimizing the energy with respect to \( b \) yields the average distance \( z_0 \) of the charge distribution from the interface and the width \( w \) of the distribution:

\[
\begin{align*}
    z_0 & = \langle z \rangle = \frac{3}{b} \left( \frac{18 \varepsilon_s \hbar^2}{11 \pi m_z e^2 n_0} \right)^{\frac{1}{3}} , \\
    w & = \sqrt{\langle z^2 \rangle - \langle z \rangle^2} = \frac{z_0}{\sqrt{3}} .
\end{align*}
\]  

(2.43)  

(2.44)

In the equation above \( \varepsilon_s \) is the dielectric constant of the semiconductor, \( m_z \) its effective mass in the \( z \)-direction and \( n_0 \) the induced surface carrier density. Note that we use a small \( n \) for surface density and a capital \( N \) for the volume density. Estimates of \( z_0 \) are given in Tab. 2.10. Parameters for the Si-FET are standard and given in the literature. At the highest possible fields, \( z_0 = 12 \, \text{Å} \), which corresponds to a few unit cells. Pentacene was chosen as an example for an organic MISFET because such devices were experimentally realized by several groups [19, 20, 18, 21, 22, 26]. In addition, theoretical bandstructure calculations are available [54]. Finally, the conclusions on the pentacene MISFET should also apply to other, related compounds such as tetracene or rubrene organic MISFET [21, 22, 23, 24, 25]. The parameters used here were taken from the thin film transistor presented in Ref. [18]. Only the effective mass \( m_z \) is not accessible by experiment and has to be estimated from band-structure calculations. Theoretical calculations yield a hopping \( t_z = 0.47 \, \text{meV} \) between the pentacene molecules in the \( z \)-direction [54]. Assuming a tight-binding band, the effective mass at the minima of the band is given by \( m_z = \hbar^2/(2 a^2 t_z) \), where \( a = 15.5 \, \text{Å} \) is the layer spacing in the \( z \)-direction [19, 20]. This yields \( m_z = 0.34 \, m_0 \). Using the surface carrier density \( n_0 = 2 \times 10^{13} \, \text{cm}^{-2} \) at the breakdown field (see Tab. 2.10), equation (2.43) gives then \( z_0 = 20 \, \text{Å} \) which is of the same order as
the layer spacing. Hence, molecular steps, as are observed when growing films, may be important in such devices [19, 20].

In the case of SUFETs the superconductor has a finite density $N_i$ of carriers which give raise to metallic screening. Electric fields are screened within the Thomas-Fermi screening length $\lambda_{TF}$. Therefore $z_0 \approx \lambda_{TF}$ for SUFETs. In cuprates (e.g. $\text{YBa}_2\text{Cu}_3\text{O}_7$) $N_i \approx 1-5 \times 10^{21}$ cm$^{-3}$ and the Thomas-Fermi screening length is estimated to be 5-10 Å (Ref. [17]). This is larger than the width of the superconducting layer (3 Å), but smaller then the unit cell ($a = 15$ Å), which means that only the first superconducting layer is affected by the electric field. Therefore, it is important that the transport in the SUFET occurs only in the first layer. Note that in a SUFET the drain and source electrodes usually contact the first layer (see Fig. 2.16).

However, the Josephson coupling among layers leads to a shortcut through the bulk. There are different possibilities to resolve this problem: (a) one uses a very thin superconductor which, ideally, is only one unit cell thick [55]. (b) The distance between superconducting layers is increased in order to suppress the Josephson coupling [56]. (c) The interlayer Josephson coupling is suppressed e.g. by a parallel magnetic field (Fraunhofer like pattern). In Ref. [55] possibility (a) was realized and changes in $T_c$ as well as an insulating phase were induced by the field effect. The ferroelectric $\text{Pb(Zr}_x\text{Ti}_{1-x})\text{O}_3$ was used as a gate dielectric and a surface carrier density $n_0 = 7 \times 10^{13}$ cm$^{-2}$ was achieved. The superconductor consisted of 1 to 2 unit cells of $\text{GdBa}_2\text{Cu}_3\text{O}_7-x$. Similarly, a single superconducting CuO$_2$-layer has been created due to inhomogeneous oxygen doping (resulting in a distribution of $T_c$ in the layers) on the surface of a $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ single crystal in Ref. [57]. Again, in this device the physics is confined to a small region at the interface and steps should play an important role. In particular, when the sample is superconducting, a step may induce a weak link. This effect can be of particular relevance in highly anisotropic layered superconductors such as the high-$T_c$ material $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ or intercalated ($\text{LaSe})_{1.14}\text{NbSe}_2$, see Ref. [58], where the thickness/coherence length $\xi \approx 3$ Å of the superconducting (CuO$_2$ or NbSe$_2$)-layers is much smaller than their distance ($d \approx 15$ Å), i.e. atomic-size steps can naturally constitute a weak link (case b).

In the following we solve first the problem of an interface step of a perfect conductor exposed to a perpendicular electric field. This is a good approximation for $h \gg z_0$ and yields an induced dipole. Knowing the charge dipole, the potential barrier across the step is calculated using the Thomas-Fermi approximation. Finally, the transmission coefficient for tunneling through the step is calculated in the WKB approximation.
Table 2.10: Comparison between different FETs. $\varepsilon_d$ and $\varepsilon_s$ are the dielectric constants of the dielectric and the semiconductor respectively. $m_z$ is the effective mass in the z-direction. $N_i$ is the intrinsic carrier density, $E_b$ is the sample dependent breakdown field and $n_0 = E_b\varepsilon_d/(4\pi e)$ is the maximum surface carrier density. $z_0$ is the distance of the charge distribution from the interface. $h$ is the step height which, for pentacene and GdBa$_2$Cu$_3$O$_{7-x}$, was taken to be the layer spacing in the z-direction. $n_i = N_i h$ is the intrinsic surface carrier density in a single layer. $k_F = \sqrt{2\pi(n_i + n_0)}$ is the Fermi-wave vector. $\langle T \rangle$ is the average transmission coefficient. $^a$Ref. [16], $^b$Ref. [18], $^c$Ref. [55], $^d$Ref. [36], $^e$See text, $^f$Ref. [17].

2.3.2 Perfect conductor approximation

In the geometry with a step of height $h$ along the y-direction (see Fig. 2.17) we model the interface by a two-dimensional grounded conductor with a potential difference $V_G$ to the gate in distance $d$. This approximation becomes exact, if the thickness of the charged area is small compared to the step height, $z_0 \ll h$. Far from the step the electric field is homogenous, $E_0 = V_G/d \approx V_G/(d + h)$, but it is distorted near the step, as a surface charge is induced there in order to compensate the potential difference $\Phi_0 = eV_G h/d$, which is realized for a flat interface with a homogeneous charge distribution. The typical equipotential curves near the step are shown in Fig.(2.18). As the system is invariant in the y-direction, we can use the conformal transformation (in the xz-plane)

$$u = x + iz = \frac{h}{\pi} \left[ \sqrt{w^2 - 1} + \log \left( w + \sqrt{w^2 - 1} \right) \right],$$

(2.45)
which maps the upper half complex plane onto the domain above the step, the cuts being on the positive real axis. The solution for the potential is then given by

$$\Phi(x, z) = -\frac{E_0 h}{\pi} \text{Im}[w(u = x + iz)]. \quad (2.46)$$

Far from the step, $w(u)$ from equation (2.45) can be expanded in orders of $h/\sqrt{x^2 + z^2}$, which yields the approximate expression

$$\Phi(x, z) = -E_0 \left(\frac{z - h}{\pi} \frac{\theta(x, z)}{x} \right), \quad \sqrt{x^2 + z^2} \gg h, \quad (2.47)$$

where $\theta$ is the polar angle in the $xz$-plane. In general, the surface charge of a perfect conductor is given by $n = \varepsilon_d E_\perp/(4\pi\varepsilon)$, where $E_\perp$ is the electric field being perpendicular to the interface and $\varepsilon_d$ is the dielectric constant of the gate insulator. Using equation (2.47) for the potential yields the asymptotic charge distribution ($x \gg h$)

$$n(x) = n_0 \left(1 - \frac{1}{\pi} \frac{h}{x}\right), \quad (2.48)$$

with the doping $n_0 = \varepsilon_d E_0/(4\pi\varepsilon)$. The exact solution is given by the parametric expression

$$n(x, z) = n_0 \left|\frac{1 - w(u)}{1 + w(u)}\right|^{\frac{1}{2}}, \quad (2.49)$$

where $w(u)$ is given by Eq. (2.45) and $u = x + iz$ is taken on the surface of the conductor. The exact result as well as the approximation equation (2.48) are shown in Fig 2.19. Obviously, the electric field induces a dipole center at the step which falls off as $x^{-1}$ far from the step.

It can be shown by the exact solution (2.49) that there is a weak divergence ($\sim x^{-1/3}$ or $\sim (h - z)^{-1/3}$ respectively) of the surface charge at the upper corner of the step due to the sharp edge, which enhances the local tunneling rate through the dielectric.
and can therefore serve as a nucleation center for a possible breakthrough of the device. The singularity at the edge can be regularized: (a) at distances from the step smaller than the local $\lambda_{TF}$, where the quantum mechanical exclusion principle comes into play, (b) geometrically due to finite step curvature. In both cases the field enhancement is of the order $(h/\lambda_c)^{1/3}$ where $\lambda_c$ is the cutoff ($\lambda_{TF}$ or finite curvature) which is at least of the order of the atomic scale ($\lambda_c \approx 1 - 2 \, \text{Å}$). Hence, ratios $h/\lambda_c$ might be of the order 10 - 20 and the field enhancement is expected to be a factor 2 - 3. This is not a big factor, but it should nevertheless be important, because steps are line defects which have a big probability to hit a “weak spot” in the dielectric where an electric breakthrough can occur. Note also that kinks in the step would lead to a further enhancement of the electric field. (c) The singularity can also be regularized due to the finite bandwidth, where the locally induced charge exceeds the filling of the band. This occurs when the potential difference $\Phi_0 = eV_G h/d$ exceeds the bandwidth. For the maximal gate fields $\Phi_0 = E_b h$ which is 2 eV for the Si-MISFET and 0.5 eV for the pentacene MISFET (see Tab. 2.10). In the latter case this is roughly the bandwidth and a complete local charge depletion can be expected [54].

2.3.3 Transmission across the step

As discussed in the introduction, the wavefunctions of the electrons confined to a flat and infinite interface can be separated into a parallel and a transverse part: $\psi_{kj}(r, z) = e^{ikr} \zeta_j(z)$ where $r = (x, z)$ and $k = (k_x, k_z)$ represent coordinate and wavevector parallel to the interface and $j = 0, 1, 2 \ldots$ labels the discrete and confined states in the transverse direction. The energies are given by

$$\epsilon_{kj} = \frac{\hbar^2 k^2}{2m_\parallel} + \epsilon_j. \quad (2.50)$$
Chapter 2. Field effect with strong electric fields

Figure 2.19: Surface charge on the perfect conductor (in units of $n_0$) along the step (distances in units of the step height $h$). Solid line: Exact solution with the divergences $x^{-1/3}$ or $(h-z)^{-1/3}$ at $(x,z)=(0,h)$. Dashed line: Approximate solution (2.48) with the $\sim 1/x$ divergence.

It can be shown that the eigenvalues $\epsilon_j$ of the tranverse part scale as $\epsilon_j \propto E_0^{2/3} \propto n_0^{2/3}$, where $E_0$ and $n_0 = \epsilon_d E_0/(4\pi e)$ are the electric field and the surface carrier density respectively (see Ref. [36]). If only the $j=0$ state is occupied (i.e. the lowest subband), then the system is two-dimensional and the Fermi energy is given by $\epsilon_F = n_0/g$, where $g = m^*/(\pi h^2)$ is the constant density of states. The condition for the occupation of only the lowest subband is $\epsilon_F < \epsilon_1 - \epsilon_0$ which holds for densities $n_0$ below a certain threshold. In Si, this threshold is $3 \times 10^{13}$ cm$^{-2}$ (using the triangular potential approximation, see Ref. [36]) which is of the same order as the maximally achievable surface densities (see Tab. 2.10). Hence, it is not clear, whether only the lowest subband is occupied. However, the presence of a step leads to charge dipole which suppresses the carrier density on the lower side of the step where the condition is then clearly satisfied. As discussed below, it is exactly this region which is of interest when calculating the transmission coefficient through the step. Therefore, we consider in the following only the lowest subband and treat the system as two-dimensional. The non-uniform charge distribution, caused by the step, can be treated in the Thomas-Fermi approximation (TFA) which locally assumes a free (here 2D) electron gas with density

$$n(r) = g\epsilon_F(r) = g[\epsilon_F - V_{\text{loc}}(r)],$$

where $\epsilon_F(r)$ is the spatially dependent Fermi Energy. At this point the result of the previous section enters by assuming that the surface carrier density $n(r) =$
\[ \int dz \, N(r, z) \] of the real system is still well approximated by the perfect conductor approximation (PCA). Note that in the PCA the induced charge is a pure surface charge with zero width and therefore differs from the real charge distribution which has a finite extension in the \( z \)-direction. However, the PCA becomes exact far from the step. Furthermore, knowing the solution of the PCA allows to calculate the local potential \( V_{\text{loc}} \) via relation (2.51). In the following the approximate solution (2.48) of the PCA is used which has the right asymptotics and which permits an analytic calculation of the transmission coefficient. Combining relations (2.48) and (2.51) yields

\[ V_{\text{loc}}(x) = \frac{1}{\pi} \frac{n_0}{g} \frac{h}{x} = \frac{h^2 n_0}{m_\parallel} \frac{h}{x}. \]  

(2.52)

The potential (2.52) acts as a potential barrier across the step for \( x > 0 \). In the WKB approximation the transmission coefficient \( T(k) \) of a mode \( k \) is given by

\[ T(k) = \exp \left( -2 \int_0^{x_0} \sqrt{\left(2m_\parallel h^2\right)\left[V_{\text{loc}}(x) - \tilde{\epsilon}_k\right]} \, dx \right), \]

(2.53)

where \( \tilde{\epsilon}_k = \epsilon_{k_0} - \frac{h^2 k_0^2}{2m_\parallel} = \frac{h^2 k_x^2}{2m_\parallel} \) is the kinetic energy along the \( x \)-direction. Using the local potential (2.52) implies \( x_0 = \frac{n_0 h}{\pi \rho_e} = \frac{2n_0 h}{\kappa_\parallel} \) and yields the analytic result

\[ T(k) = \exp \left( -2\pi n_0 \frac{h}{|k_x|} \right). \]

(2.54)

Not surprisingly, the transmission coefficient depends exponentially on the step height \( h \) and on the electric field which is proportional to the surface density \( n_0 \). In order to calculate the conductance through the step, the average \( \langle T \rangle \) over the Fermi surface of the transmission coefficient enters, which for the parabolic band is

\[ \langle T \rangle = \int_0^{2\pi} \frac{d\varphi}{2\pi} T(k_F \cos \varphi) = f \left( \frac{2\pi n_0 h}{k_F} \right), \]

(2.55)

where the function \( f \) is given by

\[ f(x) = \frac{2}{\pi} \int_0^{\pi/2} d\varphi \, e^{-x/\cos \varphi} \approx \frac{2}{\pi} \frac{e^{-x}}{\sqrt{x}}. \]

(2.56)

The approximate expression is valid for \( x \gg 1 \). In a 2D system with parabolic dispersion the Fermi wave-vector is \( k_F = \sqrt{2\pi (n_i + n_0)} \), where \( n_i \) is the intrinsic carrier density. In the MISFET \( n_i = 0 \) which yields the simple expression \( \langle T \rangle = f(k_F h) \). The conductance through the step is given by the Landauer Formula

\[ G = G_0 \langle T \rangle, \]

(2.57)
where $G_0 = \frac{2e^2}{h} \approx 12.9$ kΩ is the quantum conductance. $N = (2/\pi) k_F L$ is the number of channels for a sample of size $L$ (along the y-direction) taking into account both spins and the condition $-k_F < k_y < k_F$. The functional behavior of $f$ implies that the conductance through steps with height $h > k_F/(2\pi n_0)$ (in the MISFET $h > 1/k_F$) are exponentially suppressed.

Equation (2.55) was applied to the FET examples discussed previously and the results are summarized in Tab 2.10. An arbitrary step height $h = 20$ Å, which might be due to an artificial step, was taken for the Si-MISFET, which yields $\langle T \rangle = 0.06$ for the highest fields. In the pentacene MISFET where $1/k_F = 15$ Å which is almost the same as the interlayer spacing ($a = 15.5$ Å) and which yields $\langle T \rangle = 0.2$ for a molecular step ($h = a$) at the highest achievable dopings. Even more, at half filling, where a claim of superconductivity in pentacene was unconfirmed, the high density $n_0 = 2 \times 10^{14}$ cm$^{-2}$ leads to an even smaller transmission $\langle T \rangle = 2 \times 10^{-3}$ and hence the resulting device is significantly limited by molecular steps [13].

In lower electric fields, for the SUFET below $T_c$, the charge dipole due to the step can form a Josephson junction, which is of the SIS or SNS-type depending on the charge density in the nonsuperconducting region. The critical current $I_c$ through this junction can be estimated for a SNS tunnel junction by the Ambegaokar-Baratoff formula [59]

$$I_c R = I_c G^{-1} = \frac{\pi \Delta}{2e} \tanh \left( \frac{\beta \Delta}{2} \right),$$

where $\Delta$ is the ($s$-wave) gap of the superconductor and $G$ the conductivity from equation (2.57). $\beta$ is the inverse temperature. In this case the critical current $I_c$ depends on the external electric field exponentially via the effective thickness of the insulating region, which enters the tunnel matrix element $T$. A similar exponential dependence $I_c \sim \exp(-l/l_\beta)$ is found in field effect doped SNS-junctions with a large distance $l$ of the superconducting leads, $l \gg l_\beta = (h\beta D/2\pi)^{1/2}$ ($D \sim n^{1/2}$ Diffusion constant in normal metal), while in the opposite limit $l \ll l_\beta$ the critical current depends algebraically on $l$, $I_c \sim 1/l$, see Ref. [60]. In both cases it is seen that the superconducting transport depends sensitively on the local charge density near the step, i.e. can be easily modified by an external electric field.

Note that in a highly anisotropic layered superconductors, such as high-$T_c$-materials an atomic size step can already form a weak link in the absence of the charge dipole effect described here, because the coherence length ($\xi = 3$ Å) of the quasi 2D superconducting layers is smaller than the height $h$ of the step.

**Conclusion**

To conclude, we showed that a charge dipole is induced in the 2D electron gas near an interface step, which can lead to a (Josephson) weak link due to the local depletion of
the charge density. This forms the limiting factor for transport through an ultrathin metallic or superconducting layer and might be used for ultrasmall dissipation-free switches (SUFET). In addition to this, the field enhancement near the step in the insulating barrier can trigger the breakthrough of the dielectric and thereby limit the maximal doping level \( n_{0,\text{max}} \). Both effects are hard to avoid and pose a fundamental challenge in terms of atomically flat interfaces for any FET device with a quasi 2D (super)conducting charge density.
Chapter 3

Variational states for \( C_{60}^{n-} \)

This chapter deals with the ground states of the negatively charged \( C_{60}^{n-} \) ions which are non-trivial because of the Jahn-Teller coupling between the threefold degenerate \( T_{1u} \) LUMO and the fivefold degenerate \( H_g \) phonons. In addition, for \( n = 2, 3, 4 \), the Coulomb interaction leading to Hund's rule coupling enters the problem as well. The \( T_{1u} \otimes H_g \) Jahn-Teller problem is equivalent to the problem of a \( p \)-state equally coupled to \( E_g \) and \( T_{2g} \) vibrations which occurs in cubic systems such as CaO (See Ref. [14] and references therein). Among others, early work on this subject was done by O'Brien [14, 61, 62]. These papers are mainly concerned with \( C_{60}^{0-} \). Ref. [61] contains numerical diagonalization results for the whole coupling range and analytical results for the strong coupling limit. Later on, this limit was explored further for all fillings \( n = 1 \ldots 5 \) by the same author [63, 64] as well as in the often-cited papers of Auerbach, Manini and Tosatti [65, 66]. Both use a semiclassical (also called adiabatic) approximation to work out an effective Hamiltonian in the strong coupling limit, from which the spectrum can be deduced. Finally, the papers of Auerbach et al. [65, 66], and in more detail the thesis of Manini [67], contain also exact diagonalization results for the spectrum of all charge states in the intermediate coupling range.

In view of all this work dedicated to the \( T_{1u} \otimes H_g \) Jahn-Teller problem one might wonder why we still investigate it. The reason is that, apart from exact diagonalization, there is so far no satisfactory, analytical approach to describe the intermediate coupling regime (which is precisely the regime of \( C_{60}^{0-} \)). Therefore, we present in this work a variational ground state for all couplings which becomes exact in the limit of strong, as well as zero coupling. In addition, the calculation of the energies are mainly analytical. Here we apply the method to the charge states \( n = 1, 2 \) which, by particle-hole symmetry, are equivalent to \( n = 5, 4 \). The case \( n = 3 \) is not treated, but we believe that the proposed method is also be applicable to this case. Naturally, the variational ground state is not exact, but it bears the advantage that it is sim-
ple enough to gain a better understanding of the Jahn-Teller ground state over the whole coupling range. Furthermore, it must noted that the alternative approach, i.e. exact diagonalization, isn’t exact either because the infinite phonon Hilbert space has to be truncated. This means that the exact diagonalization becomes variational as well, but with the important difference that it fails in the strong coupling limit, where a lot of phonons are excited. Some of the ideas we present below are not new, but have already been proposed by other groups [68, 69, 70, 71]. However, we believe that our formalism is particularly well suited to construct the variational ground state. In addition, we present simplifications which reduce the numerical part of the variational method to a minimum. Finally, we develop the formalism as a tool which will be used in the subsequent chapters. Before going into the details in the following sections, we would like to sketch the main idea of the approach. At the same time, an account of older works shall be given, along with comments on our contribution to the subject.

First consider a simple model of one electronic orbital coupled to a single phonon. The Hamiltonian of such a system is (in standard notation) \( H' = a^\dagger a + g c(c^\dagger c(a^\dagger + a)) \) where the phonon frequency is set \( \omega = 1 \) and \( g \) is the dimensionless electron-phonon coupling constant. The ground state of the system with one electron is the product state \( \Psi_0 = |0\rangle_e \otimes | - g\rangle_p. \) The state \( | - g\rangle_p \) is a coherent phonon state, hence, an eigenvector of \( a \) with the eigenvalue \(-g\). The idea is to construct a similar state for the more complicated \( T_{1u} \otimes H_g \) Jahn-Teller problem. In order to do this we write the Hamiltonian in the form \( H = N_p + g(A_{ep}^\dagger + A_{ep})/\sqrt{2}. \) \( N_p \) is the phonon number operator and \( A_{ep} \) the part of the linear electron-phonon coupling term which contains the phonon annihilation operator and which corresponds to the term \( c^\dagger c a \) in \( H \). The difference to the simple Hamiltonian \( H' \) is that \( A_{ep}^\dagger \) and \( A_{ep} \) don’t have simple commutation relations such as \( a^\dagger a \). This is the reason why the \( T_{1u} \otimes H_g \) Jahn-Teller problem can’t be solved by a canonical transformation. Still, as a variational ground state, we use wavefunctions which are eigenfunctions of \( A_{ep} \). Such states are also of the form \( |\Psi\rangle = |\psi\rangle_e \otimes |q\rangle_p. \) \( |\psi\rangle_e \) is the electronic part and \( |q\rangle_p \) is a coherent state in the five-dimensional phonon space where the average displacements of the five phonon directions are given by the vector \( q \). Such states are called (generalized) Glauber states and go back to the work of Glauber on coherent states in the radiation field [72]. Glauber states were first generalized to the \( T_{1u} \otimes H_g \) Jahn-Teller problem by Judd and Vogel in order to study the strong coupling limit [68]. As will be discussed below, the Hamiltonian has accidentally \( SO(3) \) symmetry because it is equivalent to the problem of \( p \)-electrons on a spherical shell interacting with \( d \)-phonons of the same shell. As a consequence, eigenstates of the Hamiltonian have good angular momentum quantum numbers. Moreover, any rotated state \( U(\Theta)|\Psi\rangle \), where \( U(\Theta) \) is the rotation operator and \( \Theta = (\phi, \theta, \gamma) \) are the Euler angles, is an equally good variational function and has the same eigenvalue with respect to \( A_{ep} \). However, the state \( |\Psi\rangle \) is a statically distorted state and is
generally not an eigenstate of the total angular momentum. Therefore, a better trial function is obtained by projecting $|\Psi\rangle$ onto an angular momentum subspace by the use of the a projection operator $P_{lm} \propto \int d\Theta D_{mm}^l(\Theta)U(\Theta)$ where $D_{mm}^l(\Theta)$ is the Wigner D-function. The state $P_{lm}|\Psi\rangle$ is still an eigenstate $A_{\text{ep}}$ and has the same eigenvalue as $|\Psi\rangle$. It is a dynamically distorted state and gains energy from the phonon term $N_p$ through delocalization of the distortion. This projection was also introduced in the work of Judd and Vogel [68]. They considered the case of $C_{60}$ for strong coupling and their wavefunction for $C_{60}$ is the same as we use in this work. Later on, Chancey showed that states $P_{lm}|\Psi\rangle$ reduce to correct eigenstates of the Hamiltonian in the small coupling limit and gave approximate analytic expressions for the expectation value of the ground state [69]. Recently, this expectation value was calculated numerically by Dunn et al. who also introduced a proper definition of the projection operator $P_{lm}$ [70]. The same group extended the approach to $C_{70}$ [71]. However, the numerical calculations were quite involved as the calculation of the expectation value $\langle \Psi | H P_{lm} | \Psi \rangle$ resulted in four-dimensional integrals due to the two integrations in the operator $P_{lm}$. Surprisingly, at least to our knowledge, up to now nobody used the fact that $H$ is a scalar and therefore $[H, P_{lm}] = 0$. Using this property, the same expectation value is given by $\langle \Psi | H P_{lm} | \Psi \rangle$ because $P_{lm}^2 = P_{lm}$. As will be shown, this reduces the number of integrals to one which can be handled easily by a mathematica notebook. Thanks to this simplification we are able to push this approach further. Furthermore, we use the magnitude $q = |q|$ of the distortion as a variational parameter which improves the ground state energy. Additional improvements are discussed by using linear combinations with higher excited states. Special care is also given to the fact that there are multiple phonon modes in $C_{60}$. We will show that the effective mode approximation introduced by O'Brien [62] is a variational approach and that it turns out to be a very good approximation for the parameters of $C_{60}$.

### 3.1 Definition of the $T_{1u} \otimes H_g$ Jahn-Teller problem

#### 3.1.1 Hamiltonian

In what follows, we use similar notations and conventions as Chancey and O'Brien [64]. The derivation of the electron-phonon interaction term in the Hamiltonian is inspired by Ref. [65]. The $T_{1u} \otimes H_g$ Jahn-Teller problem is closely related to the five-dimensional quadrupole oscillator often encountered in nuclear physics [73]. As shown in Tab. 2.4, the $l = 1, 2$ IR's of SO(3) don't split under the icosahedral point group $I_h$ and correspond to $T_{1u}$ and $H_g$ IR's of $I_h$ respectively. Therefore, the Hamiltonian of the $T_{1u} \otimes H_g$ Jahn-Teller problem can be formulated in terms of spherical harmonics and the Hamiltonian recovers accidentally SO(3) symmetry. In order to
show this we introduce the bosonic field $\phi(\Omega)$ and the fermionic field $\psi_s(\Omega)$:

$$\phi(\Omega) = \sum_{m=-2}^{2} Y_{2m}(\Omega) a_m, \quad \psi_s(\Omega) = \sum_{m=-1}^{1} Y_{1m}(\Omega) c_{ms},$$

(3.1)

$a_m$ and $c_{ms}$ are the annihilation operators for $H_g$ ($l = 2$) vibrations and $T_{1u}$ ($l = 1$) electrons. $m$ is the z-component of the angular momentum and $s$ is the spin. The vibrational displacement field $\hat{q}(\Omega)$ and its conjugate $\hat{p}(\Omega)$ are defined as

$$\hat{q}(\Omega) = \frac{1}{\sqrt{2}} \left[ \phi^\dagger(\Omega) + \phi(\Omega) \right], \quad \hat{p}(\Omega) = \frac{i}{\sqrt{2}} \left[ \phi^\dagger(\Omega) - \phi(\Omega) \right].$$

(3.2)

Finally, if the electron density is defined by $n(\Omega) = \sum_s \psi_s^\dagger(\Omega) \psi_s(\Omega)$, the Hamiltonian can be written in the elegant form

$$H = \omega \int d\Omega \left\{ \frac{\hat{p}^2(\Omega)}{2} + \frac{\hat{q}^2(\Omega)}{2} - \sqrt{5\pi} \ g \ \hat{q}(\Omega)n(\Omega) \right\},$$

(3.3)

where $\omega$ is the phonon frequency which we set $\omega = 1$ in the following. $g$ the dimensionless coupling constant. The prefactor $-\sqrt{5\pi}$ in front of the coupling term is convention. The integration over the solid angle $\Omega$ in equation (3.3) can be carried out using the relation

$$\int d\Omega Y_{2k}(\Omega) Y_{1m}(\Omega) Y_{1m'}(\Omega) = \sqrt{\frac{3}{10\pi}} \ C_{1m \ 1m'}^{2k}$$

(3.4)

where $C_{1m_1 \ 1m_2}^{km}$ denotes the Clebsch-Gordan coefficient. The Hamiltonian takes the form

$$H = \frac{5}{2} + \sum_{m=-2}^{2} a_m^\dagger a_m - \frac{\sqrt{3}}{2} \ g \sum_{k \ m \ m'} C_{1m \ 1m'}^{2k} c_{ms}^\dagger(-1)^{m'} c_{-m's} \left[ a_k + (-1)^k a_{-k}^\dagger \right].$$

(3.5)

This form of the Hamiltonian has the advantage, that the indices of the creation and annihilation operators are the z-component of the angular momentum. Obviously, the z-component of the total angular momentum is conserved. Note that $H$ conserves the spin of the electrons. Hence, the total spin is a good quantum number of the eigenstates of $H$.

### 3.1.2 Angular momentum

**Conservation of the angular momentum**

An interesting property of the Hamiltonian (3.3) is the conservation of the total angular momentum which is apparent from the definition (3.3). Here we want to show
it more formally and thereby introduce the proper definition of the angular momentum. If \( \mathcal{L}_i \, (i = x, y, z) \) is the angular momentum acting on the spherical harmonics \( Y_{im}(\Omega) \) then the corresponding total angular momentum operator is defined by

\[
L_i = \int d\Omega \left[ \phi^\dagger(\Omega) \mathcal{L}_i \phi(\Omega) + \psi^\dagger(\Omega) \mathcal{L}_i \psi(\Omega) \right], \quad i = x, y, z. \tag{3.6}
\]

\( L_i \) is the generalization of the one particle operator \( \mathcal{L}_i \) to an operator in the Fock space and it is the sum of the electron and phonon angular momentum. Generally, it can be shown that operators generalized to the Fock space still fulfill the same commutation relations as the original one-particle operators. In particular, the operators \( L_i \) fulfill the same commutation relations as the operators \( \mathcal{L}_i \) and therefore are also angular momentum operators. In addition, it can be shown that the following relations hold:

\[
[\phi(\Omega), L_i] = \lambda_i \phi(\Omega), \quad [\phi^\dagger(\Omega), L_i] = \lambda_i \phi^\dagger(\Omega), \tag{3.7}
\]

\[
[\psi(\Omega), L_i] = \lambda_i \psi(\Omega), \quad [\psi^\dagger(\Omega), L_i] = \lambda_i \psi^\dagger(\Omega), \quad i = x, y, z.
\]

Using these relations and the definition of the Hamiltonian (3.3) implies that

\[
[H, L_i] = \int d\Omega \mathcal{L}_i \left\{ \frac{\hat{g}^2(\Omega)}{2} + \frac{\hat{q}^2(\Omega)}{2} - \sqrt{5\pi} g \hat{q}(\Omega)n(\Omega) \right\} = 0. \tag{3.8}
\]

Hence, the total angular momentum is conserved and the eigenstates of \( H \) have good quantum numbers \( l \) and \( m \), independently of the coupling strength \( g \).

**Rotation operator**

Having established the angular momentum operator (3.6) one can go on and define the rotation operator \( U(\Theta) \) in analogy to the rotation operator \( \mathcal{U}(\Theta) \) acting in the space of spherical harmonics:

\[
U(\Theta) = e^{-i\phi L_x} e^{-i\theta L_y} e^{-i\gamma L_z}, \quad \mathcal{U}(\Theta) = e^{-i\phi L_x} e^{-i\theta L_y} e^{-i\gamma L_z}. \tag{3.9}
\]

The matrix elements of \( U(\Theta) \) and \( \mathcal{U}(\Theta) \) in terms of angular momentum eigenstates are the Wigner D-functions:

\[
\int d\Omega Y^*_{im}(\Omega) \left[ U(\Theta) Y_{i'm'}(\Omega) \right] = \langle lm | U(\Theta) | l'm' \rangle = \delta_{mm'} D^l_{mm'}(\Theta). \tag{3.10}
\]

Equivalently, the Wigner D-functions can also be defined by the rotation of angular momentum eigenstates

\[
U(\Theta) Y_{lm}(\Omega) = \sum_{m'} D^l_{mm'}(\Theta) Y_{lm'}(\Omega), \quad U(\Theta) |lm \rangle = \sum_{m'} D^l_{mm'}(\Theta) |lm' \rangle. \tag{3.11}
\]
They form a complete and orthogonal basis. The orthogonality and completeness relations are \[46\]

\[
\int d\Theta \, \tilde{D}_{m_1 m'_1}^l(\Theta) \, \tilde{D}_{m_2 m'_2}^l(\Theta) = \frac{8\pi^2}{2l+1} \delta_{l_1 l_2} \delta_{m_1 m_2} \delta_{m'_1 m'_2}, \tag{3.12}
\]

where the integration is \[\int d\Theta = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\gamma.\] Correspondingly, the delta-function is \[\delta(\Theta - \Theta') = \delta(\phi - \phi') \delta(\cos \theta - \cos \theta') \delta(\gamma - \gamma').\] Finally, one is interested how the annihilation and creation operators transform under rotations. Using the commutators (3.7) and the Baker-Hausdorff formula it follows that

\[
U(\Theta)\phi(\Omega)U(\Theta)^\dagger = U(\Theta)^\dagger \phi(\Omega). \tag{3.14}
\]

Exactly the same relation holds for \(d_{l m}, \psi_{l m}, \psi_{l m}^\dagger\). From the two previous relations and the fact that \(c_{l m}^\dagger = \int d\Omega Y_{l m}(\Omega)\psi_{l m}^\dagger(\Omega)\) (idem for \(a_{l m}^\dagger\)) it follows that the creation operators transform as angular momentum eigenstates

\[
U(\Theta)c_{l m}^\dagger U(\Theta)^\dagger = \sum_{m'=-l}^l D_{m m'}^l(\Theta) c_{m'}^\dagger, \quad U(\Theta)a_{l m}^\dagger U(\Theta)^\dagger = \sum_{m'=-l}^l D_{m' m}^l(\Theta) a_{m'}^\dagger. \tag{3.15}
\]

Hence \(c_{l m}^\dagger\) and \(a_{l m}^\dagger\) are tensor operators of rank 1 and 2 respectively. Taking the conjugate of the previous relations one finds that \((-1)^{m} c_{-m}\) and \((-1)^{m} a_{-m}\) are the tensor operators formed by the annihilation operators.

**Projection operators**

Since the Wigner D-functions are a complete and orthogonal set of functions of \(\Theta\), one can project out components of the rotation operator \(U(\Theta)\):

\[
U_{m m'}^{l} = \frac{2l+1}{8\pi^2} \int d\Theta \, D_{m m'}^l(\Theta) U(\Theta). \tag{3.16}
\]

The matrix elements of the operators \(U_{m m'}^{l}\) with respect to the angular momentum eigenstates are simply given by (using the orthogonality relation (3.12))

\[
\langle l_1 m_1 \vert U_{m m'}^{l} \vert l_2 m_2 \rangle = \delta_{l_1 l_2} \delta_{m_1 m_2} \delta_{m'_1 m'_2}. \tag{3.17}
\]

Hence, \(U_{m m}^{l}\) is just the projection operator onto the angular momentum subspace \((lm)\). In the following we will denote it by \(P_{lm} = U_{m m}^{l}\). Projection operators \(P_{l 0} = U_{0 0}^{l}\) onto \(m = 0\) subspaces involve \(D_{0 0}^{l}(\Theta)\) in the definition (3.16) which is just the Legendre polynomial \(D_{0 0}^{l}(\Theta) = P_l(\cos \Theta)\). Note that \(P_{lm}\) commutes with the Hamiltonian \(H\) because \(H\) is a scalar (tensor of rank 0).
3.1.3 The real representation

Definition of the real representation

For practical purposes, it is often an advantage to work with the real sine and cosine spherical harmonics rather than with the complex spherical harmonics. In this section we present the transformation of various quantities from complex to real spherical harmonics. In order to keep things clear, quantities related to complex spherical harmonics will acquire a tilde. More details are given in appendix B. The transformation is defined by the coefficients $S_{nm}$:

$$Y_{lm}(\Omega) = \sum_{m=-l}^{l} S_{nm} \tilde{Y}_{lm}(\Omega), \quad n = -l, \ldots, l-1, l.$$  \hspace{1cm} (3.18)

The explicit form of the coefficients are given in appendix B. The real spherical harmonics $Y_{ln}$ can be expressed in terms of the real and imaginary parts of the complex spherical harmonics $\tilde{Y}_{ln}$

$$Y_{ln}(\Omega) = \begin{cases} \sqrt{2} (-1)^n \text{Im}(\tilde{Y}_{ln}) & n < 0 \\ Y_{l0} & n = 0 \\ \sqrt{2} (-1)^n \text{Re}(\tilde{Y}_{ln}) & n > 0 \end{cases}.$$ \hspace{1cm} (3.19)

The definition (3.18) determines how all other quantities have to be transformed. Requiring that the field operators $\phi(\Omega)$ and $\psi(\Omega)$ defined in (3.1) remain unchanged yields the transformation laws for creation and annihilation operators

$$c_{ns}^{\dagger} = \sum_{m} S_{nm} \tilde{c}_{m,s}, \quad c_{ns} = \sum_{m} S_{nm} (-1)^m \tilde{c}_{-m,s}.$$ \hspace{1cm} (3.20)

The operators $a_{n}^{\dagger}$ and $a_{n}$ are give by the same rules. Note that the electronic orbitals with $l = 1$ and $n = -1, 0, 1$ have $y, z$ and $x$ symmetry. From definition (3.2) it follows that phonon displacement operator $\hat{q}_{n}$ and the momentum operator $\hat{p}_{n}$ are given by

$$\hat{q}_{n} = \frac{1}{\sqrt{2}} (a_{n}^{\dagger} + a_{n}), \quad \hat{p}_{n} = \frac{i}{\sqrt{2}} (a_{n}^{\dagger} - a_{n}).$$ \hspace{1cm} (3.21)

Using the definition (3.10) of the complex Wigner D-functions $\tilde{D}_{mm'}^{l}$ gives the transformation rule

$$D_{nm'}^{l} = \sum_{mm'} S_{nm} S_{n'm'}^{*} \tilde{D}_{mm'}^{l}.$$ \hspace{1cm} (3.22)

The real Wigner D-functions $D_{nm'}^{l}$ give again the transformation rules for tensor operators, such as creation and annihilation operators, in the real representation:

$$U(\Theta) c_{ns}^{\dagger} U^{\dagger}(\Theta) = \sum_{n'} D_{n'n}^{l}(\Theta) c_{n's}^{\dagger}, \quad U(\Theta) c_{ns} U^{\dagger}(\Theta) = \sum_{n'} D_{n'n}^{l}(\Theta) c_{n's}.$$ \hspace{1cm} (3.23)
3.1. Definition of the $T_{1u} \otimes H_g$ Jahn-Teller problem

The same is valid for $a_n^\dagger$, $a_n$, $\hat{q}_n$ and $\hat{p}_n$. Finally, we shall introduce the Clebsch-Gordan coefficients of the real representation

$$R^{ln}_{l_1n_1,l_2n_2} = \sum_{mn_1m_2} S_{n_1m_1}^* S_{n_2m_2}^* \delta_{nm} C^{\text{lin}}_{l_1m_1,l_2m_2}.$$  \hspace{1cm} (3.24)

The coefficients $R^{ln}_{l_1n_1,l_2n_2}$ can be imaginary.

**Hamiltonian in the real representation**

The Hamiltonian (3.5) can be rewritten in terms of quantities in the real representation. It then takes the form

$$H = \frac{5}{2} + \sum_{n=-2}^{2} a_n^\dagger a_n - \sqrt{\frac{3}{2}} g \sum_{skn'n'} R^{2k}_{ln1n'} c_{n's}^\dagger c_{n's} \hat{q}_k$$ \hspace{1cm} (3.25)

In a wide part of the literature, the last term of (3.5), i.e. the electron-phonon coupling term $H_{ep}$, is written in the form

$$H_{ep} = \frac{g}{2} \sum_s (c_{x_s}^\dagger, c_{y_s}^\dagger, c_{z_s}^\dagger) \left( \begin{array}{ccc} \hat{q}_0 - \sqrt{3}\hat{q}_2 & -\sqrt{3}\hat{q}_{-2} & -\sqrt{3}\hat{q}_{-1} \\ -\sqrt{3}\hat{q}_{-2} & \hat{q}_0 + \sqrt{3}\hat{q}_2 & -\sqrt{3}\hat{q}_{-1} \\ -\sqrt{3}\hat{q}_{-1} & -\sqrt{3}\hat{q}_{-1} & -2\hat{q}_0 \end{array} \right) \left( \begin{array}{c} c_{x_s} \\ c_{y_s} \\ c_{z_s} \end{array} \right),$$  \hspace{1cm} (3.26)

where the basis $(c_{x_s}, c_{y_s}, c_{z_s})$ correspond to $(c_{1s}, c_{-1s}, c_{0s})$. The Hamiltonian can also be written in the form

$$H = H_p + H_{ep} = \frac{5}{2} + N_p + \frac{g}{\sqrt{2}} (A_{ep}^\dagger + A_{ep}),$$  \hspace{1cm} (3.27)

where $N_p = \sum_n a_n^\dagger a_n$ is the phonon number operator and $A_{ep}$ is defined as

$$A_{ep} = -\sqrt{\frac{3}{2}} \sum_{skn'n'} R^{2k}_{1n1n'} c_{n's}^\dagger c_{n's} \hat{q}_k.$$ \hspace{1cm} (3.28)

The operators $A_{ep}$ and $A_{ep}^\dagger$ as defined in equation (3.28) can be understood as annihilation and creation operators because they annihilate or create a phonon. However, they don’t obey simple commutation relations which is the reason why the $T_{1u} \otimes H_g$ Jahn-Teller problem doesn’t have a trivial solution such as the displaced harmonic oscillator.
3.1.4 Parametrization of the $l = 2$ distortions

The Jahn-Teller problem under consideration involves distortions of the molecule which we describe by coherent phonon states of the type

$$|q\rangle_p = \exp\left(-i \sum_{n=-2}^{2} q_n \hat{p}_n \right) |0\rangle_p = \prod_{n=-2}^{2} e^{-i q_n \hat{p}_n} |0\rangle_p. \quad (3.29)$$

The index $p$ indicates that the state belongs to the phonon part of the Hilbert space. The vector $q$ is the average displacement of the phonons and parameterizes the state. The states $|q\rangle_p$ have the following properties:

$$a_n |q\rangle_p = \frac{q_n}{\sqrt{2}} |q\rangle_p, \quad (3.30)$$
$$\langle q|\hat{q}_n|q\rangle_p = q_n, \quad (3.31)$$
$$\langle q'|q\rangle_p = e^{-\frac{1}{2} |q-q'|^2}, \quad (3.32)$$
$$U(\Theta)|q\rangle_p = |D^2(\Theta)q\rangle_e. \quad (3.33)$$

Note that the definition (3.29) differs from the usual definition of a coherent state in that the eigenvalue of the state $|q\rangle_p$ with respect to $a_n$ has an additional prefactor $1/\sqrt{2}$. With this definition, the expectation value of $\hat{q}_n$ is just $q_n$. Property (3.33) is derived from the transformation rule (3.23) and it can be used to parameterized a general state $|q\rangle_p$ in terms of the Euler angles $\Theta = (\phi, \theta, \gamma)$ and two additional
parameters, the magnitude of the distortion $q = |q| > 0$ and the shape parameter $\alpha$:

$$q(q, \alpha, \Theta) = q D^2(\Theta) q_0(\alpha),$$

(3.34)

where $q_0(\alpha) = (0, 0, \cos \alpha, 0, \sin \alpha)$ is a unit vector [64]. The shape parameter has a range $0 \leq \alpha \leq \pi/3$ as is discussed in [73]. A full coverage without repetition in the five-dimensional phase space is obtained for the Euler angles $0 \leq \phi < 2\pi, 0 \leq \theta < \pi/2, 0 \leq \gamma < \pi$ [64]. The influence of the shape parameter $\alpha$ is illustrated in Fig. 3.1 for a spherical surface which is distorted by a radial displacement $u(\Omega) \propto \sum_n q_{0n}(\alpha) Y_{2n}(\Omega)$. Using the explicit form of $D^2(\Theta)$ in the definition (3.34) yields the parametrization

$$q_2 = \frac{\sqrt{3}}{2} \sin^2 \theta \sin 2\phi \cos \alpha + \left[\frac{1 + \cos^2 \theta}{2} \sin 2\phi \cos 2\gamma + \cos \theta \cos 2\phi \sin 2\gamma \right] \sin \alpha,$$

$$q_1 = \frac{\sqrt{3}}{2} \sin 2\theta \cos \phi \cos \alpha - \left[\frac{1}{2} \sin 2\theta \sin \phi \cos 2\gamma + \sin \theta \cos \phi \sin 2\gamma \right] \sin \alpha,$$

$$q_0 = \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2}\right) \cos \alpha + \frac{\sqrt{3}}{2} \sin^2 \theta \cos 2\gamma \sin \alpha,$$

(3.35)

Furthermore, as discussed by O'Brien in Ref. [61], two independent polynomials can be constructed out of $q$ which are invariant under rotations in $SO(3)$, i.e. they don't depend on the Euler angles. These are:

$$q^2 = q_{-2}^2 + q_{-1}^2 + q_0^2 + q_1^2 + q_2^2,$$

$$q^3 \cos 3\alpha = q_0 \left( q_{-2}^2 - 3q_2^2 - 3q_{-2}^2 + \frac{3}{2} q_1^2 + \frac{3}{2} q_{-1}^2 \right) + 3\sqrt{3} \left( q_{-2} q_1 q_{-1} + \frac{1}{2} q_2 q_1^2 - \frac{1}{2} q_2 q_{-1}^2 \right).$$

(3.36)

The relevance of the coordinates defined above becomes apparent when the expectation value of the electron-phonon coupling $H_{ep}$ is taken with respect to the coherent state $|q\rangle_p$:

$$\frac{1}{\sqrt{2}} \langle q| A_{ep}^\dagger + A_{ep} |q\rangle_p = -\sqrt{\frac{3}{2}} \sum_{s k n n'} R^{2k}_{1n 1n'} c_{n's}^\dagger c_{n's} q_k.$$

(3.38)

Obviously, the degenerate $T_{1u}$ orbitals are split if $q \neq 0$. Due to the $SO(3)$ symmetry, the corresponding eigenvalues depend only on the magnitude $q$ and the shape
Chapter 3. Variational states for C\textsubscript{60}–

Figure 3.2: Splitting of the T\textsubscript{1u} levels by the electron-phonon coupling term \( H_{\text{ep}} \) in units of \( q = |q| \) as given in (3.39). The shape parameter varies between \( 0 \leq \alpha < \pi/3 \).

parameter \( \alpha \), The former gives the overall magnitude of the splitting whereas the latter determines the structure. For \( \Theta = 0 \) the splitting becomes diagonal

\[
\frac{1}{\sqrt{2}} (q|A_{\text{ep}}^{\dagger} + A_{\text{ep}}|q)_{p} = q \cos \left( \alpha - \frac{\pi}{3} \right) n_{-1} - q \cos \alpha n_{0} + q \cos \left( \alpha + \frac{\pi}{3} \right) n_{1}, \tag{3.39}
\]

where \( n_{i} = \sum_{s} c_{is}^{\dagger} c_{is} \). The levels are shown in Fig. 3.2.

3.1.5 Effective mode approximation (EMA)

In the case of C\textsubscript{60} there is not only one \( H_{g} \) orbital that couples to the T\textsubscript{1u} LUMO, but there are eight multiplets having different frequencies \( \omega_{a} \) and coupling constants \( g_{a} \). Therefore there are 40 phonon degrees of freedom and the phonon operators acquire an additional index \( a \) which denotes the multiplet. The total Hamiltonian is:

\[
H = \sum_{a=1}^{8} H_{a} = \sum_{a=1}^{8} \omega_{a} \int d\Omega \left\{ \frac{\phi_{a}^{2}(\Omega)}{2} + \frac{\phi_{a}^{2}(\Omega)}{2} - \sqrt{5\pi} g_{a} \hat{q}_{a}(\Omega)n_{i}(\Omega) \right\}, \tag{3.40}
\]

In the same way, the total angular momentum is generalized to

\[
L_{i} = \int d\Omega \left[ \sum_{a=1}^{8} \phi_{a}^{\dagger}(\Omega) L_{i} \phi_{a}(\Omega) + \psi^{\dagger}(\Omega) L_{i} \psi(\Omega) \right], \quad i = x, y, z, \tag{3.41}
\]

and, as above, it commutes with the Hamiltonian: \([L_{i}, H] = 0\). Hence, the states still have good angular momentum quantum numbers. Having defined the angular
3.1. Definition of the $T_{1u} \otimes H_g$ Jahn-Teller problem

momentum operators, the definition of the rotation operator $U(\Theta)$ and the construction of the projection operators $P_n$ is as above. Also, the transformation rules for the operators $a_{\alpha n}, a_{\alpha n}^\dagger, q_{\alpha n}, p_{\alpha n}$ under Euler rotations $\Theta$ remain as given in (3.23). The coherent states are generalized to

$$|\{q_\alpha\}\rangle_p = \exp\left(-i \sum_{\alpha n} q_{\alpha n} p_{\alpha n}\right) |0\rangle_p \tag{3.42}$$

and they have the properties,

$$a_{\alpha n} |\{q_\alpha\}\rangle_p = \frac{q_{\alpha n}}{\sqrt{2}} |\{q_\alpha\}\rangle_p, \tag{3.43}$$

$$\langle \{q_\alpha\}| \{q_\alpha\}\rangle_p = \exp\left(-\frac{1}{4} \sum_{\alpha=1}^8 |q_{\alpha} - q'_{\alpha}|^2\right). \tag{3.44}$$

O'Brien has studied in detail how the multiple mode problem can be reduced to a problem with one effective mode [62]. Here we show that the effective mode approximation (EMA) is, in fact, a variational approach. The main idea is to perform an orthogonal transformation among the different phonon multiplets which leads to new annihilation operators $b_{\alpha n}$. The transformation is defined as

$$a_{\alpha n} = \sum_{\beta=1}^8 O_{\alpha \beta} b_{\beta n}. \tag{3.45}$$

The operators $a_{\alpha n}^\dagger, q_{\alpha n}, p_{\alpha n}$ as well as $\phi_{\alpha}^\dagger$ and $\phi_{\alpha}$ transform the same way. As a consequence, the expression (3.41) for the angular momentum is invariant under such a transformation and all properties concerning rotations are conserved. Using the new phonon operators, the Hamiltonian takes the form

$$H = \omega_0 + \sum_{\alpha \beta n} \omega_{\alpha} O_{\alpha \beta} O_{\alpha \beta} b_{\beta n}^\dagger b_{\beta n} - \sqrt{\frac{3}{2}} \sum_{\alpha \beta \gamma \delta \epsilon \kappa \eta \nu \mu} \omega_{\alpha} g_{\alpha} O_{\alpha \beta} R_{1\nu 1\eta}^{2k} c_{\epsilon \kappa}^\dagger c_{\mu} q_{\beta k} \tag{3.46}$$

where $\omega_0 = \sum_{\alpha}(5/2) \omega_{\alpha}$ is the zero point energy. As a trial function a state is chosen which only contains phonon excitations of the effective mode $b_{1n}$:

$$|\Phi\rangle = F(\{b_{1n}^\dagger, c_{\epsilon \kappa}^\dagger\}) |0\rangle, \tag{3.47}$$

where $F$ is some analytic function. Taking the expectation value of $H$, every phonon operator $b_{\beta \neq 1n}$ annihilates the state $|\Phi\rangle$. As a result the expectation value becomes

$$\langle H \rangle_\Phi = \omega_0 + \sum_{\alpha n} \omega_{\alpha} O_{\alpha 1}^2 \langle b_{1n}^\dagger b_{1n} \rangle_\Phi - \sqrt{\frac{3}{2}} \sum_{\alpha \beta \gamma \delta \epsilon \kappa \eta \nu \mu} \omega_{\alpha} g_{\alpha} O_{\alpha 1} R_{1\nu 1\eta}^{2k} \langle c_{\epsilon \kappa}^\dagger c_{\mu} q_{\beta k} \rangle_\Phi. \tag{3.48}$$
\langle H \rangle_\Phi \text{ is a function of the matrix-elements } O_{\alpha 1} \text{ which can be understood as variational parameters. Minimizing } \langle H \rangle_\Phi \text{ with respect to } O_{\alpha 1} \text{ and taking into account that } O \text{ is an orthogonal matrix yields then}

\begin{equation}
O_{\alpha 1} = \frac{g_\alpha}{g_{\text{tot}}}, \quad g_{\text{tot}} = \left( \sum_{\alpha=1}^{8} g_\alpha^2 \right)^{\frac{1}{2}}.
\end{equation}

Substituting this result back one finds

\begin{equation}
\min_{\{O_{\alpha 1}\}} \langle H \rangle_\Phi \left( \{O_{\alpha 1}\} \right) = \omega_0 + \bar{\omega} \langle H_{\text{eff}} \rangle_\Phi, \quad \bar{\omega} = \sum_{\alpha=1}^{8} \omega_\alpha \frac{g_\alpha^2}{g_{\text{tot}}^2},
\end{equation}

where the effective Hamiltonian is given by

\begin{equation}
H_{\text{eff}} = \sum_{n} b_{1n}^\dagger b_{1n} - \sqrt{\frac{3}{2}} g_{\text{tot}} \sum_{skm} R_{1n1m}^{2k} c_{n,s}^\dagger c_{m,s} q_{1k}.
\end{equation}

The Hamiltonian (3.51) is equivalent to the one-mode Hamiltonian (3.25) above except that there is no zero point energy in (3.51). Using the result (3.49) of the variational procedure and the definition of the transformation \( O \), the effective mode \( b_{1n} \) can be expressed in terms of the old operators \( a_{an} \):}

\begin{equation}
b_{1n} = \sum_{\alpha=1}^{8} O_{\alpha 1} a_{an} = \sum_{\alpha=1}^{8} \frac{g_\alpha}{g_{\text{tot}}} a_{an}.
\end{equation}

Similarly it can be shown that the expectation value of the operator \( a_{an} \) for the state \( \Phi \) is

\begin{equation}
\langle a_{an} \rangle_\Phi = \frac{g_\alpha}{g_{\text{tot}}} \langle b_{1n} \rangle_\Phi
\end{equation}

The two relations are important as they allow the relate the solution of the single, effective mode problem to the multiple mode problem. In conclusion, the ground state energy for a single mode model with the parameter \( g_{\text{tot}} \) and the energy scale \( \bar{\omega} \) yields a variational estimate for the ground state energy of the multiple mode problem. In the following, with one exception, we will estimate the ground state energy of the \( C_{60} \) multiple mode problem by the effective mode approximation. Parameters used in this work are given in Tab. 3.1 and were taken from Manini [67]. This set of parameters goes back to photoemission measurements on gas-phase \( C_{60} \) done by Gunnarsson et al. [74, 75]. Results from theoretical calculations are also available, but they all yield too small coupling constants (see Ref. [76] and references therein). How the difference between between experimental and theoretical comes about is yet unclear. A possible correction to the experimental result (reduction of the coupling coefficients \( g_\alpha \) by 10 \%) might come from thermal broadening, although this effect does not explain the whole difference [76]. As can be seen from Tab. 3.1, \( g_{\text{tot}} \approx 1.5 \). Therefore, \( C_{60} \) is rather in the strong coupling regime \( g \gg 1 \).
3.1. Definition of the $T_{1u} \otimes H_2$ Jahn-Teller problem

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\omega_\alpha$ (cm$^{-1}$)</th>
<th>$\omega_\alpha$ (meV)</th>
<th>$\lambda_\alpha / N(0)$ (meV)</th>
<th>$g_\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_g(8)$</td>
<td>1575</td>
<td>195.3</td>
<td>22</td>
<td>.368</td>
</tr>
<tr>
<td>$H_g(7)$</td>
<td>1426</td>
<td>176.8</td>
<td>20</td>
<td>.368</td>
</tr>
<tr>
<td>$H_g(6)$</td>
<td>1248</td>
<td>154.7</td>
<td>0</td>
<td>.000</td>
</tr>
<tr>
<td>$H_g(5)$</td>
<td>1099</td>
<td>136.3</td>
<td>12</td>
<td>.325</td>
</tr>
<tr>
<td>$H_g(4)$</td>
<td>772.5</td>
<td>95.8</td>
<td>16</td>
<td>.448</td>
</tr>
<tr>
<td>$H_g(3)$</td>
<td>708.5</td>
<td>87.8</td>
<td>12</td>
<td>.405</td>
</tr>
<tr>
<td>$H_g(2)$</td>
<td>430.5</td>
<td>53.4</td>
<td>38</td>
<td>.924</td>
</tr>
<tr>
<td>$H_g(1)$</td>
<td>270</td>
<td>33.5</td>
<td>21</td>
<td>.868</td>
</tr>
<tr>
<td>Eff</td>
<td>581</td>
<td>72.1</td>
<td>-</td>
<td>1.532</td>
</tr>
</tbody>
</table>

Table 3.1: Frequencies and coupling constants for the vibrational modes in CeO as taken from Manini [67]. The set of parameters originates from Gunnarsson [75]. The parameter sets used in [67] and [75] differ marginally in the frequencies. The coupling strength $g_\alpha$ and the electron-phonon coupling $\lambda_\alpha / N(0)$ are related by $g_\alpha^2 = (6/5)\lambda_\alpha / N(0) / \omega_\alpha$.

3.1.6 Coulomb interaction

Electrons in the $T_{1u}$ orbital also interact via Coulomb interaction. This interaction is non-trivial if the number of electrons is $n = 2, 3, 4$ and is also referred to as the Hund's rule coupling. It favors high-spin states. In the following, we use the notation of Ref. [77]. This paper includes an ab initio calculation of the parameters for the Coulomb interaction and gives a review of older results. The Hund's rule coupling term is a scalar (tensor operator with rank 0) and therefore commutes with the angular momentum. It also conserves spin. As a consequence, it splits the charge states $n = 2, 3, 4$ into multiplets characterized by the angular momentum of the electrons and their spin. In the case $n = 2, 4$ there are 15 possible states which split into three multiplets: $1S$, $1D$ and $3P$. In order to denote them, we use the notation of atomic physics where the upper index indicates spin degeneracy and the capital letter gives the total angular momentum of the electrons. For $n = 3$ there are 20 different states which split into $2P$, $2S$ and $4S$. If the interaction of the $T_{1u}$ orbital with neighboring orbitals is neglected, then the energies of these multiplets are expressed by two parameters $U$ and $J$ [77]. The Coulomb term in the Hamiltonian takes the form:

$$H_{ee} = H_U + H_J = \frac{U}{2} N_e (N_e - 1) + \frac{J}{2} \sum_{nmns'} \left( c_{ns}^\dagger c_{ns'}^\dagger c_{ms} c_{ms} + c_{ns}^\dagger c_{ms}^\dagger c_{ns'} c_{ms'} \right) , \quad (3.54)$$

where $N_e = \sum_{ns} c_{ns}^\dagger c_{ns}$ is the number operator for the electrons. For a fixed particle number $n$, the splitting is given by $J$ and listed in Tab. 3.2. As mentioned above, high spin states are preferred. The average energy is $U \approx 3$ eV for an isolated
molecule [77, 42]. This value is strongly screened in the bulk to \( U \approx 1 - 1.5 \text{ eV} \) [42]. The splitting energy \( J \) is smaller by an order of magnitude and results from ab initio calculations vary between 50 meV to 150 meV [77]. For the isolated molecule we use a value \( J = 100 \text{ meV} \). However, in the subsequent chapters, we are interested in the effective \( J \) when \( C_{60} \) molecules form a solid. In such an environment, \( J \) might be screened just as is the charging energy \( U \) [77]. The screened value of \( J \) is accessible in magnetic susceptibility and spin relaxation experiments. Details and references are discussed in sections 3.3.4 where the effective value is found to be \( J = 60 - 80 \text{ meV} \). In the following, we set, for simplicity, \( J = \bar{\omega} \) in calculations which deal with \( C_{60} \) bulk compounds.

### 3.2 \( C_{60}^- \)

In this section we discuss the variational ground state of the Hamiltonian (3.5) for a single electron. The way how a dynamically distorted Jahn-Teller state can be constructed is discussed in detail in the sections 3.2.1 and 3.2.1. The same method will be used in the subsequent section. The limits \( g \to 0 \) (section 3.2.3) and \( g \to \infty \) (section 3.2.4) are carefully examined and it will be shown that the variational wavefunction becomes exact in both limits. In section 3.2.5, improvements of the variational wavefunction are discussed. They are particularly useful for excited states with higher angular momentum. The last section 3.2.6 treats the multiple \( H_g \) modes of \( C_{60} \) beyond the effective mode approximation (EMA) which, thereby, proofs to be a very good approximation.

#### 3.2.1 Static distortion

In order to construct a variational ground state we start with a statically distorted state of the type

\[
|\Psi_0\rangle = |\psi\rangle_e \otimes |q\rangle_p
\]

which is a product state between the electronic state \( |\psi\rangle_e \) and the coherent phonon state \( |q\rangle_p \). Applying the variational state \( |\Psi_0\rangle \) on \( H \) as given in (3.25) and using the

\[
\begin{array}{c|c|c|c|c}
 n & 2S+1A & E_{\text{mult}} & n & 2S+1A & E_{\text{mult}} \\
 \hline
 2, 3, 4 & 1^S & 4J & 3 & 2P & 2J \\
 & 1^D & J & & 2D & 0 \\
 & 3P & -J & & 4S & -3J \\
\end{array}
\]

Table 3.2: Multiplet energies of \( C_{60}^- \) for \( n = 2, 3, 4 \) relative to the average energy (spin degeneracy included). We use \( J = \bar{\omega} = 72.1 \text{ meV} \) for \( C_{60} \) bulk compounds.
relation (3.38) yields
\[ \langle \Psi_0 | H | \Psi_0 \rangle = \frac{5}{2} + \frac{q^2}{2} - \sqrt{\frac{3}{2}} g \sum_{s k n n'} R_{1n1n'}^{2k} q_{k} \langle \psi | c_{n's}^\dagger c_{n's} | \psi \rangle. \] (3.56)

The energy is minimized if \( |\psi\rangle_e \) is the eigenstate of \( H \) to the lowest eigenstate of \( - \sum_{s k n n'} R_{1n1n'}^{2k} q_{k} c_{n's}^\dagger c_{n's} \) in the subspace of one electron. Hence, the electron is put in the lowest level shown in Fig. 3.2 which is given by \( \epsilon_{b}(q) = -g \cos \alpha \). The level itself has minimal energy for \( \alpha = 0 \). Since the energy doesn’t depend on the Euler angles \( \Theta \), we choose them to be zero \( (\phi = \theta = \gamma = 0) \). As can be seen from relation (3.39), the corresponding eigenvector (for \( S_z = 1/2 \)) is then \( |\psi\rangle_e = c_{01}^\dagger |0\rangle_e \). Hence, the choice for the variational wavefunction becomes
\[ |\psi_e(q)\rangle = c_{01}^\dagger |0\rangle_e \otimes |q e_0\rangle_p = c_{01}^\dagger |q e_0\rangle. \] (3.57)

The last part of the equation is a shorter notation where the tensor products are omitted. By construction, \( |\Psi_0(q)\rangle \) is an eigenvector of \( A_{ep} \):
\[ A_{ep} |\Psi_0(q)\rangle = -\frac{q}{\sqrt{2}} |\Psi_0(q)\rangle. \] (3.58)

Under rotations it transforms as
\[ U(\Theta) |\Psi_0(q)\rangle = \sum_{n=-1}^{1} D_{n0}(\Theta) c_{n1}^\dagger |q D^2(\Theta) e_0\rangle. \] (3.59)

Due to the SO(3) symmetry, any rotated state \( U(\Theta) |\Psi_0(q)\rangle \) is an equally valid variational ground state. All these states have the same expectation value of \( H \) which is
\[ \langle \Psi_0(q) | H | \Psi_0(q) \rangle = \frac{5}{2} + \frac{q^2}{2} - gq. \] (3.60)
This energy is minimal for \( q = g \) and where it yields the following upper bound for the ground state energy:
\[ E_{0,n=1}^{stat} = \frac{5}{2} - \frac{g^2}{2}. \] (3.61)

### 3.2.2 Dynamic distortion

An energetically more favorable state is obtained when the static distortion discussed in the previous section is delocalized. This is done by projecting the variational state \( |\Psi_0\rangle \) onto an angular momentum subspace using the projection operators. Hence, the dynamically distorted Jahn-Teller state is of the form \( P_m |\Psi_0(q)\rangle \). Since \( L_2 |\Psi_0(q)\rangle = 0 \), only projections onto \( m = 0 \) subspaces will be non-zero. Furthermore, one can
verify that \( |\Psi_0(q)\rangle \) changes sign under a rotation of \( \pi \) around the \( y \)-axis. This is due to the fact that \( |\Psi_0(q)\rangle \) is odd under inversion. Therefore \( |\Psi_0(q)\rangle \) has only odd angular momentum contributions. The lowest odd angular momentum is \( l = 1 \) and the trial function for the dynamically distorted ground state is

\[
|P_0(q)\rangle = P_{10} |\Psi_0(q)\rangle = P_{10} c_{10} |q e_0\rangle ,
\]

where we have adopted the letter \( P \), as in atomic physics, to indicate that the state has orbital angular momentum \( l = 1 \). The spin degeneracy is not indicated because it is always 2 in the case of one electron. Since \( |\Psi_0(q)\rangle \) is an eigenvector of \( A_{ep} \) (equation (3.58)) and \( [A_{ep}, P_{10}] = 0 \) (\( A_{ep} \) is a scalar), it follows that \( |P_0(q)\rangle \) is also an eigenvector with the same eigenvalue:

\[
A_{ep} |P_0(q)\rangle = -\frac{q}{\sqrt{2}} |P_0(q)\rangle .
\]

The norm of the wavefunction \( |P_0(q)\rangle \) is given by

\[
\langle P_0(q)|P_0(q)\rangle = \langle \Psi_0(q)| P_{10}^2 |\Psi_0(q)\rangle = \langle \Psi_0(q)| P_{10} |\Psi_0(q)\rangle = \frac{3}{8\pi^2} \int d\Theta D_{00}^1(\Theta) \langle \Psi_0(q)| U(\Theta)|\Psi_0(q)\rangle ,
\]

where the definition of the projection operator \( P_{10} \) was introduced in the last equation. In order to evaluate this integral, we need to calculate the matrix elements \( \langle \Psi_0(q)| U(\Theta)|\Psi_0(q)\rangle \) which is a function of the distortion magnitude \( q \) and the Euler angles \( \Theta \):

\[
\langle \Psi_0(q)| U(\Theta)|\Psi_0(q)\rangle = \langle q e_0| c_{01} U(\Theta) c_{01}^\dagger |q e_0\rangle = \sum_{n=-1}^1 D_{n0}^1(\Theta) \langle q e_0| c_{01} c_{n1}^\dagger |q D^2(\Theta) e_0\rangle = D_{00}^1(\Theta) \langle q e_0| q D^2(\Theta) e_0\rangle = \cos \theta \exp \left(-\frac{3}{4} q^2 \sin^2 \theta \right).
\]

This matrix element reflects the properties discussed above. Namely, it has angular momentum \( m = 0 \) and it is odd under inversion (\( \theta \rightarrow \pi - \theta \)). In a next step the expectation value of the Hamiltonian \( H \) with respect to \( |P_0(q)\rangle \) needs to be evaluated. The electron-phonon term of the Hamiltonian is given by \( H_{ep} = g(A_{ep} + A_{ep})/\sqrt{2} \). Since \( |P_0(q)\rangle \) is an eigenvector of \( A_{ep} \) with eigenvalue \( -q/\sqrt{2} \) it follows that

\[
\frac{\langle P_0(q)| H_{ep} |P_0(q)\rangle}{\langle P_0(q)|P_0(q)\rangle} = -gq .
\]
3.2. \( \text{C}_{60} \)

Hence, the energy gain of the Jahn-Teller coupling of the dynamically distorted state is the same as for the statically distorted state. In order to evaluate the expectation value of the phonon energy, the matrix element \( \langle P_0 | N_p | P_0 \rangle \) has been calculated. As in the case of the Norm (3.64), it is given by an integral over Euler angles:

\[
\langle P_0(q)| N_p | P_0(q) \rangle = \frac{3}{8\pi^2} \int d\Theta D^1_{\text{C}_{60}}(\Theta) \langle \Psi_0(q) | N_p U(\Theta) | \Psi_0(q) \rangle. \tag{3.67}
\]

Note that \([N_p, U(\Theta)] = 0\). The evaluation of the matrix element in the integral is done as exercised in derivation (3.65), except that \(N_p\) yields an additional factor \(q^2 D^2_{11}(\Theta)/2\). One obtains

\[
\langle \Psi_0(q)| N_p U(\Theta) | \Psi_0(q) \rangle = \frac{q^2}{2} \cos \theta \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \exp \left( -\frac{3}{4} q^2 \sin^2 \theta \right). \tag{3.68}
\]

Therefore, the contribution from the term \(N_p\) to the energy is given by

\[
\frac{\langle P_0(q)| N_p | P_0(q) \rangle}{\langle P_0(q)| P_0(q) \rangle} = \frac{q^2}{2} \frac{\int_{-1}^{1} t^2 \left( \frac{3}{2} t^2 - \frac{1}{2} \right) e^{-\frac{3}{4} q^2 (1-t^2)} dt}{\int_{-1}^{1} t^2 e^{-\frac{1}{4} q^2 (1-t^2)} dt} = \frac{q^2}{2} h(q), \tag{3.69}
\]

where, in the integrals, the substitution \(t = \cos \theta\) was made. The last equality defines the function \(h(q)\) which varies smoothly from \(h(0) = 2/5\) to \(h(\infty) = 1\) as shown in Fig. 3.3. Putting the different parts together, the expectation value of \(H\) becomes

\[
E^{\text{dyn}}_0(g, q) = \frac{\langle P_0(q)| H | P_0(q) \rangle}{\langle P_0(q)| P_0(q) \rangle} = \frac{5}{2} + \frac{q^2}{2} h(q) - gq, \tag{3.70}
\]

Figure 3.3: Left panel: The function \(h(q)\). Right panel: \(q_{\text{isol}}\), which minimizes the energy \(E_0(g, q)\) given in (3.70), as a function of \(g\).

Apparently, the only difference to the statically distorted case is the factor \(h(q)\) which renormalizes the phonon energy \(q^2/2\). Hence, the contribution of the \(q^2/2\)
term is reduced which is the energy gain due to the delocalization of the distortion. In order to find the ground state energy, $E_0^{\text{dyn}}(g, q)$ has to minimized with respect to $q$ for a given coupling strength $g$. The resulting energy is show in Fig. 3.4. It compares very well with the results from exact diagonalization [65]. In the previous section it was found that the average distortion is $q = g$ in the static case. In the dynamic case, as shown in Fig. 3.3, this ratio is increased by a factor 5/2 for small $g$ and becomes 1 as $g \to \infty$.

### 3.2.3 Asymptotic behavoir for $g \to 0$

For small $g$ the electron-phonon term can be treated within perturbation theory. In the case $g = 0$, the ground state of a single electron in the $T_{1u}$ LUMO is 6-fold degenerate due to the 3 orbital and 2 spin degrees of freedom. The energy of these states is the phonon zero point energy $5/2$. The electron-phonon coupling term connects them to states with a single phonon excitation and energy $5/2 + 1$. Hence, second order perturbation theory for degenerate states has to be used. The correction term is then given by the projection of $H^{(2)} = -H_{ep}^2$ onto the degenerate ground state subspace. Using the coupling term as defined in (3.25), the matrix elements of $H^{(2)}$ in the unperturbed subspace are

$$H_{n's'ns}^{(2)} = -\langle 0| c_{n's'} H_{ep}^2 c_{ns}^\dagger|0\rangle = -\frac{3g^2}{4} \sum_{mnk} R_{1n'1'm}^2 R_{1m1'n}^2 \delta_{ss'} = -\frac{5}{4} g^2 \delta_{nn'} \delta_{ss'}.$$  \hspace{1cm} (3.71)

This is just a constant shift $-5/(4g^2)$. The degeneracy is not split due to the SO(3) symmetry (this, of course, holds for all orders). The result can be compared to the variational solution discussed above. The limit of small coupling implies $q \to 0$ and we therefore need to know the behavior of $h(q)$ for small $q$. The Taylor series of $h(q)$ around $q = 0$ can be calculated analytically expanding the exponents in the definition of $h(q)$. To lowest order one finds $h(q) = \frac{2}{5} + O(q^2)$. Minimizing the energy yields $q = \frac{5}{2} g$ as shown in Fig. 3.3. The ground state energy becomes $E = \frac{5}{2} - \frac{5}{4} g^2$. Hence, the correction agrees with the second order result. Finally, it should be noted that for $q = 0$ the variational wavefunction simply becomes

$$|P_0(q = 0)\rangle = P_{10} c_{01}^\dagger|0\rangle = c_{01}^\dagger|0\rangle$$  \hspace{1cm} (3.72)

which is the correct ground state in the absence of the electron phonon-coupling.

### 3.2.4 Asymptotic behavoir for $g \to \infty$

The limit $g \to \infty$ is discussed in Ref. [64, 65]. In these papers a semi-classical approximation is used which allows to show that the problem becomes equivalent to a rotator with a moment of inertia $I = 3g^2$ and a decoupled three-dimensional
oscillator. The rotator part corresponds to rotations of the static distortion which we have introduced above and the shape of which is illustrated in Fig. 3.1 ($\alpha = 0$). The eigenstates of the rotator are spherical harmonics with angular momentum quantum numbers $(l, m)$. As discussed, in the case of one electron only odd quantum numbers $l$ are allowed. The rotator spectrum is given by $l(l + 1)/(2l) = l(l + 1)/(6q^2)$ [65, 64]. Hence, the energy scale of the rotator excitations vanishes as $g \rightarrow \infty$. Since the rotator has two degrees of freedom, its vanishing energy scale implies that two of the five phonon degrees of freedom become soft (gapless) in the limit $g \rightarrow \infty$. On the other hand, the remaining three degrees of freedom are still harmonic oscillators with frequency 1 and correspond to vibrations around the static distortion.

As discussed above, in the limit $g \rightarrow \infty$ the distortion $q$ is equal to the coupling constant $q = g$. Therefore, we need to investigate the asymptotic behavior of the function $h(q)$ as $q \rightarrow \infty$ in order to deduce the limiting behavior of $E_0(g)$. Since $h(\infty) = 1$, the goal is to find corrections to a certain order in the small parameter $1/q$. This is best achieved by rewriting the integrals (3.64) and (3.67) which involve the integrands (3.65) and (3.68). Since the two integrands are symmetric with respect to $\theta = \pi/2$ it is enough to integrate only over $0 < \theta < \pi/2$. In this interval, the new integration variable $s = (3/4)q^2 \sin^2 \theta$ can be introduced:

\[
\langle P_0(\theta)|P_0(\theta)\rangle = \frac{2}{q^2} \int_0^{\frac{3}{4}q^2} ds e^{-s} \sqrt{1 - \frac{4}{3q^2}s}, \quad (3.73)
\]

\[
\langle P_0(\theta)|N_P|P_0(\theta)\rangle = \frac{2}{q^2} \int_0^{\frac{3}{4}q^2} ds e^{-s} \left(1 - \frac{2s}{q^2}\right) \sqrt{1 - \frac{4s}{3q^2}}. \quad (3.74)
\]

This form of the integrals allows simple expansion in orders of $1/q$ by expanding the square roots and taking the integration boundary to infinity:

\[
\langle P_0(\theta)|P_0(\theta)\rangle = \frac{2}{q^2} - \frac{4}{3q^4} - \frac{8}{9q^6} + O(q^{-8}), \quad (3.75)
\]

\[
\langle P_0(\theta)|N_P|P_0(\theta)\rangle = \frac{2}{q^2} - \frac{16}{3q^4} + \frac{40}{9q^6} + O(q^{-8}). \quad (3.76)
\]

From this limiting behavior follows that

\[
h(q) = 1 - \frac{2}{q^2} + \frac{4}{3q^4} + O(q^{-6}), \quad q \rightarrow \infty. \quad (3.77)
\]

Inserting this into (3.70) yields

\[
E(q) \approx \frac{5}{2} + \frac{q^2}{2} - gq - 1 + \frac{4}{6q^2}. \quad (3.78)
\]
The last two terms come from the $1/q$ corrections in $h(q)$. If the energy is minimized with respect to $q$ one finds $q \approx g + 4/(3g^3)$ and the asymptotic ground state energy

$$E_0(g) \approx \frac{3}{2} - \frac{g^2}{2} + \frac{2}{3g^2} \quad g \to \infty.$$  \hfill (3.79)

The first term is the zero-point energy which has been reduced from $5/2$ to $3/2$ because the asymptotic Hamiltonian contains three harmonic oscillators with frequency $1$. The second term is the Jahn-Teller energy gain and the last term is the energy of the $l = 1$ rotator excitation. The last term differs from the results of Ref. [64, 65] where they find a smaller correction $1/(3g^2)$ for the $P$ state. Hence, the variational ground state energy is correct up to the order $1$ in the limit $g \to \infty$.

Another issue is the question, whether the variational wavefunction $|P_0(q)\rangle$ becomes asymptotically equal to the wavefunction obtained from the semiclassical approximation used in Ref. [64, 65]. This is indeed the case as is shown in a rather lengthy calculation done in appendix C.

### 3.2.5 Improvement of the variational ground state

Having established a variational wavefunction for the ground state, one naturally wonders whether excited states can be constructed as well, and, closely related, how the variational ground state can be improved. In this section we shall sketch some proposition how this can be done.

The nature of the excitation spectrum of the $T_{1u} \otimes H_g$ Jahn-Teller problem with a single electron can be understood in the limits $g = 0$ and $g \to \infty$. In the former case, the vibrations are decoupled from the electron and the problem is trivially solved by product states of the electron wavefunction with the eigenfunctions of the unperturbed harmonic oscillators. In the latter case, as discussed in the previous section, there are two types of excitations: soft rotator excitations and excitations of the harmonic oscillators with frequency $1$.

In order to construct the rotator excitations we simply need to project the static distortions onto higher angular momentum subspaces. Hence, the projector $P_{10}$ in equation (3.62) needs to replaced by higher angular momentum projectors $P_{nl}$. By construction, the states obtained in this way are orthogonal to each other as they differ in angular momentum. Therefore the variational minimization procedure is analogous to the one of the $|P_0(q)\rangle$ state. One simply needs to replace the functions $D_{10}^l(\Theta) = P_l(\cos \theta)$ in the integrals (3.64) and (3.67) by a different Wigner D-functions corresponding to a higher angular momentum. In the case of a $m = 0$ we need to replace it by the Legendre polynomial $P_l(\cos \theta)$. Results of rotator excitations $l = 3, 5, 7$ are shown in Fig. 3.4. At moderated coupling, the energies differ quit substantially when compared to the exact diagonalization results.
A more involved issue is how to improve the variational rotator states. The approach presented in the following applies to all rotator states, though I will discuss it in terms of the ground state which is the $l = 1$ rotator state. Due to the variational principle, the ground state is improved by a linear combination of the state $|P_0\rangle$ and some other linearly independent states $|P_i\rangle$ such that $\langle P_i|H|P_0\rangle \neq 0$. The quality of the improved ground state obviously depends on the choice of $|P_i\rangle$. I consider four different choices:

\begin{align}
(i) \quad |P_1(q)\rangle &= H |P_0(q)\rangle \quad \text{(Lanczos)}, \\
(ii) \quad |P_1(q)\rangle &= N |P_0(q)\rangle = \frac{q}{\sqrt{2}} P_{10} a^\dagger_0 |\Psi_0(q)\rangle. \\
(iii) \quad |P_1(q)\rangle &= A_{ep}^1 |P_0(q)\rangle, \\
(iv) \quad |P_1(q)\rangle &= A_{ep}^1 |P_0(q)\rangle, \quad |P_2(q)\rangle = N |P_0(q)\rangle.
\end{align}

The first choice corresponds to a Lanczos step. The second and third choice consist in applying only the phonon term or the electron-phonon interaction term on the ground state. The second choice can also be understood as a static distortion with
Figure 3.5: Energy gain of the improved variational ground states relative to the ground state of the initial wavefunction (3.62). Dotted line: Choice (i). Dashed line: Choice (ii). Solid line: Choice (iii). The energy gain of choice (iv) falls together with the gain of choice (iii). Dash-dotted line: Asymptotic behavior $E_0 \approx -g^2/2 + 3/2 + 1/(3g^2)$ as found from the semiclassical approximation [64, 65].

A phonon excitation which is projected onto the $l = 1$ subspace. Such states have been considered in other works as well [68, 69, 70]. Since $H$, $A^t_{\text{xp}}$ and $N$ are tensor operators of rank 0, the resulting states have still the same angular momentum as $|P_0\rangle$. Note that the three wave-functions in (i) to (iii) and the initial ground state $|P_0\rangle$ are not linearly independent because the relation

$$H|P_0\rangle = \frac{5}{2}|P_0\rangle + N|P_0\rangle + \frac{g}{\sqrt{2}} \left(A^t_{\text{xp}} - \frac{q}{\sqrt{2}}\right)|P_0\rangle$$

holds. Hence, they span a 3-dimensional vector-space. The fourth choice (iv) consists in choosing the trial-function in this 3-dimensional space. All choices depend on the variational parameter $q$. Hence, $|P_0(q)\rangle$ and the additional wave-functions $|P_i(q)\rangle$ span a family of subspaces depending on $q$. The projection of $H$ onto these subspaces has eigenvalues $E_n(g, q)$. $q$ is then chosen such as to minimize the lowest eigenvalue $E_0(g, q)$. Depending on the choice of $|P_i\rangle$, the eigenvalue $E_1$ is an estimate of a harmonic oscillator excitation. The calculations for the different choices were done by a mathematica notebook. Results are shown in Fig. 3.5. The ground state is best improved by the choices (iii) and (iv). In particular, the asymptotic behavior for $g \to \infty$ becomes equal to the results of the semi-classical approximation [64, 65].
excitation energy $E_1(g)$ are shown Fig. 3.6 and compared to the exact diagonalization results [65]. Choice (iv) yields a result in reasonable agreement with the results from exact diagonalization. Finally, choice (3.82) was also applied to higher angular momentum states which yields a big improvement of the rotator energies as can be seen in Fig. 3.4.

3.2.6 Multiple modes

In section 3.1.5, the effective mode approximation was introduced. It is a variational approximation and consists in solving the single mode problem with the parameter $g = g_{\text{tot}}$ and an energy scale $\bar{\omega}$. Results for the ground state energy, also using the improved variational ground states discussed above, are shown in Tab. 3.3. The best result is only 5 % above the exact diagonalization result. In Tab. 3.3, the energies of the $l = 3$ and $l = 5$ rotator excitations are given as well. The smallest excitation energy in the system corresponds to the $l = 3$ rotator excitation and was measured experimentally by spin-relaxation studies [78]. The experimental value is 19 meV, which is quite close to the value from exact diagonalization [67] (26.5 meV). The value obtained from the variational approach (Using EMA with choice (iii), see
Table 3.3: Left table: Ground state energy of the multiple mode Jahn-Teller problem in $C_{60}$ for various variational approaches. EMA stands for effective mode approximation as discussed in section 3.1.5. The exact diagonalization result is from Ref. [67, 75]. Energies don’t contain the zero-point energy $\sum_\alpha \langle 5/2 \rangle \omega_\alpha$. Right table: Comparison of the rotator energies obtained by EMA and choice (iii) (see previous section) with the exact diagonalization results [67].

<table>
<thead>
<tr>
<th>Variational state</th>
<th>$E_0$ (meV)</th>
<th>State</th>
<th>[67]</th>
<th>Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMA, as given in (3.62)</td>
<td>-127.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EMA, improved (i)</td>
<td>-132.4</td>
<td>$P$</td>
<td>-139.6</td>
<td>-132.8</td>
</tr>
<tr>
<td>EMA, improved (ii)</td>
<td>-130.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EMA, improved (iii)</td>
<td>-132.8</td>
<td>$F$</td>
<td>-113.1</td>
<td>-92.0</td>
</tr>
<tr>
<td>EMA, improved (iv)</td>
<td>-132.8</td>
<td>$H$</td>
<td>-85.7</td>
<td>-45.4</td>
</tr>
<tr>
<td>Multiple modes</td>
<td>-129.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exact diagonalization</td>
<td>-139.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

previous section) is substantially higher (40.8 meV).

Instead of improving the ground state within the effective mode approximation (EMA), one might try to generalize the state $|\Psi_0(\theta)\rangle$ to multiple orbitals. The statically distorted state $|\Psi_0(\theta)\rangle$ is generalized to

$$|\Psi_0(\{q_\alpha\})\rangle = c_0^t |0\rangle \otimes \left[ \bigotimes_{\alpha=1}^8 |q_\alpha \phi_0\rangle_{p,\alpha} \right]$$

(3.85)

This wavefunction has eight variational parameters $q_\alpha$ which specify the distortion of each mode. It is an eigenstate of the operators $A_{\alpha}^0$, with the eigenvalues $-q_\alpha / \sqrt{2}$.

The expectation value of the Hamiltonian with respect to this state is

$$\langle \Psi_0(\{q_\alpha\}) | H | \Psi_0(\{q_\alpha\}) \rangle = \sum_{\alpha=1}^8 \omega_\alpha \left( \frac{q_\alpha^2}{2} + \frac{5}{2} - q_\alpha q_\alpha \right),$$

(3.86)

which is minimized by $q_\alpha = g_\alpha$. The dynamically distorted is obtained by projecting $|\Psi_0(\{q_\alpha\})\rangle$ onto an angular momentum subspace:

$$|P_0(\{q_\alpha\})\rangle = P_{10} |\Psi_0(\{q_\alpha\})\rangle,$$

(3.87)

The expectation value of the Hamiltonian with respect to the state $|P_0(\{q_\alpha\})\rangle$ is

$$E_0(\{q_\alpha\}) = \langle P_0(\{q_\alpha\}) | H | P_0(\{q_\alpha\}) \rangle = \sum_{\alpha=1}^8 \omega_\alpha \left( \frac{q_\alpha^2}{2} h(q) + \frac{5}{2} - g_\alpha q_\alpha \right).$$

(3.88)
The fact, that the Euclidean norm $q^2 = \sum_{\alpha=1}^{8} q_{\alpha}^2$ of the distortions enters the function $h(q)$ comes from property (3.44). In order to minimize the energy $E_0(\{q_\alpha\})$ with respect to the distortions $q_\alpha$ it is best to introduce a Lagrange multiplier $\lambda$ for the constraint $q^2 = \sum_{\alpha=1}^{8} q_{\alpha}^2$. Hence we need to minimize the function

$$F_0(\{q_\alpha\}, q, \lambda) = E_0(\{q_\alpha\}) + \frac{\lambda}{2} \left( \sum_{\alpha=1}^{8} q_{\alpha}^2 - q^2 \right)$$

(3.89)

with respect to all variables. Differentiation with respect to $q_\alpha$ yields

$$q_\alpha = \frac{\omega_\alpha q_\alpha}{\omega_\alpha h(q) + \lambda}.$$  

(3.90)

Differentiation with respect $q$ and $\lambda$ and introducing (3.90) into the resulting formulas yields two equations for $q$ and $\lambda$:

$$h'(q) \sum_{\alpha=1}^{8} \frac{\omega_\alpha^3 q_{\alpha}^2}{(\omega_\alpha h(q) + \lambda)^2} = 2 \lambda q$$

(3.91)

$$\sum_{\alpha=1}^{8} \frac{\omega_\alpha^2 q_{\alpha}^2}{(\omega_\alpha h(q) + \lambda)^2} = q^2$$

(3.92)

These two equations have to be solved numerically yielding $q$ and $\lambda$ which then are used to calculate $q_\alpha$ by equation (3.90). This yields $\lambda = 14.4$ meV and $q = 1.79$. The ground state energy obtained this way is given Tab 3.3. The energy gain with respect to the variational energy of the corresponding (i.e. non-improved) EMA is small which means that the EMA is good. In terms of the wave-function (3.87), the EMA consists in setting $q_\alpha = q_{\text{eff}}(g_\alpha/g_{\text{tot}})$ where $q_{\text{eff}}$ is obtained by minimizing the energy of the EMA. This is equivalent to setting $\lambda = 0$ rather than to minimize with respect to it. The distortions $q_\alpha$ obtained in this way from the EMA are compared to results of the full multiple mode calculation in Tab. 3.4. Indeed, the differences are rather small which means that the wavefunction of the EMA and the one of the multiple mode calculation are almost the same. This confirms again that the EMA is a good approximation. Moreover, Tab 3.3 shows that more is gained by a good solution within the EMA than by fully solving for the multiple modes. We take this as a justification to use the EMA throughout the following.

### 3.3 $C_{60}^{2-}$

In this section we consider the doubly charged $C_{60}^{2-}$ ion. In the first subsection 3.3.1 the dynamic Jahn-Teller state is derived by the method introduced in the previous
Table 3.4: Distortions $q_\alpha$ of each phonon mode in the variational ground state. The 4th column gives the result for the EMA. The 5th column is the result for the full multiple mode calculation.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\omega_\alpha$ (meV)</th>
<th>$g_\alpha$</th>
<th>$q_\alpha$, EMA</th>
<th>$q_\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_g(8)$</td>
<td>195.3</td>
<td>0.368</td>
<td>0.456</td>
<td>0.538</td>
</tr>
<tr>
<td>$H_g(7)$</td>
<td>176.8</td>
<td>0.368</td>
<td>0.456</td>
<td>0.532</td>
</tr>
<tr>
<td>$H_g(6)$</td>
<td>154.7</td>
<td>0.</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>$H_g(5)$</td>
<td>136.3</td>
<td>0.325</td>
<td>0.403</td>
<td>0.454</td>
</tr>
<tr>
<td>$H_g(4)$</td>
<td>95.8</td>
<td>0.448</td>
<td>0.556</td>
<td>0.589</td>
</tr>
<tr>
<td>$H_g(3)$</td>
<td>87.8</td>
<td>0.405</td>
<td>0.502</td>
<td>0.523</td>
</tr>
<tr>
<td>$H_g(2)$</td>
<td>53.4</td>
<td>0.924</td>
<td>1.145</td>
<td>1.051</td>
</tr>
<tr>
<td>$H_g(1)$</td>
<td>33.5</td>
<td>0.868</td>
<td>1.075</td>
<td>0.835</td>
</tr>
<tr>
<td>Total</td>
<td>1.532</td>
<td>1.899</td>
<td>1.790</td>
<td></td>
</tr>
</tbody>
</table>

3.3.1 Dynamically distorted ground state

As in the previous section, we start with a state which is statically distorted and given by the coherent state $|q e_i\rangle_p$. Again, the choice $\alpha = 0$ for the shape parameter optimizes the Jahn-Teller energy gain when the electrons are put in lowest level (see Fig. 3.2). The statically distorted state is given by

$$|^{1}\Psi_0(q)\rangle = c_{01}^\dagger c_{01}^\dagger |q e_0\rangle$$  \hspace{1cm} (3.93)

The upper index 1 indicates that the state is a singlet (spin degeneracy 1). This state is properly normalized and an eigenvector of $A_e$

$$A_e|^{1}\Psi_0(q)\rangle = -\sqrt{2}q|^{1}\Psi_0(q)\rangle.$$  \hspace{1cm} (3.94)

The eigenvalue is a factor of 2 bigger with respect to the eigenvalue of the equivalent state in $C_{60}^-$. This is due to presence of two electrons. Hence, the energy of the static distortion of $C_{60}^-$ differs from the corresponding energy in $C_{60}$ only by an additional
factor of 2 in front of the Jahn-Teller energy gain:

\[ \langle \psi_0(q)|H|\psi_0(q)\rangle = \frac{5}{2} + \frac{q^2}{2} - 2gq \]  

(3.95)

This energy is minimized by \( q = 2g \) and the variational ground state energy of the statically distorted state for \( n = 2 \) becomes

\[ E_{0,n=2}^{\text{stat}}(g) = \frac{5}{2} - 2g^2. \]  

(3.96)

Again, energy is gained when the wave-function \( |\psi_0\rangle \) is projected on the lowest allowed angular momentum subspace. Since \( |\psi_0\rangle \) has even symmetry and \( L_z|\psi_0\rangle = 0 \), only projections onto even angular momentum subspaces with \( m = 0 \) are non-vanishing. The ground state is an isotropic S state:

\[ |S_0(q)\rangle = P_{00}|\psi_0(q)\rangle. \]  

(3.97)

Note that this state has recovered full SO(3) symmetry. The expectation value of \( N_p \) with respect to this state is the same as for \( C_{60} \) because \( N_p \) only involves the phonon part. However, the electron-phonon coupling term acquires a factor 2. Therefore, the expectation value of the Hamiltonian is

\[ E_{0,n=2}(g, q) = \frac{\langle S_0(q)|H|S_0(q)\rangle}{\langle S_0(q)|S_0(q)\rangle} = \frac{5}{2} + \frac{q^2}{2} h(q) - 2gq \]  

(3.98)

In conclusion, the variational approach (without improvement) for the ground state of \( C_{60}^{2-} \) is equivalent to \( C_{60}^{2-} \) but with a doubled coupling strength: \( g \rightarrow 2g \), which is due to presence of two electrons instead of one.

As discussed in 3.2.5, rotator excitations are obtained by using projection operators for higher angular momentum in the projection (3.97). Energies of rotator states \( l = 0, 2, 4, 6 \) are shown in Fig. 3.7 together with results from exact diagonalization [67]. The variational results are in qualitative agreement, but differ quite substantially for large \( l \). In the same figure, results from an improved variational approach, discussed in subsection 3.3.3, are also shown. They agree very well with the exact diagonalization results. Finally, the asymptotic behavior of the energies, derived by O'Brien with a semiclassical approach [63], are also shown in Fig. 3.7. They are given by

\[ E_l(g) \approx -2g^2 + \frac{3}{2} + \frac{1}{12g^2} + \frac{l(l+1)}{24g^2}, \quad g \rightarrow \infty. \]  

(3.99)

As in the case of \( C_{60}^{2-} \), the improved variational approach yields the correct asymptotic behavior whereas the unimproved one discussed in this subsection doesn't.
Figure 3.7: Rotator states $^1S$, $^1D$, $^1G$, $^1I$ ($l = 0, 2, 4, 6$) in the singlet subspace ($S = 0$) and in the absence of Coulomb interaction ($U = J = 0$). The levels are plotted as a function of coupling strength $g$ and relative to the asymptotic energy $-2g^2$. Dashed lines are the result from the unimproved variational wavefunction as discussed in section 3.3.1. Solid lines correspond to the improved states and the dotted lines are the asymptotic behavior $E_i(g) = -2g^2 + 3/2 + l/(24g^2) + 1/(24g^2)$ as derived by O'Brien [63]. Stars are data from exact diagonalization [67].

### 3.3.2 Hund's rule coupling for static distortions

**Competition of Jahn-Teller effect and Hund's rule coupling**

In the case of two electrons, the Hund's rule coupling term discussed in section 3.1.6 has to be taken into account as well. We first investigate its effect on the statically distorted states. The complications arise, because with two electrons, another eigenstate of $A_{ep}$ can be constructed which also has spin $S = 0$ and angular momentum $m = 0$. Since the distortion (with $\alpha = 0$) splits the electronic levels into a singlet with energy $-gq$ and a doublet with energy $gq/2$ (see Fig. 3.2), this other state is obtained by putting the two electrons into the doublet:

$$|^1\Psi_1(q)\rangle = \frac{1}{\sqrt{2}} \left( c_{11}^t c_{17}^t - c_{-11}^{t*} c_{17}^{t*} \right) |q e_0\rangle = \frac{1}{\sqrt{2}} \left( c_{11}^t c_{17}^t + c_{-11}^{t*} c_{17}^{t*} \right) |q e_0\rangle.$$  (3.100)

In the first equality the construction operators for the complex angular momentum states are used which makes it obvious that $S = 0$ and $m = 0$. By construction,
$|\Psi_1\rangle$ is an eigenvector of $A_{ep}$ and it is orthogonal to $|\Psi_0\rangle$:

$$A_{ep}|\Psi_1(q)\rangle = \frac{1}{\sqrt{2}} q |\Psi_1(q)\rangle, \quad \langle \Psi_1 | \Psi_0 \rangle = 0.$$  \hspace{1cm} (3.101)

The state $|\Psi_1\rangle$ has a high electron-phonon coupling energy $gq$ and is very unfavorable for the Jahn-Teller effect. However, the Hund’s rule term $H_J$ couples the two states $|\Psi_0\rangle$ and $|\Psi_1\rangle$. In the basis $(|\Psi_0\rangle, |\Psi_1\rangle)$, $H_J$ has the form:

$$H_{J_{\text{ee, red}}} = \begin{pmatrix} 2J & \sqrt{2}J \\ \sqrt{2}J & 3J \end{pmatrix}.$$  \hspace{1cm} (3.102)

The eigenvectors of the matrix (3.102) are the states

$$|\Psi_S(q)\rangle = \frac{1}{\sqrt{3}} |\Psi_0\rangle + \sqrt{\frac{2}{3}} |\Psi_1\rangle = \frac{1}{\sqrt{3}} \sum_{n=-1}^{1} c_{n+}^\dagger c_{n+}^\dagger |q e_0\rangle,$$

$$|\Psi_D(q)\rangle = -\sqrt{\frac{2}{3}} |\Psi_0\rangle + \frac{1}{\sqrt{3}} |\Psi_1\rangle.$$  \hspace{1cm} (3.103)

These two states are eigenvectors of the total electron angular momentum $L^2_e$ with angular momentum $l_e = 0$ for $|\Psi_S\rangle$ and $l_e = 2$ for $|\Psi_D\rangle$. As discussed in section 3.1.6 (see Tab. 3.2), their energies with respect to the Hund’s rule term are $4J$ for $|\Psi_S\rangle$ and $J$ for $|\Psi_D\rangle$. Apparently, the electron-phonon coupling (more precisely $A_{ep}$) and the Hund’s rule term cannot be diagonalized simultaneously which means that they are in competition.

**Solution for the static distortion**

In order to investigate this competition, it is convenient to introduce the Hamiltonian $\tilde{H} = [H - (5/2)\omega]/(\omega g^2)$ where the zero point energy is subtracted and energies are normalized with the Jahn-Teller energy scale $\omega g^2$. Note that we have set the charging energy $U = 0$ because it is a constant for fixed particle number. $\tilde{H}$ has the same eigenvectors as $H$. The expectation values of $\tilde{H}$ with respect to the statically distorted state depend only on the normalized distortion $u = q/g$ and the normalized exchange energy $j = J/(\omega g^2)$. $\tilde{H}$ takes the form

$$\tilde{H}(|\Psi_0\rangle, |\Psi_1\rangle) = \frac{u^2}{2} + \begin{pmatrix} -2u + 2j & \sqrt{2}j \\ \sqrt{2}j & u + 3j \end{pmatrix},$$

$$\tilde{H}(|\Psi_S\rangle, |\Psi_D\rangle) = \frac{u^2}{2} + \begin{pmatrix} 4j & \sqrt{2}u \\ \sqrt{2}u & -u + j \end{pmatrix},$$  \hspace{1cm} (3.105)-(3.106)

which depends on the choice of basis indicated in the subscript of $\tilde{H}$. From this two representations it is obvious that the ground state is $|\Psi_0\rangle$ if $j = 0$ and $|\Psi_D\rangle$ for
Chapter 3. Variational states for $C_{60}^-$

$j \to \infty$. Hence, the ground state is solely determined by the parameter $j$. The two eigenvalues of $\hat{H}(u,j)$ are

$$
\epsilon_{\pm}(u,j) = \frac{1}{2} \left( u^2 - u + 5j \pm \sqrt{9u^2 + 6ju + 9j^2} \right).
$$

(3.107)

Minimizing $\epsilon_{-}(u,j)$ with respect to $u$ yields the normalized distortion $u(j)$ as a function of the Hund’s rule coupling strength $j$. This minimization procedure can’t be carried out analytically. However, the limiting behavior for $j \to 0$ and $j \to \infty$ can be worked out. This is done by calculating the ground state energy perturbatively for small $j$ in (3.105) and small $u$ in (3.106), respectively, which yields

$$
\epsilon_{-}(u,j) = 2j + \frac{u^2}{2} - 2u - \frac{2j^2}{3u}, \quad j \ll 1, 
$$

(3.108)

and

$$
\epsilon_{-}(u,j) = j + \frac{u^2}{2} - u - \frac{2u^2}{3j}, \quad j \gg 1.
$$

(3.109)

Minimizing these expressions yields

$$
u(j \to 0) \approx 2 - \frac{j^2}{6}, \quad u(j \to \infty) \approx 1 + \frac{4}{3j}. 
$$

(3.110)

The exact numerical solution $u(j)$ is shown in Fig. 3.8 together with the asymptotic behavior (3.110). In the limit $j \to \infty$, the Jahn-Teller distortion isn’t suppressed, but only reduced by a factor of 2. This can also be seen from the Hamiltonian (3.109). Increasing $j$ decouples the the two state $|1\Psi_S\rangle$ and $|1\Psi_D\rangle$. For positive $j > 0$ the state $|1\Psi_D\rangle$, which couples to the distortion, is lower. It is interesting to note that for negative $j < 0$, the state $|1\Psi_S\rangle$, which doesn’t couple to the distortion, would be lower and the Jahn-Teller effect would be completely suppressed for $J \to -\infty$. This is in contrast to the general wisdom where it is assumed that Hund’s rule coupling prefers a high spin state (in contrast to the Jahn-Teller effect) implies that a negative Hund’s rule coupling would enhance the Jahn-Teller distortion. Finally, the results (3.110) can be substituted back into the expressions (3.108) and (3.109) which yields

$$
\epsilon_{-}(j \to 0) \approx -2 + 2j - \frac{j^2}{3}, \quad \epsilon_{-}(j \to \infty) \approx j - \frac{1}{2} - \frac{2}{3j}.
$$

(3.111)

Taking $J = 100$ meV, $\omega = \tilde{\omega} = 72.1$ meV, $g = g_{\text{tot}} = 1.53$ for an isolated molecule (see section 3.1.6) yields $j = 0.59$. Hence, $C_{60}$ is clearly in the limit of small Hund’s rule coupling and the perturbative expressions for small $j$ are a good approximation as can also be seen in Fig. 3.8. Minimizing the energy, one finds a slightly reduced distortion of $q = 1.95\;g$ and the energy $\epsilon_{-} = -0.925$. 
High-spin/low-spin level crossing

What we have not discussed up to now are the high spin states $^3P$. The statically distorted state with $m=0$ and $S_z = 1$ is

$$|^3\Psi_P(q)\rangle = c_{11}^\dagger c_{-11}^\dagger |q e_0\rangle. \quad (3.112)$$

What concerns the Jahn-Teller effect, the $^3P$ state for $n = 2$ is equivalent to the $P$ state of $n = 1$ which is easily understood if only the $S_z = +1/2$ subspace ($c_{-11}^\dagger, c_{01}^\dagger, c_{11}^\dagger$) is considered. Putting two electrons in this subspace for $n = 2$ leaves one hole which, by particle-hole symmetry, is equivalent to putting only one electron into this subspace. Hence the spectrum is equivalent to the one of $\text{C}_{60}$ discussed in the previous section. The Hund’s rule coupling is just a constant $-J$ in the $^3P$ subspace (see Tab. 3.2). The expectation value of the Hamiltonian $\tilde{H}$ with respect to the statically distorted high spin state is

$$\langle ^3\Psi_P | \tilde{H} | ^3\Psi_P \rangle = \frac{u^2}{2} - u - j. \quad (3.113)$$

This energy is minimal for $u = 1$ which yields the energy $-1/2 - j$ for the state $|^3\Psi_P(q)\rangle$. Obviously, this energy decrease for increasing $j$ and therefore will cross the ground state of the low-spin subspace. This is shown in Fig. 3.8. If only the linear term $\varepsilon (j) \approx -2 + 2J$ is taken, then the crossing occurs at a coupling strength $j_c = 1/2$. The exact value (for static distortions) is $j_c = 0.5284$. 

Figure 3.8: Distortion $u = q/g$ (left panel) and the ground state energy $\varepsilon (j)$ of $\tilde{H} = \left( H - (5/2)\omega \right)/(\omega g^2)$ (right panel) as a function of the normalized Hund’s rule coupling $j = J/(\omega g^2)$. The solid line is the exact result for the low spin ($S = 0$), statically distorted state. The asymptotic behavior for $j \rightarrow 0$ (dotted line) and $j \rightarrow \infty$ (dashed line) is also shown. The dash-dotted line is the energy for the high-spin ($S = 1$) state. The level crossing occurs at $j_c = 0.5284$. 

$\text{3.3. C}_{60}$
3.3.3 Hund’s rule coupling for dynamic distortions

Unimproved variational states

We start this section by discussing the effect of Hund’s rule coupling using variational states as given in (3.97). The expectation value of the Hund’s rule coupling term $H_J$ involves the matrix element

$$\langle \Psi_0 | H_J U(\Theta) | \Psi_0 \rangle = J (1 + \cos^2 \theta) \exp \left(-\frac{3}{4} q^2 \sin^2 \theta \right). \quad (3.114)$$

Rotator states as given in (3.97) are $|\Psi_0(q)\rangle = P_0 \Psi_0(q)$ where $X = S, D, G, I$ stands for the total angular momentums $l = 0, 2, 4, 6$. The expectation value of $H_J$ with respect to $|\Psi_0(q)\rangle$ is given by

$$\langle |X_0(q)\rangle | H_J | X_0(q)\rangle = J \int_{-1}^{1} P_l(t) (1 + t^2) e^{-\frac{3}{4} q^2(1-t^2)} dt \int_{-1}^{1} P_l(t) t^2 e^{-\frac{3}{4} q^2(1-t^2)} dt = J h_J^{(i)}(q), \quad (3.115)$$

where $P_l(t)$ is the Legendre Polynomial. The last equation defines the functions $h_J^{(i)}(q)$ which are smoothly varying as shown in Fig. 3.9. As $H_J$ has only two eigenvalues $J$ and $4J$ in the low spin ($S = 0$) subspace, the functions $h_J^{(i)}(q)$ must be bounded by $1 \leq h_J^{(i)}(q) \leq 4$. It is instructive to discuss the limits $q \to 0$ and $q \to \infty$. The states $|X_0(q = 0)\rangle$ are solutions when the electron-phonon coupling is absent ($g = 0$) in which case the problem is trivial. Eigenstates can be written as product states of an electron- and phonon-states. In the spin $S = 0$ subspace there are one $l_e = 0$ and five $l_e = 2$ electronic states. On the other hand, the phonon ground state is the vacuum with zero angular momentum ($l_p = 0$). The first phonon excitations is 5-fold degenerate and has angular momentum $l_p = 2$. The states with two excited phonons are 15-fold degenerate and split into angular momentum $l_p = 0, 2, 4$. 

![Figure 3.9: The function $h_J^{(i)}(q)$ for angular momentum states S, D, G, I ($l = 0, 2, 4, 6$).](image-url)
3.3. \( C_{60}^2 \)

Finally, the electron and phonon angular momentum states are combined and eigenstates of the total angular momentum \( \mathbf{L} = \mathbf{L}_e + \mathbf{L}_p \) are obtained by the angular momentum addition rules. The limiting value \( h_f^{(l)}(0) \) indicates whether the electronic part of the wavefunction has angular momentum \( l_e = 0 \) (\( h_f^{(0)} = \frac{4}{\omega} \)) or \( l_e = 2 \) (\( h_f^{(2)} = \frac{1}{\omega} \)). Hence, in the limit \( q \rightarrow 0 \), the functions \( |S_0^1 \rangle \) and \( |D_0^1 \rangle \) are just the electronic \( l_e = 0 \) and \( l_e = 2 \) states without phonon excitations. The states \( |G_0^1 \rangle \) and \( |I_0^1 \rangle \) are electronic \( l_e = 2 \) states with one or two phonon excitations. On the other hand, in the limit \( q \rightarrow \infty \), the electronic part of the wavefunctions is a mixture of \( l_e = 0 \) and \( l_e = 2 \) states and the expectation value of \( H_J \) becomes a constant \( 2J \).

In order to get the ground state energy of the rotator states in the intermediate coupling regime, the energy

\[ E_{0,n=2}(g, J, q) = \langle X_0(q)|H|X_0(q)\rangle = \frac{5}{2} + \frac{q^2}{2} h_f^{(l)}(q) - 2gq + \frac{J}{\omega} h_f^{(l)}(q) \quad (3.116) \]

has to be minimized with respect to \( q \). The case \( J = \omega \) is shown in Fig. 3.10. The result is in bad agreement with the exact results of Ref. [63]. In particular for \( g \rightarrow 0 \) the energy of the \( |S_0^1 \rangle \) state is \( 4J + (5/2)\omega = 6.5\omega \) rather than \( 4.5\omega \). The reason is that the lowest \( |S_0^1 \rangle \) state for \( J > \omega/3 \) and \( g = 0 \) is an electronic \( l_e = 2 \) combined with one phonon excitation \( (l_p = 2) \).

**Improved variational states**

In order to improve the variational energies and to account for the different nature of the \( |S_0^1 \rangle \) state if \( J > \omega/3 \), we use a similar approach as presented in section 3.2.5. More precisely, a 4-dimensional subspace spanned by the following linearly independent states is used:

\[ P_0 |\psi_S(q)\rangle, \quad P_0 |\psi_D(q)\rangle, \quad A_{l_p} P_0 |\psi_S(q)\rangle, \quad A_{l_p} P_0 |\psi_D(q)\rangle. \quad (3.117) \]

\( P_0 \) is the projection operator on a angular momentum subspace. The functions \( |\psi_S(q)\rangle \) and \( |\psi_D(q)\rangle \) are defined in the previous section and have electronic angular momentum \( l_e = 0 \) and \( l_e = 2 \) respectively. The first two wavefunctions give the freedom to optimize the competition between Jahn-Teller effect and Hund’s rule coupling. The third and fourth wavefunction are according to the best improvement (choice (iii)) found in section 3.2.5. Note that \( A_{l_p} \) creates a phonon excitation which allows the different nature of the \( |S_0^1 \rangle \) state if \( J > \omega/3 \). The projection of the Hamiltonian onto this subspace is done by mathematica. Again, the lowest eigenvalue has to optimized with respect \( q \). Results for \( J = 0 \) are shown in Fig. 3.7 and are in excellent agreement with the exact diagonalization result [67]. In addition, the asymptotic behavior is as given in (3.99) [63]. The same rotator states, but for \( J = \omega \) are shown in Fig 3.10. Again, good agreement is found with the exact diagonalization results [63].
Apart from the energy gain by the improved version (3.116) of the variational wavefunction one might wonder whether the improved wavefunction differs much from the unimproved one. To quantify this, the square of the overlaps is shown in Fig. 3.11. In the case $J = 0$ the overlap is bigger than 0.95 meaning that improvement only changes the wavefunction slightly. This changes in the case $J = \omega$ where, in particular, the overlap of the $1S$ states goes to zero for $g \to 0$. This is due to the fact (discussed above) that the unimproved wavefunction doesn't yield the lowest $1S$ state if $J > \omega/3$.

### Level crossing

As discussed in the previous section, the high-spin subspace with $S = 1$ of $C_{60}^-$ is decoupled from the low-spin $S = 0$ subspace discussed so far. In the $S = 1$ subspace the Hund's rule coupling is trivially given by a constant ($-J$) and the spectrum is equivalent to the one of $C_{60}^-$. For big enough Hund's rule coupling $J$, a level crossing occurs such that the high spin $^3P$ state becomes the ground state. The crossing between low-spin and high-spin ground state defines a line in the $(g, J)$ parameter space. This is shown in Fig. 3.12 where the normalized Hund's rule coupling $j = J/(\omega g^2)$ is used. In addition, the crossing of the $^1S$ and $^1D$ state in the low spin subspace is indicated. The diagram shows that the low-spin ground state is always $^1S$. The two lines end at $(g, j) = (0, 3/4)$ which is an exact result.
that follows from the asymptotic behavior of the energy in the limit \( g \to 0 \) [65] (the zero-point energy is omitted):

\[
E(1S) \approx \frac{4J}{\omega} - 5g^2, \quad E(1D) \approx \frac{J}{\omega} - \frac{11}{4} g^2, \quad E(3P) \approx \frac{J}{\omega} - \frac{5}{4} g^2.
\] (3.118)

In the limit \( g \to \infty \) the \( ^1S - ^3P \) crossing line approaches the constant value \( j_c = 0.5284 \) derived in section 3.3.2.

### 3.3.4 Results specific to parameters of \( \text{C}_60 \)

In this section the general results of the previous sections are discussed in view of the parameters of \( \text{C}_60 \). Within the effective mode approximation (EMA), where the problem is reduced to a single mode, \( \text{C}_60 \) has a coupling constant \( g_{\text{tot}} = 1.532 \) with an energy scale \( \omega = 72.1 \text{ meV} \). The value of the Hund’s rule coupling is of the order \( J = 100 \text{ meV} \) for an isolated molecule which leads to \( j = J/\omega g^2 = 0.59 \). With these parameters, isolated \( \text{C}_60 \) is close to the low-spin/high-spin crossing of the ground state (see Fig. 3.12). This is also reflected by experiments. Measurements of the spin state of \( \text{C}_{60}^{2-} \) embedded in different matrices yield different results. Ref. [79, 80] find a high-spin (\( S = 1 \)) ground state whereas Ref. [81, 82] find a low-spin (\( S = 0 \)) ground state. Ref. [81] suggests that the gap between low- and high-spin state is presumably very small.

The reason why experimental results differ might be due to the influence of the environment of the \( \text{C}_60 \) molecule on the parameters \( (g_{\text{tot}}, J) \). The total coupling constant \( g_{\text{tot}} \) is a molecular property. It should depend little on the environment.
Figure 3.12: The solid line separates the low spin $^1S$ ground state from the high spin $^3P$ ground state in the parameter space spanned by $g$ and $j = J/(\omega g^2)$. For $g \to \infty$ the boundary approaches the constant value $j_c = 0.5284$ (dashed line) derived in section 3.3.2. At $g = 0$ it ends at $j = 3/4$. The dotted line ends at the same point and indicates the crossing of the $^1S$ and $^1D$ state in the $S = 0$ subspace. The crosses indicate the parameters for isolated $C_{60}^{2-}$ and $C_{60}^{2-}$ in bulk.

because of the robust C-C bonds. On the other hand, the Hund’s rule coupling $J$ arises from the Coulomb interaction which itself depends on the dielectric properties of the environment. This is also reflected by the fact that the charging energy $U$ is reduced by more than a factor of 2 when isolated molecules are put into a solid (see section 3.1.6). Hence, it is reasonable to assume that the Hund’s rule coupling is similarly dependent on the environment and that different experimental conclusions are due to a different effective $J$. In Fig. 3.13 the dependence of the energy levels for fixed $g_{tot}$ is shown as well as the singlet-triplet gap. To a good approximation, the levels depend linearly on $J$. The high-spin states decrease trivially by $-J$ whereas the low-spin states increase approximately by $1.75J$. The latter result is non-trivial and indicates again that the electronic part of wavefunctions in the strong coupling limit are dominated by the electronic $^2D$ state.

In solids, such as $K_4C_{60}$, the singlet-triplet gap can be estimated by magnetic susceptibility [83] as well as spin relaxation [84, 85, 86, 87]. Both quantities scale with the thermal occupation of the triplet $^3P$ state which shows an activated behavior with a gap $\Delta_{SP} \approx 50 - 100$ meV. If $\Delta_{SP}$ is associated with the singlet-triplet gap, then $J \approx 60 - 80$ meV (see Fig. 3.13). Hence the bulk value of $J$ is reduced by
Rotator energies within the EMA in $\text{C}_{60}^{2-}$ for fixed $g_{\text{tot}} = 1.532$ and as a function of the exchange energy $J$. All energies are in meV. The left panel shows the lowest rotator excitations in the low and high spin subspaces. The $1S^3P$ level-crossing occurs at $J_c = 96$ meV. The right panel shows the $1S^3P$ gap. The dotted curve (it almost falls on top of the solid one) is a linear fit $\Delta_{SP}(J) = 266 \text{meV} + 2.75J$.

In the subsequent chapters we will mainly deal with $\text{C}_{60}$ bulk compounds and we will use the exchange energy $J = \omega = 72.1$ meV.

Rotator energies in the spin $S = 0$ subspace and for $J = 0$ are shown in Tab. 3.5. They are compared to exact diagonalization results [67]. Naturally, the calculations in Ref. [67] were performed for a truncated phonon Hilbert space. Hence, these results aren't exact either but also yield an upper bound for the ground state energy. This is the reason why the energies found in the present work are actually lower than those of Ref. [67]. In addition, in Ref. [67], an extrapolation to the infinite Hilbert space was done which yields excitation energies which are roughly a factor of 3 smaller. As can be seen in equation (3.113), the asymptotic behavior of the excitation energies is given by the spectrum of a rotator $l(l + 1)/2I$ with a moment of inertia $1/I = \omega/(12g^2)$. To a good approximation, the values in Tab. 3.5 fit such a spectrum when the moment of inertia is chosen to be $1/I = \Delta E_1/3$ ($\Delta E_1$ is the lowest excitation energy). From the present calculation one obtains $1/I = 3.27$ meV which, as one would expect, is somewhat larger than the asymptotic value $1/I = \bar{\omega}/(12g_{\text{tot}}^2) = 2.56$ meV. The value from the exact diagonalization is even larger $1/I = 4.27$ meV whereas the value from the extrapolation to the infinite Hilbert space is substantially lower $1/I = 1.63$ meV. The fact that the latter result is below the asymptotic value $\bar{\omega}/(12g_{\text{tot}}^2)$ is either due to the error introduce in the extrapolation or to the fact that the calculation performed in Ref. [67] includes all phonon modes and goes beyond the effective mode approximation. To summarize, the low energy spectrum of $\text{C}_{60}^{2-}$ is a rotator spectrum where only even angular momentum states are allowed. Depending on the method of calculation, the value...
Table 3.5: Energies of the rotator state \( l = 0, 2, 4, 6 \) of \( \text{C}_{60}^{2-} \). The zero-point energy \( \omega_0 = \sum \omega_{l}(5/2)\omega_{l} \) is subtracted. Column 5-7 give the energies relative to the ground state. Results in column 2 and 5 are from exact diagonalization of a truncated Hilbert space [67]. Results in column 3 and 6 are obtained by extrapolation to an infinite Hilbert space. Column 4 and 7 are the results from the present approach using the EMA and the basis (3.117). The last line gives the inverse of the moment of inertia \( 1/I = (E_D - E_S)/3 \).

<table>
<thead>
<tr>
<th>State</th>
<th>[67]</th>
<th>[67], extr.</th>
<th>Present</th>
<th>( \Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^1S )</td>
<td>-405.9</td>
<td>-428.9</td>
<td>-406.7</td>
<td>0</td>
</tr>
<tr>
<td>( ^1D )</td>
<td>-392.8</td>
<td>-424.0</td>
<td>-396.9</td>
<td>13.1</td>
</tr>
<tr>
<td>( ^1G )</td>
<td>-367.6</td>
<td>-415.1</td>
<td>-377.3</td>
<td>38.3</td>
</tr>
<tr>
<td>( ^1I )</td>
<td>-331.1</td>
<td>-406.2</td>
<td>-350.7</td>
<td>74.8</td>
</tr>
</tbody>
</table>

\[ 1/I = \frac{(E_D - E_S)}{3}. \]

of the corresponding moment of inertia varies substantially between 1.6 – 4.3 meV.
Chapter 4

Ground state of $K_4C_{60}$ and $Na_2C_{60}$

When reviewing the research done on fullerene compounds, one first observes that much attention, both theoretical and experimental, was paid to the superconducting $A_3C_{60}$ compounds precisely because they are superconducting and the transition temperature is surprisingly high. Less effort was spent on the insulating compounds, such as $K_4C_{60}$ and $Na_2C_{60}$. Within the class of insulating alkali-doped fullerenes, the $K_4C_{60}$ and $Rb_4C_{60}$ are the best studied species. Although bandstructure calculations [88] predict them to be metallic with a partially filled $T_{1u}$ conduction band, they are insulating and non-magnetic. Experimentally, this was first shown by $\mu$SR measurements [89]. Subsequently, the insulating nature of $A_4C_{60}$ was confirmed by various other experimental techniques: The resistivity of $A_4C_{60}$ is an order of magnitude higher than in $A_3C_{60}$ [90, 91] and photoemission spectroscopy shows a gap [90, 92, 93]. Gaps are also seen in ESR [83] and NMR [84, 85, 86, 87, 94] measurements where they are found to be of the order 50-100 meV. This is the singlet-triplet gap discussed in section 3.3.4. A significantly higher gap of 500 meV is seen in optical measurements [95]. A much more recent and less studied compound is $Na_2C_{60}$ which is the only stable $A_2C_{60}$ compound known so far. Recent NMR studies show similar behavior as in $A_4C_{60}$ [87, 94, 96]. The reason for the similarity is the fact that the $C_{60}^{2-}$ and $C_{60}^{4-}$ ions are equivalent by particle-hole symmetry. More precisely, the transformation $c_{ns}^\dagger \rightarrow c_{ns}$ and $a_k^\dagger \rightarrow -a_{k'}^\dagger -a_k$ leaves the molecular Jahn-Teller Hamiltonian invariant. This property holds as long as only the $T_{1u}$ orbitals are considered. It should be noted that, although $K_4C_{60}$ and $Na_2C_{60}$ are related by particle-hole symmetry, their crystal structure is different. $K_4C_{60}$ has a bipartite bct lattice [88] while $Na_2C_{60}$ has a fcc lattice and is isostructural to the $A_3C_{60}$ compounds [97].

From the theory side, there are only a few contributions concerned with the isolating fullerene compounds. The basic understanding of $A_4C_{60}$ goes back to the work of Auerbach and Manini [65, 66]. In this work they showed that the isolated $C_{60}^{4-}$ ions have a singlet ground state where the spherical symmetry is restored by the
Chapter 4. Ground state of K$_4$C$_{60}$ and Na$_2$C$_{60}$

dynamic Jahn-Teller effect (see section 3.3.1). The physics of A$_4$C$_{60}$ is then governed by both the Coulomb interaction and Jahn-Teller effects. The understanding was and still is that the strong Coulomb energy $U$ dominates over the kinetic energy and leads to a localization of the electrons and hence to an insulating state. Once the electrons are localized, the Jahn-Teller effect comes into play which dominates over the Hund's rule coupling and favors a low-spin state. Note that Jahn-Teller splitting of C$_{60}^-$, which is of the same order as the bandwidth (0.5 eV), is too small to create an insulating state by itself. The difference between insulating A$_4$C$_{60}$ and metallic A$_3$C$_{60}$ might be explained by the fact that the C$_{60}^{1-}$ Jahn-Teller state is energetically lower than the C$_{60}^{3-}$ state which leads to an effective increase of the charging energy $U$ [75]. The question whether the dynamic Jahn-Teller effect survives in A$_4$C$_{60}$ was first addressed in Ref. [98]. This paper outlines the main concepts and ideas and is in spirit similar to work presented here. In particular, Ref. [98] distinguishes clearly between two possible scenarios. First, the ground state of A$_4$C$_{60}$ could be governed by a cooperative distortion where the vibrational coordinates can be treated as classical variables. The ground state consists then of a periodic array of statically distorted molecules. The second scenario is a ground state, where each molecule is in its molecular ground state, hence in a dynamic Jahn-Teller state. Ref. [98] calls the latter a Jahn-Teller-Mott state. As in the present work, Ref. [98] proposes an effective interaction between molecules which is mediated by second order hopping processes. And it states correctly that there should be a phase transition between the two scenario which is controlled by the ratio between the effective interaction and low energy excitations of the molecule. The model used in Ref. [98] is not specific for C$_{60}$, but is the simplest molecular Hamiltonian showing a dynamic Jahn-Teller effect, i.e. a two-level system in interaction with a two-dimensional harmonic oscillator. A work concerned more with possible phase transition is Ref. [99]. This work assumes a general interaction between the C$_{60}$ molecules and studies possible phases using a similar mean-field approximation to the one presented below. However, the nature of the interaction is not discussed. The work presented here goes beyond the results of Ref. [98] and Ref. [99] as both, the C$_{60}$ molecule and the bandstructure (leading to the effective interaction) are taken into account in way much closer to the actual materials. At the end, we obtain phases and phase diagrams which should qualitatively and, hopefully, also quantitatively describe the physics of both K$_4$C$_{60}$ and Na$_2$C$_{60}$.

The following approach starts with the isolated C$_{60}^{2-}$ ion which has been studied in detail in section 3.3.1. As discussed above, the C$_{60}^{2-}$ and C$_{60}^{4-}$ ions are equivalent by particle-hole symmetry. Therefore, below, we will mainly speak of C$_{60}^{2-}$ bearing in mind that the C$_{60}^{4-}$ ion is equivalent. The ground state of C$_{60}^{2-}$ is a $^1S$ state, hence a spin singlet with angular momentum 0. The lowest excitations in this system are rotator excitations. If C$_{60}^{2-}$ ions are brought together into a solid, the question arises, whether the $^1S$ state survives or whether molecular states will become correlated.
The additional term in the solid which has to be taken into account is the hopping between molecules. Here we treat it as a perturbation. In this way, the hopping term leads to an effective interaction between the $C_{60}^{2-}$ ions where the intermediate state contains a $C_{60}^{3-}/C_{60}^{1-}$ pair. The creation of this pair costs a charging energy $U$ which leads to an energy scale $t^2/U$ of the effective interaction ($t$ is a typical hopping energy). As will be discussed in the next section, $t^2/U$ is of the same order as the energy spacing of the lowest rotator excitation, which justifies the perturbative approach for the hopping term. Note that the particle-hole transformation, relevant for $K_4C_{60}$ leads to a negative sign in front of the kinetic energy, i.e. $t \rightarrow -t$. However, we consider second order processes where the minus sign cancels. Therefore the considerations apply equally to $K_4C_{60}$. The matrix elements of this effective interaction can be calculated using the variational rotator states for $C_{60}^{2-}$ of the previous chapter. This is done in section 4.1. In section 4.2 we will show that the low-energy physics can be mapped onto an effective model of interacting rotators. This model is then solved by a mean-field approximation for both $K_4C_{60}$ and $Na_2C_{60}$ in section 4.3. We find that in both compounds a phase transition should occur as a function of the effective interaction strength and temperature between a disordered Mott-Jahn-Teller phase and a cooperative Jahn-Teller phase. Phase diagrams and the nature of the phase transition are discussed as well.

4.1 Coupling of $C_{60}^{2-}$ ions

4.1.1 Virtual hopping

In order to derive the effective interaction due to second order hopping processes, we consider two $C_{60}$ molecules which are coupled by the hopping term

$$H_{\text{kin}} = \sum_{nm} t_{nm} (c_{2m}^\dagger c_{1n} + c_{1n}^\dagger c_{2m}).$$

(4.1)

The first index of the creation and annihilation operators denotes the molecule, the second and third denote orbital and spin respectively. Note that hopping parameters are real because the electronic orbitals of $C_{60}$ can always be chosen such that they are real. The total Hamiltonian is $H = H_{\text{mol,1}} + H_{\text{mol,2}} + H_{\text{kin}}$ and $H_{\text{kin}}$ will be treated as a perturbation. As discussed in section 3.1, the molecular Hamiltonian can be decomposed as $H_{\text{mol,i}} = (U/2)N_i(N_i - 1)/2 + H_{JT} + H_J$ where the first term is the charging energy. $H_{JT}$ is the Jahn-Teller energy and $H_J$ the Hund’s rule coupling. The biggest energy in the problem is the charging energy $U$. Given $n$ electrons per molecule, the charging energy is optimized for states with exactly $n$ electrons per molecule. States where molecule 1 and 2 are charged by $n-1$ and $n+1$ electrons respectively cost a charging energy $U$. Hence, the charge excitations
are gapped by an energy $U$. The only term in the Hamiltonian $H$ which couples to charge excitations is the kinetic energy. Within the subspace of low energy states (no charge excitations) second order hopping processes lead then to an effective interaction

$$H_{\text{eff}} = -\frac{1}{U} \mathcal{P}_0 H^2_{\text{kin}} \mathcal{P}_0,$$

(4.2)

where $\mathcal{P}_0$ is the projector on the low energy subspace. Inserting (4.1) into the definition of $H_{\text{eff}}$ yields

$$H_{\text{eff}} = \frac{2}{U} \sum_{\sigma \sigma'} t_{nm \sigma m' \sigma'} c_{1n \sigma} c_{1n' \sigma'} c_{2m \sigma} c_{2m' \sigma}$$

(4.3)

$$-\frac{1}{U} \sum_{\sigma \sigma'} t_{nm \sigma m' \sigma'} c_{1n \sigma} c_{1n' \sigma'} - \frac{1}{U} \sum_{\sigma \sigma'} t_{nm \sigma m' \sigma'} c_{2m \sigma} c_{2m' \sigma}.$$ 

The structure of $H_{\text{eff}}$ can be made more apparent by introducing the tensor operators

$$T_{\text{eff}} = \sum_{\sigma \sigma'} R_{1n \sigma} c_{1n \sigma} c_{1n' \sigma'} \leftrightarrow c_{1n \sigma} c_{1n' \sigma'} = \sum_{\sigma \sigma'} R_{1n \sigma} T_{\text{eff}}.$$

(4.4)

The definition (4.4) is for a real basis (real spherical harmonics) and $R_{1n \sigma}$ are the corresponding Clebsch-Gordan coefficients. As the electron annihilation and creation operators are tensor operators of rank 1, the tensor operator $T_{\text{eff}}$ can have rank $L = 0, 1, 2$. The explicit form of these tensor operators is (the index $i$ is dropped)

$$T_{00} = -\frac{1}{\sqrt{3}} \sum_{l=-1}^{1} c_{l0}^\dagger c_{l0},$$

$$T_{11} = \frac{1}{\sqrt{3}} (c_{1s}^\dagger c_{1s'} - c_{1s}^\dagger c_{0s}, c_{1s}^\dagger c_{-1s'} - c_{-1s}^\dagger c_{1s'}, c_{1s}^\dagger c_{0s'} - c_{0s}^\dagger c_{1s'})$$

$$T_{22} = \frac{1}{\sqrt{6}} \left( 3 \left[ c_{1s}^\dagger c_{-1s'} + c_{-1s}^\dagger c_{1s'} \right], 3 \left[ c_{1s}^\dagger c_{0s'} + c_{0s}^\dagger c_{1s'} \right], 2 c_{0s}^\dagger c_{0s'} - c_{-1s}^\dagger c_{-1s'}, c_{1s}^\dagger c_{1s'} - c_{1s}^\dagger c_{1s'}, c_{0s}^\dagger c_{0s'} + c_{0s}^\dagger c_{0s'} \right).$$

(4.5)

In the formula above, the indices $(-1, 0, 1)$ correspond to $(y, z, x)$ symmetry of $p$-orbitals. Some of the tensors have a simple interpretation. $-\sqrt{3} T_{00}$ is the number operator for electrons with spin $s$. The angular momentum of the electrons is $L = -\sqrt{2} \sum_{l}(L_{11}, L_{1-1}, L_{10})$. Finally, as can be seen from equation (3.5), the electron-phonon coupling term in the Hamiltonian can also be written as $-\sqrt{3}/2 g \sum_{k} T_{2k}^s T_{2k}^s$. $T_{2k}^s$ and $\hat{q}_k$ are both tensor operators of rank 2 and the electron-phonon coupling term is the simplest scalar (rank 0) which can be constructed out of these two tensor operators. Using the right side of definition (4.4) the effective interaction reads

$$H_{\text{eff}} = 2 \sum_{LNN'} K_{LN LN'} T_{2s}^s T_{2s}^{s'} + \frac{1}{\sqrt{3}} \sum_{LNN} \left( K_{LNN} T_{2s}^s + K_{000} T_{2s}^{s'} \right).$$

(4.6)
4.1. Coupling of $C_{60}^2$ ions

where the coupling matrix $K_{LN L'N'}$ is given by

$$K_{LN L'N'} = \frac{1}{U} \sum_{nn' mm'} R_{1n1n'}^{LN} R_{1m1m'}^{L'N'} t_{nm} t_{n'm'}.$$  \hspace{1cm} (4.7)

Relation (4.6) expresses the effective interaction in terms of tensor operators which simplifies the subsequent analysis because the eigenstates of molecules in absence of $H_{kin}$ have good angular momentum. One verifies that the coupling matrix $K_{LN L'N'}$ vanish if $L$ and $L'$ have different parity. Therefore coupling between odd and even tensor operators is forbidden. Furthermore, if the hopping is of the simple form $t_{nm} = t \delta_{nm}$ then the coupling matrix reduces to $K_{LN L'N'} = t^2/U \delta_{LL'} \delta_{NN'}$.

4.1.2 Matrix elements of tensor operator

General expression

The aim is to calculate the matrix elements of a general tensor operator $T_{LN}$ with respect to angular momentum states $|ln\rangle$ which involves the Wigner-Eckhart theorem. In the previous section angular momentum eigenstates with $m = 0$ were constructed be projecting statically distorted states $|\psi\rangle$ onto angular momentum subspaces by the projection operator $P_0$. The states $|\psi\rangle$ themselves were constructed such that $L_z |\psi\rangle = 0$. Angular momentum states with $m \neq 0$ can be constructed from the states $|\psi\rangle$ using the operators $U_{nn'}^l$, defined in (3.16):

$$|ln, \psi\rangle = U_{n0}^l |\psi\rangle. \hspace{1cm} (4.8)$$

The normlized matrix elements of the tensor operator $T_{LN}$ between such states are then given by

$$\frac{\langle l_2 n_2, \psi_2 | T_{LN} | l_1 n_1, \psi_1 \rangle}{\sqrt{\langle l_2 n_2, \psi_2 | l_2 n_2, \psi_2 \rangle \langle l_1 n_1, \psi_1 | l_1 n_1, \psi_1 \rangle}} = \frac{\langle \psi_2 | U_{0n_2}^{l_2} T_{LN} U_{n_0}^{l_1} | \psi_1 \rangle}{\sqrt{\langle \psi_2 | P_{l_0} \psi_2 \rangle \langle \psi_1 | P_{l_1} \psi_1 \rangle}}. \hspace{1cm} (4.9)$$

The direct evaluation of the right side of (4.9) is quite involved as both operators $U_{nn'}^l$ contain an integral over Euler angles. However, using the formula for a triple product of Wigner D-functions [46], one can show that the operator expressions as appearing on the right side of (4.9) can be rewritten as

$$U_{n_2 n_2}^{l_2} T_{LN} U_{n_1 n_1}^{l_1} = R_{L^2 N^2 L^1 N^1}^{l_2 n_2} \frac{2l_1 + 1}{2l_2 + 1} \sum_{N'n'} R_{L^{l_2} N^{l_2} L^1 N^1}^{n_2 n_2} U_{n_1 n_1}^{l_1 l_2}. \hspace{1cm} (4.10)$$

The first Clebsch-Gordan on the right side is a consequence of the Wigner-Eckhardt theorem. If expression (4.10) is substituted into the matrix element (4.9) one obtains

$$\frac{\langle l_2 n_2, \psi_2 | T_{LN} | l_1 n_1, \psi_1 \rangle}{\sqrt{\langle l_2 n_2, \psi_2 | l_2 n_2, \psi_2 \rangle \langle l_1 n_1, \psi_1 | l_1 n_1, \psi_1 \rangle}} = R_{L^2 N^2 L^1 N^1}^{l_2 n_2} t(l_1 l_2 L, \psi_1 \psi_2), \hspace{1cm} (4.11)$$
Table 4.1: Parameter $t(l_1l_2L)$ entering relation (4.11) for the matrix elements of $T_{LN}^{s'}$ with respect to the rotator states $|lm\rangle$ in $C_{60}$. The second column gives the result for finite coupling $g$ using the improved variational states introduced in (3.117). The third column is the result for $g \to \infty$ as given in (4.18). The last column is the ratio of the second over the third column.

<table>
<thead>
<tr>
<th>$l(l_1l_2L)$</th>
<th>$g = 1.532, J/\omega = 1$</th>
<th>$g \to \infty, J = 0$</th>
<th>Ratio (C2/C3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t(221)</td>
<td>0.0635</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>t(441)</td>
<td>0.0749</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>t(022)</td>
<td>0.3887</td>
<td>$\sqrt{2/15} = 0.3651$</td>
<td>1.065</td>
</tr>
<tr>
<td>t(222)</td>
<td>-0.4504</td>
<td>$-2/\sqrt{21} = -0.4364$</td>
<td>1.032</td>
</tr>
<tr>
<td>t(242)</td>
<td>0.4442</td>
<td>$2/\sqrt{21} = 0.4364$</td>
<td>1.018</td>
</tr>
<tr>
<td>t(442)</td>
<td>-0.4219</td>
<td>$-\sqrt{40/231} = -0.4161$</td>
<td>1.014</td>
</tr>
</tbody>
</table>

Note that the matrix elements now only contain one operator $U_{nm'}$, which substantially simplifies the calculations. Note that the previous formula also hold for complex spherical harmonics. One only needs to replace the Clebsch-Gordan coefficients $C_{lm}^{lm'}$ by $C_{lm}^{lm'}$.

Strong coupling limit

The parameter $t(l_1l_2L, \Psi_1\Psi_2)$ can be calculated exactly in the limit $g \to \infty$. The lowest excitations of $C_{60}$ are rotator excitations in the spin singlet subspace (see section 3.3.4). The spin triplet states are separated by a gap of 50-100 meV and I don't consider them here. As discussed in section 3.3.1, the rotator states are given by

$$|ln\rangle = U_{ln}^{l_{n0}}|\Psi\rangle \quad \text{with} \quad |\Psi\rangle = c_{01}^l c_{01}^l|2g e_0\rangle,$$

(4.13)

Note that I have put the variational parameter $g = g$ which is correct in the limit for $g \to \infty$. Due to the symmetry of $|\Psi\rangle$, only even values of $l$ are allowed. The tensor operators of interest are $T_{LN}^{s'}$ as introduced in (4.4) (the index $i$ dropped, because I consider a single molecule). Since I restrict the considerations to the singlet subspace, only matrix elements of tensor operators with $s = s'$ will be non-zero. In order to calculate the parameter $t(l_1l_2L)$ appearing in (4.11), matrix elements of the type $\langle \Psi | U_{ln} T_{LN}^{s'} | \Psi \rangle$ have to be evaluated. They are given by

$$\langle \Psi | U_{ln} T_{LN}^{s'} | \Psi \rangle = \frac{2l_{n0} + 1}{8\pi^2} \int d\Theta D_{ln}^{l_{n0}}(\Theta) \langle \Psi | U(\Theta) T_{LN}^{s'} | \Psi \rangle$$

(4.14)
4.1 Coupling of $C_{60}^{2-}$ ions

Figure 4.1: Parameter $t(022)$ (solid line), $t(221)$ (dotted line) and $-t(222)$ (dashed line) entering relation (4.11) as a function of $g$ and for $J = 0$. See also caption of Tab. 4.1.

$$= \frac{2l + 1}{8\pi^2} \int d\Theta D_{0n}^l(\Theta) \langle 0 | c_{01} c_{01}^\dagger U(\Theta) T_{LN}^{ss} c_{01}^\dagger c_{01} | 0 \rangle e^{-3g^2 \sin^2 \theta}.$$  

Because $T_{LN}^{ss'}$ is purely electronic, the electron and phonon contributions to the matrix element $\langle \Psi | U(\Theta) T_{LN}^{ss'} | \Psi \rangle$ can be separated as was done in the second equality. The exponential is due to the phonon coherent state. Due to this exponential, the main contribution to the integral come from the points $\theta = 0, \pi$. At these points

$$\langle 0 | c_{01} c_{01}^\dagger U(\Theta) T_{LN}^{ss} c_{01}^\dagger c_{01} | 0 \rangle = \langle 0 | c_{01} c_{01}^\dagger T_{LN}^{ss} c_{01}^\dagger c_{01} | 0 \rangle,$$  

for $\theta = 0, \pi$, (4.15)

because $c_{01}^\dagger c_{01}^\dagger | 0 \rangle$ is invariant under a rotation $\theta = \pi$. Using the explicit form of the tensor operators $T_{LN}^{ss}$ on verifies that

$$\langle 0 | c_{01} c_{01}^\dagger T_{LN}^{ss} c_{01}^\dagger c_{01} | 0 \rangle = \begin{cases} \sqrt{2/3} \delta_{N0} & L = 2 \\ 0 & L = 1 \\ -1/3 & L = 0 \end{cases}.$$  

(4.16)

Apparently, the matrix elements of $T_{LN}^{ss}$, i.e of the angular momentum, vanish in lowest order (no $1/g$ correction). This is a result which was already found by O'Brien in the case of $C_{60}$ [61]. The reason is, that in the strong coupling limit, the Jahn-Teller splitting of the orbitals is big such that transitions between orbitals are negligible in which case the expectation value of the angular momentum vanishes. Now we are in a position to evaluate the expression (4.14) approximately by replacing the factors in front of the exponential $e^{-3g^2 \sin^2 \theta}$ by their value at $\theta = 0, \pi$ as given in (4.16). The Wigner D-function simply becomes $\delta_{n0}$. In this way, one obtains for the tensor
operators $T^{n\mu}$

\[ \langle \Psi | U_{0n}T_{2n}^{\mu n} | \Psi \rangle \approx \delta_{n0}(2l + 1)\sqrt{\frac{2}{3}} I(g), \quad I(g) = \int_{-1}^{1} dt \ e^{-3g^2(1-t^2)}. \]  

(4.17)

Similarly, it can be shown that $\langle \Psi | U_{0l}T_{00}^{\mu \nu} | \Psi \rangle \approx -(2l + 1)I(g)/\sqrt{3}$. Likewise, the normalization factors become $\langle \Psi | P_{0l} | \Psi \rangle \approx (2l + 1)I(g)$. Inserting this into (4.11) yields the matrix elements of the tensor operator $T_{LN}^{n\mu}$ with respect to low energy rotator states $|ln\rangle$ of $C_{60}^2$ in the strong coupling limit $g \to \infty$:

\[ \frac{\langle l_2n_2 | T_{LN}^{n\mu} | l_1n_1 \rangle}{\sqrt{\langle l_2n_2 | l_2n_2 \rangle \langle l_1n_1 | l_1n_1 \rangle}} = \delta_{\nu\nu'} R_{LNN_1n_1}^{l_2n_2} \begin{cases} \sqrt{\frac{2}{3}} \sqrt{\frac{2l_1+1}{2l_2+1}} R_{0010}^{000} & L = 2 \\ 0 & L = 1 \\ -\frac{1}{\sqrt{3}} & L = 0 \end{cases}. \]  

(4.18)

Note that the relation $R_{2010}^{000} = C_{2010}^{000}$ holds. In the previous chapter variational states for the rotator states of $C_{60}^2$ were derived. With these states the matrix elements of the tensor operator $T_{LN}^{n\mu}$ can be calculated for finite $g$ by relation (4.11). Results are given in Tab. 4.1. As can be seen, the limit $g \to \infty$ is in good agreement with the finite $g$ results from the variational solution. The biggest deviation is less than 7%. Fig. 4.1 shows the dependence of some matrix elements on the electron-phonon coupling $g$.

In the following we will use the matrix elements (4.18) from the strong coupling limit $g \to \infty$ which simplifies the coupling $H_{eff}$ (relation (4.6)) between molecules further. In particular, the $L = 1$ tensor operators can be neglected. Furthermore, the $L = 0$ tensor operator is just a constant $T_{00}^{n\mu} = -\delta_{\nu\nu'}/\sqrt{3}$. Taking this into account in relation (4.6), one finds the effective coupling

\[ H_{eff} = 4 \sum_{NN'} K_{2N2N'} T_{2N}^{1\dagger} T_{2N'}^{2\dagger}, \quad \frac{2}{\sqrt{3}} \sum_{N} \left( K_{2N00} T_{2N}^{1\dagger} + K_{002N} T_{2N}^{2\dagger} \right) + \frac{4}{3} K_{0000}. \]  

(4.19)

4.2 Effective model

4.2.1 Rotator Hamiltonian

As discussed in section 3.3.1, the spectrum of $C_{60}^2$ in the strong coupling limit $g \to \infty$ is given by the spectrum of a rotator with a moment of inertia $I = 12g^2/\omega$ and where only even states are allowed. In the case of the finite coupling constant $g_{tot} = 1.532$, the spectrum of the low energy excitations is indeed well approximated by the rotator spectrum $l(l+1)/(2I)$ (see section 3.3.4). Likewise, it was shown
4.2. Effective model

above that the strong coupling limit \( g \to \infty \) gives also a very good description of the matrix elements involved in the coupling of a set of \( \text{C}^{2-}_{60} \) molecules. For these reasons, a system of coupled \( \text{C}^{2-}_{60} \) molecules can be mapped onto a system of coupled rotators such that the low energy excitations are the same. The effective rotator Hamiltonian is given by three terms \( H_{\text{rot}} = H_{\text{rot}}^0 + H_{\text{rot}}^1 + H_{\text{rot}}^e \) and the Hilbert space is restricted to even angular momentum states. \( H_{\text{rot}}^0 = \sum_i L_i^2/(2I) \), where the sum runs over all sites, describes the spectrum of a single \( \text{C}^{2-}_{60} \). \( H_{\text{rot}}^1 \) and \( H_{\text{rot}}^e \) correspond to the first and second term of \( H_{\text{eff}} \) as given in (4.19). They describe the interaction among molecules and an external field respectively. Eigenstates of \( H_{\text{rot}}^0 \) are spherical harmonics \( Y_{lm}(\Omega) \) with eigenvalues \( l(l+1)/(2I) \) (and \( \hbar = 1 \)).

Second rank tensor operators entering \( H_{\text{rot}}^1 \) and \( H_{\text{rot}}^e \) are defined by

\[
\tau_{ij} = \sum \frac{L_i^2}{2I} Y^{*}_{iN} Y_{iN}(\Omega_i), \tag{4.20}
\]

The matrix elements of these tensor operators are [46]

\[
\int d\Omega_i Y^{*}_{iN}(\Omega_i) \tau_{ij} Y_{iN}(\Omega_i) = \sqrt{\frac{2l_i + 1}{2l_j + 1}} R_{ij}^{l_0} R_{ij}^{l_0} R_{ij}^{l_0} R_{ij}^{l_0}, \tag{4.21}
\]

Up to a constant factor \( \sqrt{2/3} \), they are the same as in relation (4.18) for \( L = 2 \) tensor operators. Therefore, \( H_{\text{eff}} \) given in (4.19) can be rewritten in terms of the tensor operators \( \tau_{ij} \). In order to simplify the notation of what follows, the five-dimensional vector \( \tau_i = (\tau_{-2}, \ldots, \tau_2) \) is introduced. The Hamiltonian for a lattice (bct for \( \text{K}_4\text{C}_{60} \) and fcc for \( \text{Na}_2\text{C}_{60} \)) of coupled rotators takes then the form

\[
H_{\text{rot}} = \sum_i \frac{L_i^2}{2I} + \frac{1}{2} \sum_{i,j} \tau_{ij} \cdot (\mathcal{K}_{ij} \tau_i) - \sum_i \mathbf{h}_e \cdot \tau_i. \tag{4.22}
\]

\( \mathcal{K}_{ij} = \mathcal{K}_{ji} \) is a five-dimensional matrix with elements \( \mathcal{K}_{iN}^{i'N'} = (8/3)K_{iN}^{i'N'} \), where \( K_{iN}^{i'N'} \) is the effective interaction as defined in (4.7) between the molecules on site \( i \) and \( j \). \( \mathbf{h}_e \) is the external field given by \( h_{eN} = (2\sqrt{2}/3) \sum_j K_{jN}^{iN} \). The Hamiltonian is simplified assuming \( t_{nm} = t \delta_{nm} \) for nearest neighbors. This, as discussed above, yields the coupling matrix \( K_{LNN'} = t^2/\delta_{LL'} \delta_{NN'} \) and the rotator Hamiltonian becomes

\[
H_{\text{rot}} = \sum_i \frac{L_i^2}{2I} + \lambda \sum \tau_{ij} \cdot \tau_i, \tag{4.23}
\]

where second sum runs over pairs of nearest neighbors and \( \lambda = 8t^2/(3U) \).

The definition of \( H_{\text{rot}} \) given above has one drawback, namely that the angular momentum \( L_i \) and the operators \( \tau_{ij} \) are not in an obvious way conjugate variables. In order to resolve this, we write \( L_i \) and \( \tau_{ij} \) in terms of \( n_i = (n_{ix}, n_{iy}, n_{iz}) \) and
\( v_t = \partial_t n_t \), which are the position and velocity of the rotator. Obviously the vector \( n \) is subject to the constraint \( |n| = 1 \). With these variables, the angular momentum is given by \( L_t = n_t \times v_t \). On the other hand, the operators \( \tau_{i,N} \) can be expressed in terms of the vectors \( n_t \):

\[
\tau_i = \left( \sqrt{3} n_{ix} n_{iy} \sqrt{3} n_{ix} n_{iy} n_{iz}^2 - \frac{n_{ix}^2 + n_{iy}^2}{2}, \sqrt{3} n_{ix} n_{iz}, \sqrt{3} n_{iz}^2 - \frac{n_{iy}^2}{2} \right). \tag{4.24}
\]

Since \( \tau_{i,N} \) as given in (4.20) can be parametrized by two angles \( \theta_i, \phi_i \), there are three constraints upon the five components of \( \tau_{i,N} \). Using the form (4.24) and the constraint \( |n| = 1 \) one easily verifies that the following constraints hold:

\[
\begin{align*}
\tau_{i-2}^2 + \tau_{i-1}^2 + \tau_i^2 + \tau_{i+1}^2 + \tau_{i+2}^2 &= 1, \\
3 \left( \tau_{i+1}^2 + \tau_{i-1}^2 \right) + 2 \left( \tau_{i+1} + 1 \right) (2 \tau_{i+1} + 1) &= 0, \\
2 \tau_{i-1} \tau_{i+2} - \tau_{i-2} \left( \tau_{i+1}^2 - \tau_{i-1}^2 \right) &= 0.
\end{align*} \tag{4.25}
\]

Finally, we define the conjugate variable \( \pi_{i,N} = \partial_t \tau_{i,N} \). It can be shown that \( L_t^2 = \pi_i^2 \), where \( \pi_i = (\pi_{i-2}, \ldots, \pi_{i+2}) \). Hence, the Hamiltonian takes the form

\[
H_{rot} = \frac{1}{2I} \sum_i \pi_i^2 + \frac{1}{2} \sum_{i,j} \tau_j \cdot (\mathcal{K}_{ij} \tau_i) - \sum_i \hbar_e \cdot \tau_i. \tag{4.26}
\]

In this way the Hamiltonian can be written in terms of the conjugate variables \( (\tau_{i,N}, \pi_{i,N}) \) which are subject to the rather complicated constraints (4.25). Note that if the second and third constraints were absent, one would recover a non-linear sigma model with a five-dimensional vector \( \tau_i \) and the constraint \( \tau_i^2 = 1 \). In absence of all constraints, \( \pi_i^2 \) becomes just the Laplace operator in a five-dimensional space.

As discussed in (3.1.4), the five-dimensional coordinates can be written in terms of the Euler angels \( \Theta = (\phi, \theta, \gamma) \), the shape parameter \( \alpha \) and the magnitude \( q \). The Laplace operator can then be expressed in these variables which is done in Ref. [63]. Imposing the constraints (4.25), the Laplace operators reduces correctly to the Hamiltonian of a rotator parameterized by \( (\theta, \phi) \) [63].

### 4.2.2 Parameters for \( K_4C_{60} \) and \( Na_2C_{60} \)

#### Moment of inertia \( 1/I \)

In this section the parameters relevant for \( Na_2C_{60} \) and \( K_4C_{60} \) are discussed. Values for the moment of inertia \( I \) were discussed in section 3.3.4. Since it is a molecular property, it doesn't depend on the material (\( Na_2C_{60} \) or \( K_4C_{60} \)). Values range between \( 1/I = 1.63 - 4.37 \) meV depending on the type of calculation. In the strong coupling limit, \( I = 12g^2/\omega \). With \( \omega = 72.1 \) meV and \( g_{tot} = 1.532 \) one obtains \( 1/I = 2.56 \) meV.
4.2. Effective model

Figure 4.2: Left panel: Electronic bandstructure in bct K$_4$C$_{60}$. The bands are tight-binding bands calculated by Gunnarsson et al. in Ref. [100]. Right panel: Eigenvalues of the coupling term in the rotator Hamiltonian.

**Coupling and external field in K$_4$C$_{60}$**

The calculation of the effective coupling matrices $\mathcal{K}^{ij}$ and the external fields $h_e$ entering the rotator Hamiltonian (4.22) requires the knowledge of the electronic bandstructure because the effective interaction is due to virtual hopping processes. For this purpose we use the tight-binding bands derived in Ref. [100]. They are shown in Fig. 4.2. The bandwidth is 0.56 eV. As discussed in detail in Ref. [100], nearest neighbor as well as next nearest neighbor hopping is relevant. The latter stems from hopping processes via the K ions and contributes 40% to the total bandwidth. Knowing all hopping matrix elements, $\mathcal{K}^{ij}$ and $h_e$ are calculated from (4.7). The Coulomb energy $U = 1.27$ eV is used [42]. The coupling term $\sum_{ij} \tau_j \cdot (\mathcal{K}^{ij} \tau_i)/2$ is a quadratic form in $\tau_i$. It has the periodicity of the lattice and its eigenvalues can be drawn in a bandstructure-like way. They are shown in the right panel of Fig. 4.2. For each k-vector a $5 \times 5$ matrix $\mathcal{K}(k)$ has to be diagonalized which yields five bands. The bct lattice of K$_4$C$_{60}$ can be imagined as a bcc lattice with a slight compression (10%) in the c-direction [88]. In the following, when discussing lattice- or k-vectors we will neglect this compression and treat the positions of the C$_{60}$ molecules as in the bcc lattice. In the bct lattice, the labelling of the high-symmetry points is almost unchanged, with $\Gamma$, $H$, $P$, $X$, $M$ of the bct zone corresponding to $\Gamma$, $H$, $P$, $N$, $H$ of the bcc zone, respectively. The highest eigenvalue (6.65 meV) of the distortion bands occurs at the $\Gamma$-point. The lowest eigenvalue (-7.00 meV) occurs at the equivalent points $H = (0, 0, 2\pi)$ and $M = (2\pi, 0, 0)$. Since the nearest neighbors are at positions ($\pm 1/2, \pm 1/2, \pm 1/2$), the distortive order at the $H$-point (or $M$-point) correspond to a staggered distortion in the bipartite bct lattice. Below we will do a mean-field approximation where uniform and staggered distortions are considered. In this calculation only the matrices $\mathcal{K}(k)$ for $k = \Gamma, H$ are used. They are given
Table 4.2: Non-zero matrix-elements of $K(k)$ at the high-symmetry points $k = \Gamma, H$ of the bct lattice of $K_4C_{60}$ and $k = X$ of the fcc lattice of $Na_2C_{60}$. Most matrix elements $K_{NN'}(k)$ vanish because of the mirror symmetries of the bct and fcc lattice. There is one remaining off-diagonal element $K_{02}(k)$ coupling the 0 and 2-component. This leaves a $2 \times 2$ matrix to diagonalize. The eigenvalues are $E_-$ and $E_+$. Note that in the case of $Na_2C_{60}$ there are three different $X$-points: $X^a = (2\pi, 0, 0)$, $X^b = (0, 2\pi, 0)$ and $X^c = (0, 0, 2\pi)$ with different matrices $K_{X^a}$, $K_{X^b}$ and $K_{X^c}$. However, the eigenvalues if these matrices are the same.

in Tab. 4.2. The zeros in the matrices are due to symmetries of the bct lattice, namely the three mirror planes which coincide with coordinates planes. The reason that $K_\Gamma \neq -K_H$ are the next nearest hopping terms. The width of the distortion band is $W_D = 13.65$ meV. As can be seen from Fig. 4.2, the electronic bands as well as the distortive bands are roughly parallel which means that diagonal hopping is dominant. In this case the hopping term is approximatively given by $t_{nm} = t_\delta_{nm}$ and the coupling term takes the form (4.23) where a single constant $\lambda$ enters. The distortion bands become 5-fold degenerate and the bandwidth is given by $W_D = 8 \lambda$ (There are 8 nearest neighbors in the bct lattice). Hence, the appropriate coupling constant to choose is $\lambda = W_D/8 = 1.71$ meV. Finally the external field $h_e$ is found to be

$$h_e = (0, 0, 1.43, 0, 3.21) \text{ meV}.$$ (4.27)

Again, the zeros are due to the mirror symmetries of the lattice. The magnitude of the field is $|h_e| = 3.52$ meV and the shape parameter is $\alpha_e = 0.3 \pi \approx \pi/3$.

**Coupling in $Na_2C_{60}$**

$Na_2C_{60}$ has a fcc lattice with a lattice constant $a = 14.184$ Å [97]. It is isostructural to $K_3C_{60}$ which has a slightly larger lattice constant $a = 14.24$ Å [101]. To our knowledge, there are no bandstructure calculations for $Na_2C_{60}$. Since $Na_2C_{60}$ and $K_3C_{60}$ have the same lattice and almost the same lattice constant, we will use the bandstructure of $K_3C_{60}$. Furthermore, we assume a unidirectional structure where all molecules have the same orientation although the real structure is more complicated [97]. LDA calculations predict a bandwidth of $W = 0.6$ eV for $K_3C_{60}$ [101].
4.3 Mean-field solution

The LDA bands are well approximated by a nearest neighbor tight-binding model. We use the tight-binding parametrization given in Ref. [39] with an overall scaling such that the bandwidth is $W = 0.6$ eV. The resulting bands are shown in Fig. 4.3. Eigenvalues for the distortion coupling term are calculated as discussed above for $K_4C_{60}$. The resulting distortion bands are also shown in Fig. 4.3. The lowest eigenvalue occurs at the $\Gamma$-points. The multiplicity of the $\Gamma$-point in the Brillouin-zone is threefold leading to three different matrices $\mathcal{K}_{\Gamma}$, $\mathcal{K}_{X}$, and $\mathcal{K}_{X'}$ which have the same eigenvalues. They are given in Tab. 4.2. Again, the zeros in $\mathcal{K}_{X}$ are due to the mirror symmetries of the fcc lattice. Since the fcc lattice has higher symmetry, the external field $h_e$ vanishes in $Na_2C_{60}$ because the $C_{60}$ ions feel a cubic environment.

4.3 Mean-field solution

The Hamiltonian (4.22) is solved within a mean-field approximation. For this purpose, we will calculate the free energy $F_0(m, \beta)$ for a single molecule, where $m = \langle \tau \rangle$ is the expectation value of the operator $\tau = (\tau_{1-2} \ldots \tau_{12})$. This expectation value is related to the average distortion of the molecule and, in the following, we simply will refer to it as the distortion. It is the equivalent to the magnetization in a magnetic system. $\beta$ is the inverse temperature. In the mean field approximation, the free energy per $C_{60}$ of the interacting system is approximated by

$$F\left(\{m_i\}, \beta\right) = \frac{1}{N} \left[ \sum_i F_0(m_i, \beta) + \frac{1}{2} \sum_{i,j} m_j \cdot (\mathbf{K}^{ij} m_i) - \sum_i h_e \cdot m_i \right], \quad (4.28)$$

where $N$ is the number of $C_{60}$ sites. $F\left(\{m_i\}, \beta\right)$ has to be minimized with respect to the variables $\{m_i\}$. 

Figure 4.3: *Left panel:* Electronic bandstructure of fcc $Na_2C_{60}$. The bands are tight-binding bands with a width $W = 0.6$ eV [39]. *Right panel:* Eigenvalues of the coupling term in the rotator Hamiltonian of $Na_2C_{60}$. 
4.3.1 The local free energy $F_0$

Expansion for small fields

The local free energy $F_0$ can be derived from the thermodynamic potential

$$A_0(h, \beta) = -\frac{\ln[Z_0(h, \beta)]}{\beta}, \quad Z_0(h, \beta) = \text{Tr} \exp \left[-\beta \left( \frac{L^2}{2I} - h \cdot \tau \right) \right], \quad (4.29)$$

where $Z_0$ is the partition function of a single molecule. The free energy is then given by the Legendre transform of $A_0$:

$$F_0(m, \beta) = \max_{h} \left[ A_0(h, \beta) + h \cdot m \right]. \quad (4.30)$$

Since the thermodynamic quantities $Z_0$, $A_0$ and $F_0$ describe a single molecule, i.e. a finite system, they have to be analytic functions of all their respective variables. As discussed in section 3.1.4, five-dimensional vectors such as $m$ and $h$ can be parameterized in terms of the Euler angles $\Theta = (\phi, \theta, \gamma)$ as well as the magnitude $m = |m|$ and the shape parameter $\alpha$. Since the Hamiltonian of a single molecule (or rotator) is $SO(3)$ invariant, it follows that thermodynamic potentials don't depend on the Euler angles, i.e. $A_0 = A_0(h, \alpha, \beta), \quad F_0 = F_0(m, \alpha, \beta) \quad \text{etc.}$ Out of a 5-vector, two polynomials can be constructed which are independent of the Euler angles and takes the values $q^2$ and $q^3(\cos 3\alpha)$. The two polynomials are given in 3.36. As a consequence, the analyticity condition implies that the thermodynamic potentials are functions of $q^2$ and $q^3(\cos 3\alpha)$ ($q$ standing for $h$ or $m$). Hence, for example, $F_0$ has to be of the form

$$F_0(m, \alpha, \beta) = f_0(\beta) + f_2(\beta) m^2 + f_3(\beta) m^3 \cos(3\alpha) + f_4(\beta) m^4 + O(m^5). \quad (4.31)$$

Likewise, $Z_0(h, \beta)$ and $A_0(h, \beta)$ are of the same form. Their power expansion for small $h$ is given by the functions $z_i(\beta)$ and $a_i(\beta)$ respectively. The functions $f_i(\beta)$, $z_i(\beta)$ and $a_i(\beta)$ are not independent. Knowing one set defines the two others by definitions (4.29) and (4.30). In a straightforward way, the definition (4.29) implies

$$a_0 = -\frac{\ln[z_0]}{\beta}, \quad a_2 = -\frac{z_2}{\beta z_0}, \quad a_3 = -\frac{z_3}{\beta z_0}, \quad a_4 = -\frac{z_4}{\beta z_0} + \frac{z_2^2}{2\beta z_0^2}, \quad (4.32)$$

where the dependence on the inverse temperature $\beta$ was not explicitly written. The relation between $a_i(\beta)$ and $f_i(\beta)$ is given by (4.30). Since $F_0$ and $A_0$ are independent of the Euler angels we can choose $\Theta = 0$ for both, $m$ and $h$, which maximizes the term $h \cdot m$ in (4.30) and yields

$$F_0(m, \alpha, \beta) = \max_{h, \alpha'} \left[ A(h, \alpha', \beta) + h \cdot m \cos(\alpha - \alpha') \right]. \quad (4.33)$$
Expanding \( h \) and \( \alpha \) in powers of \( m \) and optimizing the expansion coefficients such as to maximize (4.33) one finds

\[
\alpha' = \alpha - \frac{3a_3 \sin(3\alpha)}{(2a_2)^2} m + O(m^2), \quad h = -\frac{m}{2a_2} - \frac{3a_3 \cos(3\alpha)}{(2a_2)^3} m^2 + O(m^3). \tag{4.34}
\]

Reinserting this results in (4.33) yields:

\[
f_0 = a_0, \quad f_2 = -\frac{1}{4a_2}, \quad f_3 = -\frac{a_3}{(2a_2)^3}, \quad f_4 = \frac{a_4}{(2a_2)^4} - \frac{9a_3^2}{2(2a_2)^5}. \tag{4.35}
\]

**Limit \( T = 0 \)**

We start with the limit \( T = 0 \), i.e. \( \beta \to \infty \). In this limit, the partition function is given by \( Z_0(h, \beta) = \exp[-\beta \epsilon_0(h)] \), where \( \epsilon_0(h) \) is the lowest eigenvalue of \( L^2/(2I) - h \cdot \tau \). It follows that \( \mathcal{A}_0(h) = \epsilon_0(h) \). Using perturbation theory, one finds

\[
\mathcal{A}_0(h) = \epsilon_0(h) = -\frac{I}{15} h^2 - \frac{2I^2}{315} h^3 \cos(3\alpha) + \frac{13I^3}{23625} h^4 \tag{4.36}
\]

Using relations (4.35) we find the local free energy

\[
F_0(m, \alpha) = \frac{1}{T} \left[ \frac{15}{4} m^2 - \frac{75}{28} m^3 \cos(3\alpha) + \frac{1185}{196} m^4 \right]. \tag{4.37}
\]

**Classical limit \( T \to \infty \)**

In this limit, the temperature is much bigger than the typical energy scale of the rotator. Or in terms of the inverse temperature: \( \beta \ll I \). As a consequence, the \( L^2 \) term can be neglected and \( \tau \) can treated as a classical variable. The partition function is then given by

\[
Z_0(h, \beta) = \int \frac{d\Omega}{4\pi} \exp \left[ \beta h \cdot \tau(\Omega) \right], \tag{4.38}
\]

where the components of \( \tau(\Omega) \) are given by (4.20). Again, we can choose the Euler angle \( \Theta = 0 \) for \( h \) which yields

\[
Z_0(h, \alpha, \beta) = \int \frac{d\Omega}{4\pi} \exp \left\{ \beta h \left[ \cos \alpha \left( \frac{3}{2} \cos^2 \theta + \frac{1}{2} \right) + \frac{\sqrt{3}}{2} \sin \alpha \sin^2 \theta \cos 2\phi \right] \right\}. \tag{4.39}
\]

This integral cannot be calculated analytically. However, the exponential can be developed in powers of \( \beta h \) which allows to calculate the power expansion of \( Z_0 \):

\[
Z_0(h, \alpha, \beta) = 1 + \frac{(\beta h)^2}{10} + \frac{(\beta h)^3}{105} \cos(3\alpha) + \frac{(\beta h)^4}{280}. \tag{4.40}
\]
Using relations (4.32) and (4.35) yields the free energy

\[ F_0(m, \alpha, \beta) = \frac{1}{\beta} \left[ \frac{5}{2} m^2 - \frac{25}{21} m^3 \cos(3\alpha) + \frac{425}{196} m^4 \right]. \]  

\( a_2(\beta) \) at finite temperature

In the case of finite temperature, we will derive a convenient sum which allows to evaluate the functions \( a_2(\beta) \) and \( f_2(\beta) \). As is discussed in the next section, \( f_2(\beta) \) is the relevant quantity for the phase transition. In order to derive the expression, the following relation is used:

\[ \partial^2 \lambda \left( \text{Tr} e^{A + \lambda B} \right) = \sum_{nm} |B_{nm}|^2 \frac{e^{A_n} - e^{A_m}}{A_n - A_m}, \]  

where \( A \) and \( B \) are two operators which, in general, don’t commute. The indices \( n \) and \( m \) run over a basis, in which \( A \) is diagonal with eigenvalues \( A_n \). The matrix elements of \( B \) in this basis are \( B_{nm} \). Formula (4.42) can be derived by expanding the exponential and then doing the derivatives. Comparing to the definition (4.29) of the partition function yields the correspondence \( A = -\beta L^2/(2I), B = \beta (h \cdot \tau)/h \) and \( \lambda = h \). The sum over \( n \) in (4.42) becomes a sum over all even angular momentum states \( (lm) \). The eigenvalues of \( A \) are \( A_l = -((\beta/I) l(l+1)/2 \) and don’t depend on \( m \). Furthermore, using sum rules for Clebsch-Gordan coefficients [46] and the matrix elements (4.21) one can show that

\[ \sum_{m_1 m_2} B_{l_2 m_2 l_1 m_1}^2 = \frac{\beta^2}{h^2} \sum_{m_1 m_2} |\langle l_2 m_2 | h \cdot \tau | l_1 m_1 \rangle|^2 = \beta^2 \frac{2l_1 + 1}{5} \left( R_{20 l_1 0} \right)^2. \]  

Figure 4.4: The function \( a_2(x) \) as given in (4.44) the dashed line is the behavior \( a_2(x) \approx x/10 \) for small \( x \).
4.3. Mean-field solution

Note again that $R^{\gamma\gamma}_0 = C^{\gamma\gamma}_0$. Inserting this into (4.42) and carrying out some cumbersome algebra yields finally $a_2(\beta) = I \hat{a}_2(\beta/I)$, where

$$
\hat{a}_2(x) = -\frac{\sum_l \exp \left[ -\frac{\pi}{2}(l+1) \right]}{\sum_l \exp \left[ -\frac{\pi}{2}(l+1) \right]} \binom{l(l+1)(2l+1)}{10(2l-1)(2l+3)} x + \frac{3(2l+1)}{5(2l-1)(2l+3)} \frac{3(2l+1)}{5(2l-1)(2l+3)^2}, \quad \text{l even.} \tag{4.44}
$$

The sums in (4.44) run over even $l$ and can easily be evaluated with a computer. The function $\hat{a}_2(x)$ is shown in Fig. 4.4. One verifies that $\lim_{x\to\infty} \hat{a}_2(x) = -1/15$, which is just the behavior predicted in (4.36). To work out the behavior for small $x$ is much more involved and is not discussed here. Only the result shall be stated:

$$
\hat{a}_2(x) = -\frac{x}{10} + \frac{x^2}{20} - \frac{x^3}{75} + O(x^4). \tag{4.45}
$$

Taking only the first term one obtains $a_2(\beta) = -\beta/10$ which yields the same second order term $f_2 = 5/(5\beta)$ in (4.41).

4.3.2 Solution for K\textsubscript{4}C\textsubscript{60}

In a bipartite lattice, such as the bct lattice of K\textsubscript{4}C\textsubscript{60}, one expects a solution of the type $m_i = m_0 \pm m_s$ where $m_0$ is the ferrodistortive moment and $m_s$ is a staggered moment with different sign on the two sublattices. The free energy (4.28) per site becomes then

$$
F(m_0, m_s, \beta) = \frac{1}{2} [F_0(m_0 + m_s, \beta) + F_0(m_0 - m_s, \beta)] + m_0 \cdot (K_\Gamma m_0) + m_s \cdot (K_H m_s) + h_s \cdot m_0. \tag{4.46}
$$

The matrices $K_\Gamma$ and $K_H$ are the Fourier transform of the coupling matrices $K^{ij}$ at the high symmetry points $\Gamma$ and $H$ of the bct lattice. The moments on sublattice 1 and 2 are $m_1 = m_0 + m_s$ and $m_2 = m_0 - m_s$ respectively. In terms of $m_1$ and $m_2$ the free energy becomes

$$
F(m_1, m_2, \beta) = \frac{1}{2} F_0(m_1, \beta) + \frac{1}{2} F_0(m_2, \beta) + \frac{1}{4} m_1 \cdot ([K_\Gamma + K_H] m_1) \tag{4.47}
+ \frac{1}{4} m_2 \cdot ([K_\Gamma + K_H] m_2) + \frac{1}{2} m_1 \cdot ([K_\Gamma - K_H] m_2) + \frac{1}{2} h_s \cdot (m_1 + m_2).
$$

Isotropic coupling

We first consider the case of isotropic coupling, which corresponds to the Hamiltonian (4.23). In what follows, we derive a phase diagram for the isotropic model. This phase diagram is generic and, as will be shown subsequently, taking into account the anisotropy only leads to a minor shift of the phase transition line.
If the coupling is isotropic, then the external field vanishes $h_\varepsilon = 0$. The coupling matrices are given by $K_{T,N,N'} = -K_{H,N,N'} = \kappa \delta_{N,N'}$ where $\kappa = z \lambda / 2$ with $z = 8$ being the number of nearest neighbors in the bct lattice. Using equation (4.47), the free energy becomes

$$F(m_1, m_2, \beta) = \frac{1}{2} F_0(m_1, \beta) + \frac{1}{2} F_0(m_2, \beta) + \kappa m_1 \cdot m_2. \tag{4.48}$$

The free energy as given in (4.48) has to be minimized with respect to $m_1$ and $m_2$ which, in general, are 10 parameters. In order to simplify the minimization, we make the ansatz

$$m_1 = m(0, 0, \cos \alpha, 0, \sin \alpha), \quad m_2 = m(0, 0, \cos \alpha', 0, \sin \alpha'), \quad \alpha' = \frac{4\pi}{3} - \alpha. \tag{4.49}$$

Using relations (3.36), one verifies that the distortions $m_1$ and $m_2$ have the same magnitude and shape parameters, namely $m$ and $\alpha$. However, they are rotated with respect to each other: $m_2$ results from rotating $m_1$ by the Euler angles $\phi = \theta = \gamma = \pi/2$. Inserting the ansatz in (4.48) and using the expansion (4.31) yields the free energy (the dependence on the inverse temperature is omitted)

$$F(m, \alpha) = f_2 m^2 + f_3 m^3 \cos(3\alpha) + f_4 m^4 - \kappa m^2 \cos\left(\frac{\pi}{3} - 2\alpha\right). \tag{4.50}$$
The advantage of ansatz (4.49) is now apparent. For $0 < \alpha < \pi/6$ both, the third order term (with $f_3 < 0$) and the coupling term are negative. The third order term is optimized for $\alpha = 0$ whereas the coupling term is optimized for $\alpha = \pi/6$. Near the phase transition, where $m$ is small, the coupling term dominates over the third order term and we therefore set $\alpha = \pi/6 - \delta$, where $\delta$ should be small. Inserting this into (4.50) and expanding in $\delta$ yields

$$F(m, \delta) = f_2 m^2 + 3 f_3 m^3 \delta + f_4 m^4 - \kappa m^2 (1 - 2 \delta^2) + O(\delta^3).$$

(4.51)

Minimizing $F(m, \delta)$ with respect to $\delta$ one finds

$$\delta = \frac{3 f_3 m}{4 \kappa}.$$  

(4.52)

Hence, $\delta$ is proportional to $m$ which justifies the assumption that $\delta$ is a small parameter. In addition, after reinsertion of $\delta$, the third order term in (4.51) becomes a fourth order term in $m$:

$$F(m) = (f_2 - \kappa) m^2 + \left( f_4 - \frac{9 f_3^2}{8 \kappa} \right) m^4.$$ 

(4.53)

This free energy describes a second order phase transition if the coefficient of the fourth order term is positive. Assuming this being the case, the phase transition occurs if $\kappa = f_2(\beta)$. This condition gives the phase transition line in a $T$-$\kappa$ phase diagram. All one needs to know to draw it is the coefficient $f_2(\beta)$ which can be obtained from $a_2(\beta)$ as calculated above. Right at the phase transition, the condition for the fourth order term to be positive becomes $f_4 > 9 f_3^2/(8 f_2)$, which is fulfilled in both, the low and high temperature phase. The corresponding phase diagram is shown in Fig. 4.5. Also shown in Fig. 4.5 are the magnitude $m$ and the shape parameter $\alpha$ in the ordered phase at $T = 0$. Near the phase transition $\alpha \approx \pi/6$. In the limit $\kappa \to \infty$ one approaches $m = 1$ and $\alpha = 0$ which correspond to statically distorted state where molecular levels are split into a low-energy singlet and a high-energy doublet. From ansatz (4.49) it can be seen that in sublattice 1 the $n = 0$ level ($z$-symmetry) lies lowest whereas on sublattice 2 it is the $n = -1$ level ($y$-symmetry). It is interesting to note that we would recover the same result when we would do a simple bandstructure calculating and treating the phonon coordinates as classical variables. Optimizing the ground state energy with respect to the classical phonon coordinates for a filling of 2 electrons per molecule would yield a staggered distortion with the same order.

**Parameters of $K_4C_{60}$**

In this section we explore the effect of taking into account the actual bandstructure of $K_4C_{60}$ which leads to an anisotropic coupling and an external field $h_z$. The
Figure 4.6: Left panel: Ferrodistortive moment $m_0 = (0,0,m_{0,0},0,m_{0,2})$ as a function of the moment of inertia $1/I$ in $K_4C_{60}$ at $T = 0$. $m_0$ minimizes (4.54) assuming $m_s = 0$. Right panel: Lowest eigenvalue of $K' + K_H$ as given in (4.55) where $K'_{NN'} = \delta_{m_N m_{N'}} F_0(m_0)/2$ ($m_0$ is given on the left panel). A staggered moment $m_s \neq 0$ develops when the eigenvalue becomes negative which occurs for $1/I_e = 1.54$ meV. The dotted line is the result when only the constant term $15/(4I)$ of (4.55) is taken into account.
given in Tab. 4.2. The lowest eigenvalue of $\mathcal{K}' + \mathcal{K}_H$ occurs for $(N, N') = (-1, -1)$ and is given by

$$(\mathcal{K}' + \mathcal{K}_H)_{-1,-1} = \frac{15}{4I} \left[ 1 - \frac{15}{14} (m_{0,0} - \sqrt{3} m_{0,2}) + \frac{158}{49} (m_{0,0}^2 + m_{0,2}^2) \right] + \mathcal{K}_H_{-1,-1}.$$  

As already discussed, the phase transition occurs when this eigenvalue becomes negative. For small $m_0$, only the constant term in the square bracket of (4.54) is important and the phase transition occurs if $15/(4I) = f_2 = |\mathcal{K}_H_{-1,-1}|$. This criterion is equivalent to the one found above for the isotropic case. Hence, if only the constant term is taken into account, then one recovers the phase diagram given in Fig. 4.5 (with the $\kappa$-axis being the magnitude of the lowest eigenvalue of coupling matrix). The finite field $m_0$ reduces the critical $1/\gamma_c$ to lower values of $1/I$ (i.e. it shifts the phase boundary in Fig. 4.5 somewhat to the right). This is shown in the right panel of Fig. 4.6. For the parameters used here, the critical moment of inertia is $1/I_c = 1.54$ meV. This value is rather lower than $1/I$ of $K_4C_{60}$ which are of the order $1.6 - 4.5$ meV. Nevertheless, the system is expect to be close to the phase transition and applying pressure might drive it into the staggered phase (see discussion at the end of the chapter). In the staggered phase, the distortion is given by $\mathbf{m}_i = (0, \pm m_0, m_{0,0,0}, m_{0,2})$. The shape parameter of the staggered moment is again $\alpha = \pi/6$ which correspond to a biaxial symmetry (see Fig. 3.1) as in the case of the isotropic coupling.

### 4.3.3 Solution for Na$_2$C$_{60}$

In Na$_2$C$_{60}$ the external field $h_0$ vanishes. The reason is the high symmetry of the fcc lattice where the $\text{C}_{60}$ ions feel a cubic environment. Since $h_0 = 0$, there will be no distortion if the coupling is small. As discussed in section 4.2.2, the biggest negative eigenvalues of the coupling matrix occur at the $X$-points. They are given in Tab. 4.2. The two lowest eigenvalues are $\kappa(X) = -10.11$ meV and $\kappa_1(X) = -9.93$ meV. They are almost degenerate and we consider both in the following. Since there are three different $X$-points in the Brioullin zone, the eigenvectors corresponding to eigenvalues $\kappa_0(X)$ and $\kappa_1(X)$ depend on the $X$-point. In the case $X^a = (2\pi, 0, 0)$, $\kappa(X^a)$ is almost diagonal as can be seen from Tab. 4.2. There is a small off-diagonal element $\kappa_{02}(X^a) = 0.5$ meV which we will neglect in the following. Under this assumption the eigenvectors of $\kappa_0$ and $\kappa_1$ for the three different $X$-points ($X^b = (0, 2\pi, 0)$ and $X^c = (0, 0, 2\pi)$) are

\[
\begin{align*}
\mathbf{n}_0^a &= e^{2\pi i r_x} \left( 1, 0, 0, 0, 0 \right), & \mathbf{n}_1^a &= e^{2\pi i r_x} \left( 0, 0, 1, 0, 0 \right), \\
\mathbf{n}_0^b &= e^{2\pi i r_y} \left( 0, 0, 0, 1, 0 \right), & \mathbf{n}_1^b &= e^{2\pi i r_y} \left( 0, 0, -\frac{1}{2}, 0, -\frac{\sqrt{3}}{2} \right),
\end{align*}
\]  

(4.56)
Figure 4.7: Distorted phase of Na$_2$C$_{60}$ represented as distorted spheres. The distorted spheres point along the four diagonals of the cube. The new unit cell is the cube shown and contains four molecules which are distorted along different directions.

\[ \mathbf{n}_{0,i} = e^{2\pi i x_{i,t}} (0,1,0,0,0), \quad \mathbf{n}_{r,i} = e^{2\pi i r_{x,t}} \left( 0,0,-\frac{1}{2},0,\frac{\sqrt{3}}{2} \right). \]

The index \( i \) indicates the site at position \( (r_{x,i}, r_{y,i}, r_{z,i}) \) (the lattice constant is set \( a = 1 \)). The vectors are normalized such that \( |\mathbf{n}_{0,i}| = |\mathbf{n}_{r,i}| = 1 \). If, for example, the magnetization is set \( \mathbf{m}_i = m \mathbf{n}_{0,i} \), then the free energy per particle given in (4.28) becomes

\[ F'({\mathbf{m}_i}, \beta) = \frac{1}{2} [F_0(m_{i=0}, \beta) + F_0(-m_{i=0}, \beta)] + \kappa_0 m^2. \] (4.57)

This relation holds also for the other eigenvectors. Since the free energy in (4.57) is invariant under \( \mathbf{m}_i \rightarrow -\mathbf{m}_i \), one expects a second order transition as discussed for the isotropic case. Since the vectors \( \mathbf{n}_{0,i}, \mathbf{n}_{r,i}, \mathbf{n}_{\sigma,i} \) have the same eigenvalue \( \kappa_0 \), any linear combination of them still has the same eigenvalue \( \kappa_0 \) and minimizes the energy of the coupling term. The same holds for the eigenvalue \( \kappa_1 \). Hence, the magnetization can also chosen to be

\[ \mathbf{m}_{0,i} = \frac{m}{\sqrt{3}} (\mathbf{n}_{0,i}^a + \mathbf{n}_{0,i}^b + \mathbf{n}_{0,i}^c), \quad \mathbf{m}_{r,i} = \frac{m}{\sqrt{3}} (\mathbf{n}_{r,i}^a + \mathbf{n}_{r,i}^b + \mathbf{n}_{r,i}^c). \] (4.58)
4.3. Mean-field solution

Figure 4.8: Left panel: Free energy $IF(m) = IF_0(m, \alpha = 0, T = 0) - x c m^2$ of Na$_2$C$_6$O$_{3}$ at the critical coupling $x_c = |\kappa_0| = 3.3257$ where the first order phase transition occurs. Right panel: Magnetization $m$ as a function of the parameter $x = |\kappa_0|$ for $T = 0$. The jump of $m$ at the first order phase transition is indicated by the dashed line. The critical magnetization is $m_c = 0.356$. Near the phase transition, $m(x)$ is not single-valued because of metastable states.

Again, the free energy can be worked out and one finds

$$F_0(m, \alpha = 0, \beta)$$. In the previous relations the local free energy is written as a function of the magnitude of the distortion $m$ and the shape parameter $\alpha$. In the second equation of (4.59), one can introduce $m' = (2m)/\sqrt{3}$, which yields

$$F_0(m', \alpha = 0, \beta) + \kappa_1 m^2.$$ (4.60)

Obviously, in the case $\kappa_0 = \kappa_1$ the minimal values of $F_0(m', \alpha = 0, \beta)$ are always a factor $3/4$ smaller than those of $F_0(m, \alpha = 0, \beta)$. Hence, $m_{0,i}$ minimizes the free energy. The fact that $\kappa_0$ is slightly lower than $\kappa_1$ favors the $m_{0,i}$ distortion additionally.

Comparing the free energy $F_0(m', \alpha = 0, \beta)$ to the free energy $F_0(m, \alpha = 0, \beta)$ of (4.57), the third order term in $m$ is important. From the $T = 0$ and $T \rightarrow \infty$ expansions (4.37) and (4.41) of $F_0$, it can be seen that the third order term of $F_0(m', \alpha = 0, \beta)$ is negative for $\alpha = 0$. This term is absent in (4.57). Therefore, the free energy $F_0(m', \alpha = 0, \beta)$ is lower than the free energy $F_0(m, \alpha = 0, \beta)$ given in (4.57) and the magnetization $m_{0,i}$ is favorable. In addition, due to the third order term, the phase transition will be of first order. $m_{0,i}$ is shown in Fig. 4.7.

We consider the case $T = 0$ in some detail. At $T = 0$ the overall energy scale of the local free energy is given by the inverse of the moment of inertia $1/I$. The
phase transition occurs for some critical, dimensionless value $x_c = |\kappa_0| I$. Numerical calculations yield $x_c = 3.3257$. The free energy (4.59) right at the phase transition is shown in Fig. 4.8. Since it is a first order phase transition, there are two minima with the same energy. The two minima are separated by a small barrier of the order $IF \approx 3 \times 10^{-3}$. The magnetization as function of the dimensionless coupling $x = |\kappa_0| I$ is also shown in Fig. 4.8. As can be seen, the region where there is a second metastable minimum is small $3.276 < x < 3.75$. The upper limit is $IF_2(T = 0) = 15/4$ where the second order phase transition would occur if the third order term were absent (see equation (4.37)). In the limit $T \to \infty$ the qualitative behavior is found to be similar, but with an overall energy scale $1/\beta$ instead of $1/I$. The critical coupling is given by $x_c(T \to \infty) = |\kappa_0| \beta = 2.2707$ and the critical field is $m_c(T \to \infty) = 0.429$. Again, the critical coupling is close to the second order phase transition $\beta f_2(T \to \infty) = 5/2$. In both limits, we find that the condition for the phase transition is close to the condition $|\kappa_0| = f_2(\beta)$ (within 10%) which is the condition for the second order phase transition in the case of isotropic coupling in a bipartite lattice. Therefore, the phase diagram for Na$_2$C$_6$O should look similar to the one for the isotropic bipartite lattice shown in Fig. 4.5 (where $\kappa$ has to be replaced by $|\kappa_0|$). In fact, one expects a first order transition line which is slightly shifted to the left with respect to the second order phase transition of Fig. 4.5.

4.4 Discussion

In the previous section we found for both compounds, K$_4$C$_{60}$ and Na$_2$C$_{60}$, a phase transition from a Jahn-Teller-Mott state where the molecular dynamics is uncorrelated to a cooperative Jahn-Teller state where the distortions on different molecules are correlated. The nature of the transition, i.e. first or second order, depends on the lattice. In the bipartite bet lattice of K$_4$C$_{60}$ a second order phase transition to a staggered moment occurs. Generally, we expect such a transition in any bipartite lattice. On the other hand, the fcc lattice of Na$_2$C$_{60}$ is not bipartite which renders the transition weakly first order. Also, the resulting order is more complicated and leads to a superstructure with four molecules in the unit cell, each of which is distorted along a different direction. The phase diagrams of the two materials are expected to be similar to the one shown in Fig. 4.5 for the isotropic case where the phase-transition line is given by the condition $\kappa_c = f_2(\beta_c)$. This means that the transition occurs when the lowest eigenvalue of the coupling term in the free energy (4.28) cancels the quadratic term in the local free energy $F_0$. The external field $h_c$ in K$_4$C$_{60}$ and the weak first order transition in Na$_2$C$_{60}$ only lead to slight shifts of the phase-transition line in Fig. 4.5. For $T = 0$ a quantum phase transition is expected. Using a moment of inertia $1/I = \bar{\omega}/(12g^2_{\text{tot}}) = 2.56$ meV yields a critical value $\kappa^* = 9.6$ meV. Since the lowest eigenvalues of the coupling term is $-7$ meV...
and \(-10.1\) meV for \(K_4C_{60}\) and \(Na_2C_{60}\) respectively, we expect the former to be in the uncorrelated state whereas the latter should show a cooperative Jahn-Teller distortion. Of course, at finite temperature, thermal fluctuations kill the correlations and we expect a phase-transition in \(Na_2C_{60}\) to an uncorrelated phase at around 30 K (see Fig. 4.5).

It is not clear, how this transition can be detected experimentally. The main problem is that the two phases on either side of the transition are insulators and non-magnetic which excludes a number of simple experiments as possible probes of the transition. A direct way to see it would be a careful diffraction experiment, such as x-ray diffraction, with which the crystal structure can be determined. This was done for \(K_4C_{60}\) and \(Rb_4C_{60}\) in Ref. [102] where no indication of a quadrupole distortion (\(l = 2\)) was found. The authors exclude quadrupole distortions beyond a 0.04 Å difference in the equatorial and polar radii of the \(C_{60}\) molecule. However, this does not imply that Jahn-Teller distortions are absent. First, the C-C bonds are stiff and therefore displacement are expected to be small. Second, those Jahn-Teller modes which are higher in energy have phonon eigenvectors which correspond to higher angular momentum distortions (\(l > 2\)) when the \(C_{60}\) molecule is modelled as a spherical shell [103]. Hence, these modes have little overlap with a quadrupole distortion and their distortion can't be probed by a quadrupole measurement.

A local probe of the distortion is given by spectroscopic measurements of phonon frequencies because the splitting of the frequencies depends on the local symmetry of the molecule and therefore on its distortion. In Ref. [104] the two high-frequency \(T_{1u}\) modes were measured by infrared spectroscopy. The \(T_{1u}(4)\) mode appears as a triplet below 250 K and changes to a doublet at higher temperatures. This suggest a phase transitions from biaxial symmetry of the molecule below 250 K to an axial symmetry above. A transition at 250 K would require a lowest eigenvalue of the effective coupling of the order \(-60\) meV rather then \(-7\) meV. Hence, the energy scale of the transition seen in Ref. [104] is much higher than the energy scale of the phase transition that we propose. Interestingly, although the energy scale is wrong, the phase transition that we propose suggests the same change in symmetry as observed in Ref. [104]. Namely, in the ordered phase (low temperature) a stagger moment is expected which corresponds to biaxial distortions. At higher temperature, where the staggered moment is absent, there is still the uniform moment induced by the external field \(h_0\) which correspond to an axial symmetry (because the shape parameter of \(h_0\) is \(\alpha \approx \pi/3\)).

In Ref. [105] a phase transition at 50 K in \(Na_2C_{60}\) was detected by spin resonance as well as Raman spectroscopy. The phase transition was attributed to a metal-insulator transition. Hence, here the critical temperature of the transition is in agreement with the critical temperature of our transition (30 K, see above), but the proposed nature of the transition is different. In particular, Ref. [105] suggests a metallic state above 50 K whereas our high-temperature state is a state where the
molecules are uncorrelated and charges are localized. Therefore it is an insulator. However, one experimental observation involved in the conclusion of Ref. [105] still agrees with our picture. Namely, a large narrowing of the $H_g(2)$ line-width below 50 K is observed. Generally, we expect a bigger line-width for the dynamic Jahn-Teller state than for the static one. Hence, in the low-temperature phase where the Jahn-Teller effect is cooperative and phonon coordinates are statically displaced, the line-width should be small. On the other hand, in the high temperature phase where molecules are uncorrelated and in a dynamic Jahn-Teller state, one expects a bigger line-width. This agrees with the observations of Ref. [105].

Finally, we want to note that the phase transition proposed above can be tuned by applying pressure which increases the hopping between molecules. As a consequence, the effective coupling is increased as well and the system is driven towards or into the ordered phase. The dependence of the hopping on the lattice constant is to a good approximation given by the factor $\exp(-\delta a/\text{Å})$ [39], where $\delta a$ is the change of the cubic lattice constant. The change of the lattice constant $\delta a$ is related to the pressure $P$ by the isothermal bulk modulus $B$ via $\delta a/a = -P/(3B)$ ($a = 14$ Å in fcc $C_{60}$). Therefore

$$\kappa \propto t^2 \propto \exp \left( \frac{28}{3} \frac{P}{B} \right) \approx \exp \left( 10 \frac{P}{B} \right),$$

where $\kappa$ and $t$ are the energy scales of the effective interaction and the hopping respectively. Bulk moduli in $C_{60}$ compounds are of the order 20 GPa which corresponds 200 kbar [106, 107]. Applying, for example, a pressure of 10 kbar increases the effective coupling $\kappa$ by a factor $\exp(1/2) = 1.65$. This would easily drive $K_4C_{60}$ into the ordered phase. Experimentally, the closely related $Rb_4C_{60}$ under pressure (up to 12 kbar) was investigated by NMR [86]. At $T = 0$ a metallic phase appears at an applied pressure of roughly 8 kbar. At this pressure, the lowest eigenvalue of effective coupling in $K_4C_{60}$ is roughly $-7 \exp(8/20) \approx -10$ meV which corresponds to the critical value $\kappa^*$ of the phase transition. Whether this is just an accidental coincidence or whether the transition seen in Ref. [86] is related to transition presented here is unclear. The difficulty is that the NMR experiment of Ref. [86] probes the spin and it is not obvious in which way the phase transition to a cooperative Jahn-Teller state influences the spin dynamics.
Chapter 5

Photoemission of $K_n C_{60}$

Alkali-metal-doped $C_{60}$ has been investigated extensively by photoemission spectroscopy (PES) in bulk systems (Ref. [108, 109, 93] and references therein). Recently, Yang et al. measured the electronic band dispersion of $K_3 C_{60}$ in a monolayer system on Ag(111) by angle resolved PES (ARPES) [15]. They investigated a monolayer systems of $K_n C_{60}$ on a Ag(111) surface. $C_{60}$ on Ag(111) forms a triangular lattice which is commensurate with the Ag(111) surface and which has a nearest neighbor separation $a = 10 \text{ Å}$ equal to the one in bulk [110]. By comparing angle integrated spectra (AIPES) from several experiments a generic feature emerges which is the striking difference between the spectra of metallic $K_3 C_{60}$ and the insulating $K_4 C_{60}$ and $K_6 C_{60}$: $K_3 C_{60}$ shows a metallic spectra with a sharp Fermi edge and distinct structures whereas the insulating phases display a broad Gaussian-peak.

In the present work we address this difference. The key ingredient is the large change in coupling strength to the low-energy ($\omega \approx 10 \text{ meV}$) optic vibrations of the $K^+$ ions. These modes cause a net shift of the $C_{60}$ molecular levels and their interaction is efficiently screened in metallic $K_3 C_{60}$ where it is reduced by a factor $10^{-4}-10^{-2}$ [111, 112, 113]. However, in the insulating phases, where metallic screening is absent, they couple strongly ($g \approx 7$, see below) due to the direct Coulomb interaction of the ionic charge with the photoemission hole. The resulting physics is best illustrated by the toy-model $H = \omega [a^\dagger a + g c^\dagger c (a^\dagger + a)]$ where a single electron is coupled to a harmonic oscillator. The corresponding photoemission spectrum is a Poisson distribution $P(\epsilon) = \sum_n g^{2n} e^{-g^2}/n! \delta(\epsilon + |n-g^2|\omega)$ where $g^2$ is the average number of excited phonons emitted during the photoemission process. In the insulating phases $g^2 \approx 50$ is very large and as a result the spectrum becomes incoherent resulting in a Gaussian-like shape. In the following we treat the metallic and insulating phases separately. In section 5.1, using the non-crossing approximation (NCA), it is shown that the spectrum of metallic $K_3 C_{60}$ is dominated by the coupling to the intramolecular $C_{60}$ modes. In the next section 5.2 the coupling to the optic K-modes is derived. In the last section 5.3 we use moment expansion to calculate position
and width of the Gaussian-like spectra of K₄C₆₀ and K₆C₆₀.

5.1 Non-Crossing approximation (NCA) for K₃C₆₀

In this section the photoemission spectrum of metallic K₃C₆₀ is calculated using NCA [114]. A similar calculation was performed by Liechtenstein et al. where they showed that the width of the plasmon in K₃C₆₀ can be explained by electron-phonon coupling [115]. The Hamiltonian used for the NCA consists of two parts, the kinetic energy of the electrons and on-site Jahn-Teller coupling as discussed in section 3.1.5. We neglect the Coulomb interaction in the NCA. This is justified in a monolayer adsorbed on Ag(111) where U is reduced by the proximity of the metal [116]. Here we restrict our attention to such systems. As will be shown below, all what enters the NCA from the kinetic energy term in Hamiltonian is the bare density of states (DOS). Hence, we don’t bother to describe the detailed form of the kinetic energy term but assume simply a square DOS with width \( W = 0.5 \text{ meV} \). The vibronic part as given in section 3.1.5 describes the coupling of the electrons to the 8 intramolecular \( H_g \) modes:

\[
H_{\text{vib}}^H = \sum_{jak} \omega_a \left[ \frac{1}{2} a_j^{\dagger} a_j a_j^{\dagger} a_j - \frac{\sqrt{3}}{2} g_a \sum_{s m n} R_{1n1m}^{2k} c_{js}^{\dagger} c_{js} (a_j^{\dagger} a_j + a_j a_j^{\dagger}) \right]. \tag{5.1}
\]

This Hamiltonian is described in detail throughout the section 3.1. Here we have in addition the index \( j \) which denotes the site in the lattice. Parameters for the energies \( \omega_a \) and the coupling constant \( g_a \) are given in Tab. 3.1.

In the NCA, the electron self-energy is approximated by the diagram shown in Fig. 5.1. The interacting Green’s function, which itself contains the self-energy, en-
5.1. Non-Crossing approximation (NCA) for $K_3C_{60}$

This requires to determine the self-energy self-consistently which is done iteratively. In the present problem the Green's function $G_{nm}(\omega, \mathbf{k})$ and self-energy $\Sigma_{nm}(\omega, \mathbf{k})$ are $3 \times 3$ matrices because there are three orbitals per molecule and therefore three bands. The free phonon propagator $D^0_0(\omega)$ is a scalar and depends only on frequency and the multiplet because the phonons are dispersionless and degenerate within a multiplet. As a consequence, only the local Green's function $G_{nm}^{\text{loc}} = 1/N \sum_{\mathbf{k}} G_{nm}(\omega, \mathbf{k})$ enters which renders the self-energy $\Sigma_{nm}(\omega, \mathbf{k}) = \Sigma_{nm}(\omega)$ local as well. This is consequence of including only non-crossing diagrams. Quantities would become momentum dependent when vertex corrections were included. From a computational point of view, the advantage is that integrations over momentum drop. The diagram of Fig. 5.1 translates (for $T = 0$) into

$$\Sigma_{nm}(E) = i \sum_{\alpha kn'} \frac{3}{4} \omega_\alpha^2 g_\alpha^2 R^{2k}_{1n1n'} R^{2k}_{1m1m'} \int \frac{d\omega}{2\pi} D^0_0(\omega) G_{nm}^{\text{loc}}(E - \omega). \quad (5.2)$$

Equation (5.2) can be simplified further when the symmetry of the lattice is used. Generally, the momentum dependent Green’s function transforms as $G_{nm}(\omega, \mathbf{k}') = \sum_{n'm'} D_{nm'}^1(\mathcal{R}) D_{nn'}^1(\mathcal{R}) G_{n'm'}(\omega, \mathbf{k})$ under a point-group symmetry transformation $\mathcal{R}$ which takes $\mathbf{k}$ into $\mathbf{k}'$. The matrices $D_{nn'}^1$ are the Wigner D-functions. The same relation holds for the self-energy. In our case only local, momentum-independent quantities enter and therefore $G_{nm}^{\text{loc}}$ and $\Sigma_{nm}^{\text{loc}}$ have to be invariant under all transformation $\mathcal{R}$ which belong to the point-group of the lattice. In particular, one can show that in a cubic environment

$$G_{nm}^{\text{loc}}(\omega) = G^{\text{loc}}(\omega) \delta_{nm}, \quad \Sigma_{nm}(\omega) = \hat{\Sigma}(\omega) \delta_{nm}, \quad (5.3)$$

where $G^{\text{loc}}(\omega)$ and $\hat{\Sigma}(\omega)$ are scalars. Note that this is equivalent to the fact that $l = 1$ orbitals don’t split in a cubic environment. The symmetry of the trigonal lattice of $C_{60}$ molecules on Ag(111) is reduced but still has a 3-fold axis. In this case the Green’s function has an off-diagonal part of the form $G_{nm}^{\text{off-diag}}(\omega)(1 - \delta_{nm})$. We performed calculations using a tight-binding model which fits the band-structure proposed in Ref. [15]. This calculation included the off-diagonal part. Deviations (in the DOS) to the case where the off-diagonal part was neglected turned out to be of the order of 1 % or less. Hence, we use the Green’s function and self-energy as given in (5.3). Inserting this in (5.2) leaves a sum over a product of $R^{2k}_{1n1n'}$ coefficients which is

$$\sum_{\alpha kn'} \frac{3}{4} R^{2k}_{1n1n'} R^{2k}_{1m1m'} \delta_{n'm'} = \frac{5}{4} \delta_{nm}. \quad (5.4)$$

Using relations (5.3) and (5.4) simplifies (5.2) to the scalar equation

$$\hat{\Sigma}(E) = i \sum_{\alpha} \frac{5}{4} \omega_\alpha^2 g_\alpha^2 \int \frac{d\omega}{2\pi} D^0_0(\omega) G^{\text{loc}}(E - \omega). \quad (5.5)$$
Figure 5.2: Solution of the NCA at half filling ($\mu = 0$) which corresponds to K$_3$C$_{60}$. *Upper panel:* Occupied part of the interacting DOS. *Lower panel:* Advanced self-energy. *Inset:* Occupied DOS (solid line) convoluted with a Gaussian ($\sigma = 10$ meV) and compared to the experimental spectrum of the monolayer (dashed line) [15].

Thus, the problem is simplified to a single band interacting with a set of non-degenerate phonon modes. As the Green’s function $G^{\text{loc}}$ in (5.5) contains the self-energy $\Sigma$, relation (5.5) is a complicated equation for the self-energy which is solved iteratively. This is best done, using advanced quantities. Since the free phonon propagator $D^0_q(\omega) = 2\omega_q/(\omega^2 - \omega_q + i\delta)$ enters (5.5), the integral over $\omega$ can be done analytically which yields the advanced self-energy

$$\text{Im} \left[ \Sigma^A(\omega) \right] = \sum_\alpha \frac{\pi}{4} \omega_\alpha^2 \delta^2 \left[ \rho(\omega - \omega_\alpha) \theta(\omega - \omega_\alpha - \mu) + \rho(\omega + \omega_\alpha) \theta(\mu - \omega - \omega_\alpha) \right],$$

$$\text{Re} \left[ \Sigma^A(\omega) \right] = \frac{1}{\pi} \oint dx \frac{\text{Im} \left[ \Sigma^A(x) \right]}{\omega - x},$$

where $\theta$ is the stepfunction and $\mu$ the chemical potential. In (5.7) the principle part
of the integral is taken. \( \rho(\omega) \) is the interacting density of states given by

\[
\rho(\omega) = \int d\epsilon \rho_0(\epsilon) \frac{1}{\pi} \text{Im} \left[ \hat{G}^A(\epsilon, \omega) \right],
\]

where \( \rho_0(\omega) \) is the bare DOS and \( \hat{G}^A(\epsilon, \omega) = 1/(\omega - \Sigma^A(\omega) - \epsilon - i\delta) \) is the advanced Green's function. Equation (5.6) to (5.8) are solved iteratively using parameters of Tab. 3.1. The iteration is stable and converges within five steps. As stated above, in (5.5), the band-structure only enters via the bare DOS which we chose to be a generic square DOS with a width \( W = 0.5 \text{ eV} \). Using other bare DOS revealed that the interacting DOS depends only weakly on the form of the bare DOS. The result for half-filling (\( \mu = 0 \)), which corresponds to \( \text{K}_3\text{C}_6\text{O} \), is shown in Fig. 5.2. The interacting DOS shows an overall structure, such as a dip at 0.2 eV and a second hump at 0.4 eV, which agrees well with the AIPES of the monolayer system [15].

### 5.2 Vibrations of the ionic lattice

In \( \text{K}_\sigma\text{C}_6\text{O} \), electrons can couple to the lattice either via change in hopping integrals or via Coulomb interaction with the ionic charges. The former mechanism was studied in detail and it was found that the corresponding coupling constant is negligible compared to the coupling of the intramolecular modes [6]. The latter mechanism was studied in much less detail because in superconducting \( \text{K}_3\text{C}_6\text{O} \) it is assumed to be small due to screening [111, 112, 113] (as was discussed in the introduction to this chapter). However, in the insulating compounds screening is absent. As a consequence, the photoemission hole in insulating \( \text{K}_\sigma\text{C}_6\text{O} \) will couple strongly to the vibrations of the ionic lattice via Coulomb interaction. Below we give an estimate of the corresponding coupling constant.

In \( \text{K}_\sigma\text{C}_6\text{O} \), the mass ratio \( \frac{M_{\text{C}_6\text{O}}}{M_\text{K}} = 18.4 \) is big which allows to separate the lattice vibrations into acoustic modes and optic dispersionless \( K \)-modes. Generally, acoustic modes only couple little to electric fields. In particular, the coupling vanishes for \( \mathbf{q} \rightarrow 0 \). The coupling to the acoustic modes is involved because both \( \omega_{\mathbf{q}\alpha} \) and \( g_{\mathbf{q}\alpha} \) are \( \mathbf{q} \) dependent. We used a simple spring model to estimate the coupling constant. It was parameterized by a phonon frequency of 5 meV at the Brillouin zone boundary [117]. We found an average frequency \( \bar{\omega}_\alpha = 3.8 \text{ meV} \) and average coupling constant \( \bar{g}_\alpha = 2.63 \). Although \( \bar{g}_\alpha > 1 \), the energy scale \( \bar{\omega}_\alpha \) is two orders of magnitude smaller than the energies of the intramolecular modes. Therefore we neglect the coupling to the acoustic modes in the following.

Since the mass ratio is big, the optic modes are essentially vibrations of the K-ions in a rigid C\_6O matrix. Frequencies of the K-ions are assumed to be dispersionless. They were measured by EELS [118] where it was observed that K-ions close to the surface have substantially lower frequencies. As photoemission is surface sensitive, we use
these values which are \( \omega_K = 8.9 \text{ meV} \) and \( \omega_K = 10.9 \text{ meV} \) for \( K_4C_{60} \) and \( K_6C_{60} \) respectively [118]. In order to derive the coupling constant we consider a single \( C_{60} \) site which has an ionic charge \( -N_e e \) and which interacts with the surrounding positively charged K-ions. The positions of the K-ions are denoted by the index \( r \) and the electric field at these positions, due to the charge \( -N_e e \), is supposed to be \( -N_e E_r \) (\( E_r \) is the electric field due to a charge \( e \) at the origin). The electrostatic interaction energy yields then the electron-phonon coupling term:

\[
H_{\text{ep}, K} = -N_e \sum_r e \delta q_r \cdot E_r,
\]

(5.9)

where \( \delta q_r \) is the displacement of the K-ion at position \( r \) from its equilibrium position. This displacement can be expressed with phonon construction and displacement operators: \( \delta q_{rn} = \sqrt{\hbar/(2M_K \omega_K)} (a_{rn} + a_{rn}^\dagger) \). Here we introduce \( \hbar \) exceptionally. The index \( n \) denotes the components of the 3-dimensional vector \( \delta q_r \). Introducing this relation into (5.9) yields the coupling constant \( g_{K, rn} \)

\[
H_{\text{ep}, K} = -\sum_r \sqrt{\frac{\hbar}{2M_K \omega_K}} e E_{rn} N_e (a_{rn} + a_{rn}^\dagger) = -\sum_r \omega_K g_{K, rn} N_e (a_{rn} + a_{rn}^\dagger). \quad (5.10)
\]

Since all the phonon modes are degenerate we can introduce an effective breathing mode \( a^\dagger \propto \sum_r E_{rn} a_{rn}^\dagger \) such that the charge on the \( C_{60} \) ion couples to this one mode only. Note that the breathing modes corresponding to different \( C_{60} \) ions are in general not orthogonal to each other. However, below we shown that the problem can be reduced to a single \( C_{60} \) ion for which the effective mode is then well defined. The coupling constant to this mode is given by

\[
g^2 = \frac{e^2 \hbar}{2M_K \omega_K^3} \sum_r E_r^2. \quad (5.11)
\]

The sum in (5.11) depends on the lattice. Furthermore, for photoemission experiments we should consider the surface layers rather than the bulk. However, the precise structure of the surface is not known and might also depend on the type of experiment (monolayer systems or thin films). Therefore, we consider the bcc lattice of \( K_6C_{60} \) which has a cubic lattice constant \( a = 11.39 \text{ Å} \). Each \( C_{60} \) molecule is surrounded by 24 K-ions located at \( (0, 0.5, 0.25)a \) [101]. Considering the bare coupling to the closest by K-ions yields \( g_K = 11 \). However, as discussed in the first chapter, \( C_{60} \) molecules are highly polarizable and will screen the electric field of the ionic charges. In order to have an estimate of the screening, we use a multipole expansions as discussed in section 2.2.1. Fig. 5.3 shows the electric field strength \( E_r = |E_r| \) at the positions of the \( C_{60} \) and K-ions surrounding a charge \( e \) at the origin. The electric field is shown as a function of the number of multipoles included.
5.2. Vibrations of the ionic lattice

Figure 5.3: Electric field strength \( E_r = |E_r| \) at the positions of the Ceo and K-ions surrounding a charge \( e \) at the origin and calculated using multipole expansion. The electric field is shown as a function of the number of multipoles included in the expansion.

in the multipole expansion. The electric fields entering (5.11) are reduced by 40 % which yields a coupling constant \( g_K = 6.6 \). In \( K_4C_{60} \) distances between \( C_{60} \) and K-ions are almost the same as in \( K_6C_{60} \), however, every \( C_{60} \) is surrounded by 16 K-ions instead of 24. This reduces \( g_K \) in \( K_4C_{60} \) by a factor \( \sqrt{2/3} \) with respect to \( K_6C_{60} \). Taking also into account the difference in \( \omega_K \) we find \( g_K = 7.3 \) for \( K_4C_{60} \). In both compounds, \( K_4C_{60} \) and \( K_6C_{60} \), \( g_K > 1 \) which means that electrons are strongly coupled to the optic lattice vibrations.

There is yet another type of phonon modes, the intramolecular \( A_g \) modes, which couple to the total charge \( N_e \) on the molecule. There are two such modes in \( C_{60} \), but one has vanishing coupling constant [74]. The coupling term in the Hamiltonian is of the same form as the coupling to the effective breathing mode discussed above. Frequency and coupling constant of the mode with non-vanishing coupling constant are \( \omega_{A_g} = 182 \) meV and \( g_{A_g} = 3\lambda_{A_g}/(2\omega_{A_g}N[0]) = 0.3 \) [74] (see also section 3.1.5).
5.3 Moment expansion of the photoemission spectrum

The spectrum of an angle resolved photoemission (ARPES) experiment $I(k, \omega)$ is proportional to the one-electron removal spectral function

$$I(k, \omega) \propto A^-(k, \omega) = \sum_n |\langle \Phi^N_{n-1}|c_k|^\Phi^N_0 \rangle|^2 \delta[\omega - (E^N_0 - E^N_{n-1})]. \quad (5.12)$$

In this formula, $|\Phi^N_0\rangle$ is the $n$th eigenstate of the system with $N$ electrons. The energy of this state is $E^N_n$. The sum in (5.12) runs over all eigenstates of the system with $N - 1$ electrons. The matrix-element entering equation (5.12) stems from Fermi's golden rule. In general, it depends also on the energy and polarization of the electron [119]. In fact, the dependence of the intensity on the photon energy in $\text{C}_6\text{O}$ has strong modulations [120, 121]. However, when probing at a constant energy and if only one band is considered, the spectrum of this band should be well approximated by relation (5.12). The spectrum $I(k, \omega)$ can also be understood as a distribution function in the variable $\omega$. In order to calculate the moments of this distribution, it is convenient to calculate the Fourier transform. Some lines of algebra yield

$$K(k, t) = \int d\omega e^{-i\omega t} I(k, \omega) \propto \langle \Phi^N_0 | c^+_k e^{i\omega H} c_k e^{-i\omega H} | \Phi^N_0 \rangle. \quad (5.13)$$

The right side of relation (5.13) is just $\langle \Phi^N_0 | c^+_k c_k(t) | \Phi^N_0 \rangle$. Therefore, $K(k, t)$ is closely related to the one-particle Green’s function which, in contrast to $K(k, t)$, involves the time order operator. Using the Baker-Hausdorff formula, $K(k, t)$ can be expanded in powers of $t$

$$K(k, t) = \sum_m \frac{(-it)^m}{m!} \mu_m(k), \quad (5.14)$$

where $\mu_m$ is $m$th moment of $I(k, \omega)$ and given by

$$\mu_m(k) = \int d\omega \omega^m I(k, \omega) \propto \langle \Phi^N_0 | c^+_k [\ldots [c_k, H], H \ldots] | \Phi^N_0 \rangle. \quad (5.15)$$

The factor of proportionality in (5.15) is given by the normalization condition $\mu_0 = 1$. In the following we are mainly interested in the angle integrated spectrum (AIPES) which means that all $k$-dependent quantities are integrated over $k$. The moments of the integrated spectrum $I(\omega)$ are then given by

$$\mu_m = \int d\omega \omega^m I(\omega) = \frac{1}{N} \sum_{j \alpha} \langle \Phi^N_0 | c^+_j c_{j \alpha} [\ldots [c_{j \alpha}, H], H \ldots] | \Phi^N_0 \rangle, \quad (5.16)$$
where the sum runs over positions $j$, orbitals $n$ and spin $\sigma$. The factor $1/N$ normalizes the moments properly such that $\mu_0 = 1$.

The main goal of the following is to calculate the position and the width of the distribution, hence the first and the second moment. Usually, in a photoemission experiment, the position of the spectrum is only known relative to the edge of the spectrum, which itself is determined by the chemical potential $\mu = E_0^N - E_0^{N-1}$. Formally, this can be seen by rewriting the delta-function in (5.12) as $\delta(\omega - \mu + \Delta E_a^{N-1})$, where $\Delta E_a^{N-1} = E_a^{N-1} - E_0^{N-1}$ are the excitation energies of the system with $N - 1$ electrons. Obviously, the spectrum is zero for $\omega > \mu$. The mean value of the spectrum relative to this edge is therefore given by $\Delta \mu_1 = \mu_1 - \mu$. Using relation (5.16) and the definition of the chemical potential one shows that

$$\Delta \mu_1 = -\frac{1}{N} \sum_{jmn} \left[ \langle \Phi_0^N | c_{j,mn}^\dagger H c_{j,mn} | \Phi_0^N \rangle - \langle \Phi_0^N | H | \Phi_0^{N-1} \rangle \right],$$

(5.17)

where the second term in the bracket is just $E_0^{N-1}$. If the Hamiltonian consists of different terms $H = \sum_{\nu} H_{\nu}$, then, by replacing $H$ with $H_{\nu}$ in relation (5.17), we can associate a $\Delta \mu_{\nu}^1$ to each term $H_{\nu}$ such that $\Delta \mu_1 = \sum_{\nu} \Delta \mu_{\nu}^1$. The width of the distribution is given by

$$\sigma^2 = \mu_2 - \mu_1^2.$$  

(5.18)

As will be shown in below, the Hamiltonian can also be split into a sum $H = \sum_{\nu} H_{\nu}$ such that the total width $\sigma^2 = \sum_{\nu} \sigma_{\nu}^2$ becomes a sum over contributions from each term. However, in the case of the width this is not a general property, but only holds for suitably chosen divisions of the Hamiltonian into parts $H_{\nu}$.

### 5.3.1 Kinetic energy and the rest

To start, we separate the Hamiltonian as $H = H_{\text{kin}} + H'$ where $H_{\text{kin}}$ is the kinetic energy which contains hopping processes from one site to another. $H'$ contains all other terms in the Hamiltonian, such as phonon energies, electron-phonon interaction and on-site Coulomb interactions. $H'$ is assumed to be the sum of molecular Hamiltonians $H_j'$ and therefore leaves the on-site particle number $N_{e,j} = \sum_{\sigma} c_{j,mn}^\dagger c_{j,mn}$ unchanged, i.e. $[H', N_{e,j}] = 0$. This separation will allow us to treat the contributions of the kinetic energy and those of the rest ($H'$) separately. Below, when dealing with the $H'$-part, the problem will reduce to a molecular problem where the spectrum of a single molecule has to be calculated. This is a consequence of the fact that the ground states of the insulating phases are product states of molecular ground states:

$$|\Phi_0^N\rangle = \bigotimes_j |\Phi_{0,j}^N\rangle,$$

(5.19)
where $\Phi_{0,j}^\pi$ is the ground state of $C_{60}^{\pi-}$. This is trivial in the case of $K_6C_{60}$ where the LUMO-band is filled and where $|\Phi_{0,j}^\pi\rangle = \sum_n c_{j,n\sigma}^\dagger |0\rangle$. In the case of $K_4C_{60}$ this is less obvious, but, as was shown in chapter 4, the ground state of $K_4C_{60}$ is presumably also of the form (5.19) with $|\Phi_{0,j}^\sigma\rangle = |\langle S\rangle\rangle$, i.e. the molecular states are uncorrelated dynamic Jahn-Teller states. Note that a ground state of type (5.19) is an eigenfunction of the molecular particle number $N_{\sigma,j}$ with eigenvalue 4 and 6 in the case of $K_4C_{60}$ and $K_6C_{60}$ respectively. We are interested in the first and second moment of the integrated spectrum $I(\omega)$ which are given by relation (5.16). Obviously, the contributions to the first moment of $H_{\text{kin}}$ and $H'$ are additive. In addition, applying $H_{\text{kin}}$ once on the ground moves an electron from one site to another and yields a state orthogonal to the ground state. Therefore the contribution of $H_{\text{kin}}$ to $\mu_1$ vanishes and one obtains

$$\mu_1 = \frac{1}{x} \sum_{n\sigma} \langle \Phi_{0,j}^\pi | c_{j,n\sigma}^\dagger [c_{j,n\sigma}, H'_j] | \Phi_{0,j}^\pi \rangle.$$  \hspace{1cm} (5.20)

Note that the sum over all sites dropped because each site yields the same contribution. The expression for the second moment requires to apply the Hamiltonian twice. Again, the mixed term $H_{\text{kin}}H'$ vanishes because it produces a state orthogonal to the ground state. Therefore the second moment is of the form

$$\mu_2 = \mu_{\text{kin}}^2 + \frac{1}{x} \sum_{n\sigma} \langle \Phi_{0,j}^\pi | c_{j,n\sigma}^\dagger [c_{j,n\sigma}, H'_j, H'_j] | \Phi_{0,j}^\pi \rangle.$$  \hspace{1cm} (5.21)

$\mu_2^\text{kin}$ arises from processes where an electron hops off and back to the same site. It is just the second moment of the bare band structure. Note that the previous formula have the advantage that the calculations are reduced to a molecular problem. The contribution of the kinetic energy to the chemical potential is $\mu_{\text{kin}} = \langle H_{\text{kin}} \rangle_{\Phi_0^{N-1}} - \langle H_{\text{kin}} \rangle_{\Phi_0^{N-1}}$. The first term vanishes because electrons in the ground state (5.19) are completely localized and don’t have any kinetic energy. The second term of $\mu_{\text{kin}}$ depends on the nature of the state $\Phi_0^{N-1}$ which contains one photoemission hole. Here we assume that the coupling to the optic K-mode is strong such that the hole forms a small polaron [122] which means that it is localized and that it only has little kinetic energy. Hence, the second term vanishes as well. In summary, both the first moment $\mu_{\text{kin}}^1$ and the chemical potential $\mu_{\text{kin}}$ vanish and therefore $\Delta \mu_{\text{kin}}^1 = 0$. The contribution to the width from the kinetic energy is $\sigma_{\text{kin}}^2 = \mu_{\text{kin}}^2$ because the first moment vanishes. As mentioned above, $\mu_{\text{kin}}^2$ is the second moment of the bare density of state. As in section 5.1 we assume a quadratic bare density of states with width $W = 0.5$ eV and centered around 0. This yields $\sigma_{\text{kin}} = W/\sqrt{12} = 0.144$ meV.
5.3.2 Optic phonon mode

In this subsection we consider a single molecule. The site index \( j \) will be dropped in the following. The Hamiltonian \( H' \) of the single molecule is again separated into

\[
H' = H_{\text{vib}} + H'' = \omega_0 \left[ a^\dagger a - g N_e (a^\dagger + a) \right] + H''.
\]

\( H_{\text{vib}} \) describes a generic optic phonon mode with energy \( \omega_0 \) which couples to the total charge \( N_e \) on the molecule. In our case this is either the effective breathing mode of the K-ions surrounding the molecule or an intramolecular \( A_g \) mode. \( H'' \) contains all remaining terms (Jahn-Teller modes, Coulomb interaction or other optic modes), but doesn’t contain any phonon operators \( a \) or \( a^\dagger \). The ground state of \( H' \) is \( |\Phi_0^g\rangle \) and can be written as \( |\Phi_0^g\rangle = D(xg)|\phi_0^g\rangle \), where \( |\phi_0^g\rangle \) is the ground state of \( H'' \) with energy \( E_0^g \). \( |\phi_0^g\rangle \) doesn’t contain any excitations of the optic phonon mode under consideration. \( D(xg) \) creates a coherent phonon state \( |\alpha\rangle \) with \( \alpha = xg \) which is the ground state of \( H_{\text{vib}} \). By construction, \( |\Phi_0^g\rangle \) is the ground state of \( H' \) with the energy \( E_0^g = -\omega_0 x^2 g^2 + E_0'' \). In order to calculate the spectrum of the single molecule we use the Fourier transform as given in relation (5.13):

\[
K'(t) = \frac{1}{x} \sum_{n_\sigma} \langle \Phi_0^g | c_{n_\sigma}^\dagger e^{it H'} c_{n_\sigma} e^{-it H'} | \Phi_0^g \rangle.
\]

The Hamiltonian (5.22) can now be substituted into (5.23). Furthermore, the particle number \( N_e \) appearing in the Hamiltonian can replaced by \( x - 1 \) in the first exponential and by \( x \) in the second one. As a consequence, parts of the Hamiltonian which are due to \( H_{\text{vib}} \) only involve operators \( a \) and \( a^\dagger \) and commute with all other terms. It can be shown that this allows to write the Fourier transform as a product \( K'(t) = K_{\text{vib}}(t) K''(t) \) where \( K_{\text{vib}}(t) \) and \( K''(t) \) are the Fourier transforms of the spectra if \( H' = H_{\text{vib}} \) and \( H' = H'' \) respectively. This implies that \( I'(\omega) \) is the convolution of two spectra \( I_{\text{vib}}(\omega) \) and \( I''(\omega) \). Therefore, the average position and the width of the two distributions are additive. The spectrum \( I_{\text{vib}}(\omega) \) can be worked out exactly and the result is a poisson distribution:

\[
I_{\text{vib}}(\omega) = \sum_n \frac{g^{2n} e^{-g^2}}{n!} \delta(\omega - [g^2 - 2xy^2 - n] \omega_0)
\]

The mean value is \( \mu_{\text{vib}} = -2x \omega_0 g^2 \) whereas the contribution of \( H_{\text{vib}} \) to the chemical potential is \( \mu_{\text{vib}} = (1 - 2x) \omega_0 g^2 \). On the other hand the width of a Poisson as given in (5.24) is well known. In summary, we have

\[
\Delta \mu_{\text{vib}} = -\omega_0 g^2, \quad \sigma_{\text{vib}} = \omega_0 g.
\]

If \( g \gg 1 \) and the energy \( \omega_0 \) is too small to be resolved, then the Poisson distribution \( I_{\text{vib}} \) will look like a gaussian with width \( \sigma_{\text{vib}} \). These conditions are fulfilled for the
optic K-modes. Since $I'$ is the convolution of $I_{\text{opt}}$ with $I''$, it follows that possible structures of $I''$ will be smeared by the convolution with $I_{\text{opt}}$. Therefore, $I'$ is expected to be smooth and close to a gaussian as well. This, we believe, is the reason why the spectra of the insulating K₄C₆₀ and K₆C₆₀ phases look like a gaussian.

5.3.3 Coulomb interaction and Jahn-Teller modes

As was discussed in chapter 3, the ground state of the C₆₀ ions is not trivial due to the Jahn-Teller interaction and Hund’s rule coupling. Likewise, photoemission spectra of C₆₀ ions are not trivial neither and they can’t be expressed by a simple distribution (5.24) as was the case for the optic modes discussed above. The reason is that both, $H_g$ Jahn-Teller modes as well as the Hund’s rule term couple to orbital fluctuations rather than to the total charge on the molecule. As a consequence we limit us to the calculation of the first and second moment as given in (5.20) and (5.21) respectively. The Coulomb interaction as given in (3.54) contains also the charging energy $U$ which simply yields a shift of the total spectrum. This can be understood when looking at the Fourier transform (5.23) and replacing the particle number operator $N_e$ in $H_J$ by $x - 1$ and $x$ as was discussed above. Again, the same shift appears in the chemical potential and therefore cancels when the spectrum is drawn relative to the chemical potential. As consequence, we only have to worry about the Hund’s rule coupling part of the Coulomb interaction. Therefore, the remaining part of the Hamiltonian $H''$, which we consider below, consists of the sum over all $H_g$ modes as discussed in section 3.1.5 and the Hund’s rule coupling discussed in section 3.1.6:

$$H'' = \sum_\alpha \omega_\alpha \left( \frac{5}{2} + N_{p,\alpha} + H_{ep,\alpha} \right) + H_J. \quad (5.26)$$

Below we treat the case of K₄C₆₀ and K₆C₆₀ separately. We start with the latter which is the simpler case.

K₆C₆₀

As can be seen from relation (5.20), the first moment is obtained by calculating the expectation value of

$$\frac{1}{x} \sum_{n\sigma} c_{n\sigma}^i [c_{n\sigma}, H''] = \frac{1}{x} \left( \sum_\alpha \omega_\alpha H_{ep,\alpha} + 2H_J \right), \quad (5.27)$$

where $x$ is the number of electrons on the ion. It can be verified that the equality is an exact operator relation. The factor of 2 in front $H_J$ is due to the fact that $H_J$ contains two electron construction operators. Relation (5.27) implies that the first
5.3. Moment expansion of the photoemission spectrum

The moment expansion of the photoemission spectrum is given by the expectation values of the electron-phonon coupling term and the Hund’s rule term. In the case of K$_6$C$_{60}$, photoemission creates a single hole in an otherwise full band. Therefore, Hund’s rule coupling is absent in the spectrum of K$_6$C$_{60}$. In addition, the C$_{60}^-$ ion has no Jahn-Teller distortion and the ground state of K$_6$C$_{60}$ doesn’t contain any excited $H_g$ modes. Hence, the expectation value of $H_{ep,a}$ vanishes and $\mu''_1 = 0$. However, the contribution to the chemical potential from the electron-phonon coupling term is $\mu'' = -E_{0}^{a=5} = -E_{0}^{a=1}$ (neglecting the zero point energies). The second equality results from particle-hole symmetry. Values for the ground state energy of $E_{0}^{a=1}$ are discussed in Tab. 3.3. Here we use the value from Ref. [67] which yields $\Delta \mu''_1 = -\mu'' = -139.6$ meV. Calculating the second moment involves twice the electron-phonon coupling term which allows to create and destroy a phonon. This leads to contributions of the order $\omega^2 g^2_a$. Working out the commutators in relation (5.21) yields a sum as given (5.4) and one finds

$$\mu''_2 = (\sigma'')^2 = \frac{5}{4} \sum_{a} \omega^2 g^2_a. \tag{5.28}$$

The second moment is equal to the width due to the vanishing first moment. Hence, each $H_g$ mode contributes $(5/4)\omega^2 g^2_a$ to the total width of the spectrum. Using the values from Tab. 3.1 we find the total width $\sigma'' = 149$ meV.

K$_4$C$_{60}$

In K$_4$C$_{60}$ there is in addition the Hund’s rule term which complicates the calculation. Here we only give the result. When doing the calculations, one can profit from the particle-hole symmetry which implies that removing an electron (i.e. photoemission) from a C$_{60}^-$ is equivalent to adding an electron to C$_{60}^+$ (i.e. inverse photoemission). A variational ground state for C$_{60}^-$ was constructed in section 3.3.3 and we use this state to calculate the expectation values. Furthermore, we also calculate the leading terms (in $g^{-2}$) for the strong coupling limit $g \to \infty$ which turns out to be a good approximation. In the strong coupling limit, the expectation values of the two terms appearing (5.27) are $\langle H_{ep,a} \rangle = -4g^2_a$ and $\langle H_J \rangle = 2J$ (see section 3.3.1 and section 3.3.3 respectively). Therefore, the first moment in the strong coupling limit is given by

$$\mu'_{1,\infty} = -\sum_{a} \omega_a g^2_a + J = -\bar{\omega} g^2_{\text{tot}} + J. \tag{5.29}$$

In the case of finite coupling, using the parameters $g_{\text{tot}} = 1.532$ and $J/\bar{\omega} = 1$, we obtain $\mu'_{1} = -1.001 \bar{\omega} g^2_{\text{tot}} + 0.875 J$. On the other hand, the chemical potential in the strong coupling limit is given by (see Ref. [63])

$$\mu''_{\infty} = -\frac{1}{2} \bar{\omega} (g^2_{\text{tot}} - 1) + J. \tag{5.30}$$
Therefore we obtain

$$\Delta \mu_{1,\infty}'' = \mu_{1,\infty}'' - \mu_{\infty}'' = -\frac{1}{2} \bar{\omega} (g_{\text{tot}}^2 + 1). \quad (5.31)$$

In order to calculate this value for finite coupling we would need to know the ground state energy of C_{60}^3 for finite \( J \neq 0 \). Unfortunately, only energies for \( J = 0 \) are known from Ref. [67]. Since the value \( \Delta \mu_{1,\infty}'' \) doesn’t depend on \( J \), we calculate with \( J = 0 \). From Ref. [67] we have \( \mu'' = -69.3 \) meV which yields \( \Delta \mu_{1,\infty}'' = -100 \) meV.

In the strong coupling limit the leading terms of the second moment take the form

$$\mu_{2,\infty}'' = \frac{5}{4} \sum_{\alpha} \omega_{\alpha}^2 g_{\alpha}^2 + 2 \bar{\omega}^2 g_{\text{tot}}^2 + 2J^2 - 2J \bar{\omega} g_{\text{tot}}^2 - J \bar{\omega}. \quad (5.32)$$

The first three terms contain twice the electron-phonon interaction \( H_{ep} \), the forth term contains twice the Hund’s rule term \( H_J \) and the last two terms are the mixed terms. In order to discuss the difference to K_{6}C_{60}, it is more instructive to consider the width

$$(\sigma''^2) = \mu_{2,\infty}'' - (\mu_{1,\infty}''^2) = \frac{5}{4} \sum_{\alpha} \omega_{\alpha}^2 g_{\alpha}^2 - 3 \bar{\omega}^2 g_{\text{tot}}^2 + J^2 - J \bar{\omega}. \quad (5.33)$$

The first term is equal to the width in K_{6}C_{60}. The second term is a correction due to the dynamic Jahn-Teller ground state. Note that this correction would vanish in the case of a static distortion. The third term is the increase of the width due to the Hund’s rule term and the last term is a correction due to the interplay between the Jahn-Teller term and the Hund’s rule coupling. Again, in the case of finite coupling, there are in addition higher order corrections and one obtains (with the same parameter as above) the width

$$(\sigma')^2 = \frac{5}{4} \sum_{\alpha} \omega_{\alpha}^2 g_{\alpha}^2 - 0.812 \frac{3}{8} \bar{\omega}^2 g_{\text{tot}}^2 + 0.984 J^2 - 0.925 J \bar{\omega}. \quad (5.34)$$

Using the values from Tab. 3.1 and \( J = \bar{\omega} \) yields \( \sigma'' = 137 \) meV which is somewhat smaller than in K_{6}C_{60}.

### 5.3.4 Summary and results

Collecting the results from above we find the total mean value \( \Delta \mu_1 \) and the total width \( \sigma^2 \):

$$\Delta \mu_1 = -\omega_{K}^2 g_{K}^2 - \omega_{A_2}^2 g_{A_2}^2 + \Delta \mu_1'', \quad (5.35)$$

$$\sigma^2 = \frac{W^2}{12} + \omega_{K}^2 g_{K}^2 + \omega_{A_2}^2 g_{A_2}^2 + (\sigma'')^2. \quad (5.36)$$
Using the values given above and in the previous section yields $\Delta \mu_1 = -592$ meV and $\sigma = 217$ meV for $K_4C_{60}$ and $\Delta \mu_1 = -633$ meV and $\sigma = 226$ meV for $K_6C_{60}$. Hence, the relative average position and the width turn out to be similar in the two compounds. The reason for the similar value of $\Delta \mu_1$ is the fact that it is dominated by the contribution of the optic K-mode which is comparable in the two compounds. Note that the contribution $-\omega_K g_K^2$ of the K-mode is proportional to $\omega_K^{-2}$ because $g_K^2$ is proportional to $\omega_K^{-3}$ (see equation (5.11)). Hence, $\Delta \mu_1$ depends sensitively on $\omega_K$. On the other hand the width is equally dominated by the contributions from the kinetic energy and the term $(5/4) \sum_\alpha \omega_\alpha^2 g_\alpha^2$. Since these two quantities don’t change upon doping, the width of the $K_4C_{60}$ and $K_6C_{60}$ spectra are almost the same. Gaussians with the position and width given above are shown in Fig. 5.4 and compared to the experiment. Good agreement in both, the position and width, is found.
Figure 5.4: Gaussian fit (solid curves) to the photoemission spectrum using the first and second moment and plotted with respect to the chemical potential. The dashed curves are the experimental data (Ref. [109] for $K_6C_{60}$, Ref. [93] for $K_4C_{60}$) from photoemission experiments on bulk compounds.
Appendix A

Icosahedral Clebsch-Gordan coefficients and coupling matrices

A.1 Icosahedral Clebsch-Gordan coefficients

Clebsch-Gordan coefficients and the closely related Wigner-Eckhardt theorem are best known from SO(3) symmetry and angular momentum addition. However, the concept is more general and applies to every group, in particular to the icosahedral symmetry $I_h$. A detailed and thorough treatment for all three-dimensional point groups is given in Ref. [48]. Clebsch-Gordan coefficients for $I_h$ can be deduced from various Wigner 3jm symbols tabulated in this book. However, the procedure requires extensive book keeping and is somewhat cumbersome. In the present work we adopt a less sophisticated method which can be easily carried out using mathematica. The idea is to construct partner functions for the IR of $I_h$ based on spherical harmonics and then calculate products of three partners which are proportional to the Clebsch-Gordan coefficients of $I_h$. The spherical harmonics based partner functions are denoted by $Y_{lxk}(\Omega)$ where the labelling from section 2.2.2 is used. $l$ denotes the total angular momentum (IR of SO(3)), $x$ is the IR of $I_h$ and $k$ denotes the residual degeneracy. In order for the $k$-indices to be defined we consider the molecule oriented with the 5-fold axis parallel to the $z$-axis. This allows to label the states within a multiplet unambiguously with its $C_5$ index $k$. The ordered basis of a $T_{1u}$ subspace has $k$-indices $(0,1,-1)$ whereas the ordered basis of an $H_u$ subspace is given by $(0,1,-1,2,-2)$. Note that in the case of applied $l = 1$ or $l = 2$ potential, the $k$ index corresponds to the $m$ index of the spherical harmonics. The function $Y_{lxk}(\Omega)$ is a linear combination of $Y_{lm}(\Omega)$ and coefficients are given in Ref. [48]. The IR's $x$ which can be constructed from a angular momentum subspace $l$ are shown in Tab. 2.4. The Clebsch-Gordan
The normalization factor $\mathcal{N}$ is chosen such that $\sum_{k_1 k_2} |C_{k_1 k_2}^k|^2 = 1$. A subtle point arises when factors in products of IR of $I_h$ appear more than once. An example is $H_u \otimes H_u = A_g \oplus T_{1g} \oplus T_{2g} \oplus 2G_g \oplus 2H_g$ which implies that there are two sets of Clebsch-Gordan coefficients for products of partnerfunctions which belong all to $H$ symmetry. This requires the additional multiplicity $\lambda$ index in the Clebsch-Gordan coefficient $C_{k_2 k_1}^k(\lambda; x_2 x_1; x)$. There is a freedom how to choose these two sets because any orthogonal transformation among $\lambda = 1$ and $\lambda = 2$ yields two equally appropriate sets. Our choice follows Ref. [48].

In the following we will represent the coefficients $C_{k_2 k_1}^k(\lambda; x_2 x_1; x)$ as matrices with respect to the indices $k_1$ and $k_2$. In order to reduce the number of matrices, we will give the coupling matrices for $(lm) = (10), (20)$ potentials, which are rotated around the $y$-axis by an angle $\theta$. The resulting matrices are then given by

$$C^\theta(\lambda; x_2 x_1; x) = \sum_k d^l_{0k}(\theta) C^k(\lambda; x_2 x_1; x), \quad (A.2)$$

where $d^l_{0k}(\theta)$ is the rotation matrix of the spherical harmonics in a given $l$-subspace (see Appendix B.2). Below, the coupling matrices $C^\theta(\lambda; x_1 x_2; x)$ which are needed to calculate the splitting of the HOMO and LUMO are given. They are traceless $\text{Tr} C^\theta = 0$ and normalized such that $\text{Tr} (C^\theta)^T C^\theta = 1$. The coupling matrices which describe the splitting of the LUMO are

$$C^\theta(T_{1u} T_{1g}; T_{1u}) = \frac{1}{2} \begin{pmatrix} 0 & -\sin \theta & -\sin \theta \\ -\sin \theta & -\sqrt{2} \cos \theta & 0 \\ -\sin \theta & 0 & \sqrt{2} \cos \theta \end{pmatrix}, \quad (A.3)$$

$$C^\theta(T_{1u} T_{1u}; H_g) = \frac{1}{4} \begin{pmatrix} -4 \sqrt{3} + 2 \sqrt{6} \sin^2 \theta & \sqrt{3} \sin 2\theta & -\sqrt{3} \sin 2\theta \\ \sqrt{3} \sin 2\theta & 2 \sqrt{\frac{3}{2}} - \sqrt{6} \sin^2 \theta & \sqrt{6} \sin^2 \theta \\ -\sqrt{3} \sin 2\theta & \sqrt{6} \sin^2 \theta & 2 \sqrt{\frac{3}{2}} - \sqrt{6} \sin^2 \theta \end{pmatrix}. \quad (A.4)$$

The eigenvalues of these two matrices are independent of $\theta$ and given by $(0, -\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}})$ and $(-\frac{3}{\sqrt{6}}, \frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}})$ which implies that the splitting is independent of the orientation of the molecule with respect to the direction of the applied $l = 1$ and $l = 2$ potentials. The coupling of the HOMO ($H_u$) to the lower lying $H_g$ and $G_g$ levels is given by

$$C^\theta(H_u H_g; T_{1u}) = \quad (A.5)$$
### A.2 Perturbation theory

In this section we discuss the calculation of the level splitting for arbitrary directions within perturbation theory using the coupling constants of Tab. 2.7. As discussed above, we restrict the analysis to $l = 1$ and $l = 2$ external potentials, which corresponds to $x = T_{1u}$ and $x = H_g$ potentials in the icosahedral symmetry $I_h$. In first order perturbation theory, the splitting of the levels in the degenerate subspace $E_{nx}$

\[
\begin{pmatrix}
0 & \sqrt{3} \sin \theta & -\sqrt{3} \sin \theta & 0 & 0 \\
\sqrt{3} \sin \theta & -\sqrt{5} \cos \theta & 0 & \sqrt{2} \sin \theta & 0 \\
-\sqrt{3} \sin \theta & 0 & \sqrt{2} \cos \theta & 0 & -\sqrt{2} \sin \theta \\
0 & \sqrt{2} \sin \theta & 0 & -2\sqrt{2} \cos \theta & 0 \\
0 & 0 & -\sqrt{2} \sin \theta & 0 & 2\sqrt{2} \cos \theta
\end{pmatrix},
\]

\[
\frac{1}{2\sqrt[5]{5}} C^6(H_uG_g; T_{1u}) =
\begin{pmatrix}
\sqrt{3} \sin \theta & 2\sqrt{5} \cos \theta & 0 & -\frac{1}{\sqrt{5}} \sin \theta & 0 \\
-\sqrt{3} \sin \theta & 0 & -2\sqrt{5} \cos \theta & 0 & \frac{1}{\sqrt{5}} \sin \theta \\
0 & -\sqrt{2} \sin \theta & 0 & -\sqrt{2} \cos \theta & -\frac{3}{\sqrt{5}} \sin \theta \\
0 & 0 & \sqrt{2} \sin \theta & 0 & \frac{3}{\sqrt{5}} \sin \theta \\
0 & 0 & 0 & \sqrt{2} \cos \theta & 0
\end{pmatrix}.
\]

The coupling of the HOMO among themselves is given by

\[
C^6(1; H_uH_u; H_g) =
\begin{pmatrix}
-8 + 12 \sin^2 \theta & \sqrt{3} \sin 2\theta & \sqrt{5} \sin 2\theta & 0 & 0 \\
\sqrt{3} \sin 2\theta & 2 - 3 \sin^2 \theta & -3 \sin^2 \theta & -3 \sin 2\theta & 3 \sin^2 \theta \\
\sqrt{3} \sin 2\theta & -3 \sin^2 \theta & 2 - 3 \sin^2 \theta & 3 \sin^2 \theta & -3 \sin 2\theta \\
\sqrt{3} \sin 2\theta & -3 \sin 2\theta & 3 \sin^2 \theta & 2 - 3 \sin^2 \theta & 3 \sin 2\theta \\
\sqrt{3} \sin 2\theta & 3 \sin^2 \theta & -3 \sin 2\theta & 3 \sin 2\theta & 2 - 3 \sin^2 \theta
\end{pmatrix}
\]

\[
\frac{1}{4\sqrt{5}} C^6(2; H_uH_u; H_g) =
\begin{pmatrix}
0 & \sqrt{3} \sin 2\theta & \sqrt{5} \sin 2\theta & -\sqrt{3} \sin^2 \theta & -\sqrt{3} \sin^2 \theta \\
\sqrt{3} \sin 2\theta & 2 - 3 \sin^2 \theta & \sin^2 \theta & \sin 2\theta & \sin^2 \theta \\
\sqrt{3} \sin 2\theta & \sin^2 \theta & 2 - 3 \sin^2 \theta & \sin^2 \theta & \sin 2\theta \\
-\sqrt{3} \sin^2 \theta & \sin 2\theta & \sin^2 \theta & -2 + 3 \sin^2 \theta & \sin 2\theta \\
-\sqrt{3} \sin^2 \theta & \sin^2 \theta & \sin 2\theta & \sin 2\theta & -2 + 3 \sin^2 \theta
\end{pmatrix}
\]
is given by the eigenvalues of the matrix

$$H_{k_1 k_2}^{(1)}(nx) = \langle nx k_2 | V^{\text{eff}}| nx k_1 \rangle.$$  \hfill (A.9)

This matrix vanishes in the case of an odd potential and the splitting is given by the second order expression

$$H_{k_1 k_2}^{(2)}(nx) = \sum_{\langle n' x' \rangle} \sum_{k'} \frac{\langle nx k_2 | V^{\text{eff}} | n' x' k' \rangle \langle n' x' k' | V^{\text{eff}} | nx k_1 \rangle}{E_{nx} - E_{n' x'}}.$$  \hfill (A.10)

Using the previous relations and equation (2.33), the coupling matrix for an even \( l = 2 \) potential is given by

$$H^{(1)}(nx ; \theta) = V_{10} \sum_{\lambda} t_{\lambda}(nx nx ; H_g) C_{\lambda}^\theta(xx ; H_g).$$  \hfill (A.11)

Note that the multiplicity label \( \lambda \) is only relevant for the HOMO \( H_a \). The coupling matrix for the odd \( l = 1 \) potential is

$$H^{(2)}(nx ; \theta) = V_{10}^2 \sum_{\langle n' x' \rangle} t(nx n x' ; T_{1u})^2 \frac{C_{\theta}(xx' ; T_{1u})^T C_{\theta}(xx' ; T_{1u})}{E_{nx} - E_{n' x'}}.$$  \hfill (A.12)

In the following we restrict the sum over subspaces \( \mathcal{E}_{n' x'} \) closest in energy to \( \mathcal{E}_{nx} \) which is the \( T_{1g} \) subspace in the case of the LUMO and the \( H_g \) and \( G_g \) subspaces in the case of the the HOMO (see Fig 2.8). In equation (A.12) the product \( C_{\theta}(xx' ; T_{1u})^T C_{\theta}(xx' ; T_{1u}) \) enters. For the matrices given in (A.3), (A.5) and (A.6) these products can be expressed in terms of the \( l = 2 \) coupling matrices (A.4), (A.7) and (A.8):

$$C_{\theta}(T_{1u} T_{1g} ; T_{1u})^T C_{\theta}(T_{1u} T_{1g} ; T_{1u}) = \frac{1}{3} + \frac{1}{\sqrt{6}} C_{\theta}(T_{1u} T_{1u} ; H_g),$$  \hfill (A.13)

$$C_{\theta}(H_u H_g ; T_{1u})^T C_{\theta}(H_u H_g ; T_{1u}) =$$

$$\frac{1}{5} + \frac{\sqrt{5}}{10} C_{\theta}(1 ; H_u H_u ; H_g) - \frac{3}{10} C_{\theta}(2 ; H_u H_u ; H_g),$$

$$C_{\theta}(H_u G_g ; T_{1u})^T C_{\theta}(H_u G_g ; T_{1u}) =$$

$$\frac{1}{5} + \frac{\sqrt{5}}{10} C_{\theta}(1 ; H_u H_u ; H_g) + \frac{3}{10} C_{\theta}(2 ; H_u H_u ; H_g).$$  \hfill (A.15)

Using the results above, we can now calculate the perturbative Hamiltonians \( H'(T_{1u} , \theta) \) and \( H'(H_u , \theta) \) which describe the levelsplitting of the LUMO and HOMO respectively for an applied external potential which consists of an \( (lm) = (10) \) and
(lm) = (20) component making an angle $\theta$ to the five-fold axis of the molecule. Neglecting the constant term in (A.13) on obtains for the LUMO:

$$H'(T_{1u}, \theta) = \left(V_{10}^2 c_1 + V_{20} c_2\right) C^0(T_{1u}T_{1u}; H_g),$$

(A.16)

with

$$c_1 = \frac{1}{\sqrt{6}} \frac{t(T_{1u}T_{1g}; T_{1u})^2}{E_{T_{1u}} - E_{T_{1g}}}, \quad c_2 = t(T_{1u}T_{1u}; H_g).$$

(A.17)

Equation (A.16) implies that the contributions of the $l = 1$ and $l = 2$ external potential to the splitting of the LUMO add up trivially. Similarly one obtains for the HOMO:

$$H'(H_u, \theta) = V_{10}^2 d_1 \left[ \cos \delta_1 C^0(1; H_uH_u; H_g) + \sin \delta_1 C^0(2; H_uH_u; H_g) \right] +$$

$$V_{20} d_2 \left[ \cos \delta_2 C^0(1; H_uH_u; H_g) + \sin \delta_2 C^0(2; H_uH_u; H_g) \right],$$

(A.18)

with

$$d_1 \cos \delta_1 = \frac{\sqrt{5}}{10} \left[ \frac{t(H_u H_g; T_{1u})^2}{E_{H_u} - E_{H_g}} + \frac{t(H_u G_g; T_{1u})^2}{E_{H_u} - E_{G_g}} \right],$$

$$d_1 \sin \delta_1 = \frac{3}{10} \left[ - \frac{t(H_u H_g; T_{1u})^2}{E_{H_u} - E_{H_g}} + \frac{t(H_u G_g; T_{1u})^2}{E_{H_u} - E_{G_g}} \right]$$

(A.19)

$$d_2 \cos \delta_2 = t_1(H_u H_u; H_g), \quad d_2 \sin \delta_2 = t_2(H_u H_u; H_g).$$

In (A.18) the contributions of the $l = 1$ and $l = 2$ potentials only add up trivially if $\delta_1 = \delta_2$ because $C^0(1; H_uH_u; H_g)$ and $C^0(2; H_uH_u; H_g)$ don't commute. Using the values in Tab. 2.7 and the energies of Fig. 2.8 yields the values $\delta_1 = 0.064$ and $\delta_2 = 0.037$, which are almost equal when compared to $\pi$. This can be understood by the following remarks: $\delta_1 = 0$ in the case of $t(H_u H_g; T_{1u}) = t(H_u G_g; T_{1u})$ and $E_{H_g} = E_{G_g}$. Furthermore, it can be shown that $\delta_2 = \arctan(1/\sqrt{125}) \approx 0.090$ assuming that the angular dependence of the HOMO is given by $l = 5$ spherical harmonics. Taking an average value of $\delta = 0.050$ yields the approximate relation

$$H'(H_u, \theta) \approx \left(V_{10}^2 d_1 + V_{20} d_2\right) \left[ \cos \delta C^0(1; H_uH_u; H_g) + \sin \delta C^0(2; H_uH_u; H_g) \right],$$

(A.20)

which shows that, to a good approximation, the contributions of the $l = 1$ and $l = 2$ potential to the splitting of the HOMO add up trivially.
Appendix B

Real spherical harmonics

In this appendix the transformation to real spherical harmonics is introduced. This transformation applies not only to spherical harmonics, but to all quantities depending on the angular momentum quantum numbers \((lm)\), such as the Wigner D-functions, Clebsch-Gordan coefficients etc. Below we will discuss the transformation rules for spherical harmonics and the Wigner D-functions. For the purpose of a clear notation, quantities in the complex spherical harmonics basis will be written with a tilde.

B.1 Definition of the transformation matrix

The transformation can be defined as

\[
Y_{in} = \begin{cases} 
  b_n Y_{in} + b_{-n} Y_{-in}, & n \geq 0, \\
  i \left( b_n Y_{in} - b_{-n} Y_{-in} \right), & n < 0,
\end{cases}
\]

with

\[
b_n = \begin{cases} 
  (-1)^n \frac{i^n}{\sqrt{2}}, & n > 0, \\
  \frac{1}{\sqrt{2}}, & n = 0, \\
  \frac{i^n}{\sqrt{2}}, & n < 0.
\end{cases}
\]

From this definition it is obvious that the \(\phi\)-dependence of \(Y_{in}(\theta, \phi)\) is \(\cos(n\phi)\) for positive \(n\) and \(\sin(n\phi)\) for negative \(n\). The real spherical harmonics can also be understood as real and imaginary part of the complex spherical harmonics. The correspondence is given in relation (3.19). The transformation can be written in terms of transformation coefficients \(S_{nm}\):

\[
Y_{in}(\Omega) = \sum_{m=-l}^{l} S_{nm} Y_{im}(\Omega), \quad \text{with} \quad S_{nm} = \sqrt{\text{sign}(n)} \left[ \delta_{nm} + \text{sign}(n) \delta_{n-m} \right] b_m. \quad (B.2)
\]
The coefficients $S_{nm}$ are best represented as a matrix. For $-2 \geq n, m \geq 2$, $S$ takes the form

$$
S = \begin{pmatrix}
\frac{i}{\sqrt{2}} & 0 & 0 & 0 & -\frac{i}{\sqrt{2}} \\
0 & \frac{i}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & \frac{i}{\sqrt{2}} & 0 & -\frac{i}{\sqrt{2}} & 0 \\
\frac{i}{\sqrt{2}} & 0 & 0 & 0 & \frac{i}{\sqrt{2}}
\end{pmatrix}.
$$

(B.3)

The explicit form of the real spherical harmonics for $l = 1, 2$ is

$$(Y_{1-1} \ldots Y_{11}) = \sqrt{\frac{3}{4\pi}} (\sin \theta \sin \phi, \cos \theta, \sin \theta \cos \phi),$$

(B.4)

$$(Y_{2-2} \ldots Y_{22}) = \sqrt{\frac{5}{4\pi}} \left(\frac{\sqrt{3}}{2} \sin^2 \theta \sin 2\phi, \frac{\sqrt{3}}{2} \sin 2\theta \sin \phi, \frac{3}{2} \cos^2 \theta - \frac{1}{2}, \frac{\sqrt{3}}{2} \sin 2\theta \cos \phi, \frac{\sqrt{3}}{2} \sin^2 \theta \cos 2\phi\right).$$

(B.5)

B.2 Real Wigner D-functions

Using the definition of the Wigner D-functions (3.10), the transformation rules for them can be worked out:

$$D_{nm'}^l = \sum_{nm''} S_{nm''}^* S_{n'm'} D_{nm''}^l.$$  

(B.6)

The complex Wigner D-functions are of the form $\tilde{D}_{nm'}^l = e^{-i\phi m} d_{nm'}^l(\theta)e^{-i\gamma m'}$. Similarly, real Wigner D-functions can be written as a product of three matrices $D^l = r^l(\phi) d^l(\theta) r^l(\gamma)$. The matrix $r^l(\phi)$ is the transform of the factor $e^{-i\phi m}$. The matrix elements $r_{nm'}^l(\phi) = r_{nm'}^l(\phi)$ are independent of the total angular momentum $l$ and are given by

$$r_{nm'}(\phi) = \begin{cases} 
\cos n'\phi, & n = n', \\
\sin n'\phi, & n = -n', |n| \neq 0, \\
0, & \text{otherwise}.
\end{cases}$$

(B.7)

The functions $d_{nm'}$ transform also according the rule (B.6). The matrices $d^l(\theta)$ give the orthogonal matrices for the rotations of the real spherical harmonics around the $y$-axis by an angle $\theta$. For $l = 1, 2$ these matrices are given by

$$d^l(\theta) = \begin{pmatrix} 
1 & 0 & 0 \\
0 & \cos \theta & \sin \theta \\
0 & -\sin \theta & \cos \theta
\end{pmatrix},$$

(B.8)
\[ d^2(\theta) = \begin{pmatrix}
  \cos \theta & \sin \theta & 0 & 0 & 0 \\
  -\sin \theta & \cos \theta & 0 & 0 & 0 \\
  0 & 0 & \frac{3}{2} \cos^2 \theta - \frac{1}{2} & -\frac{\sqrt{3}}{2} \sin 2\theta & \frac{\sqrt{3}}{2} \sin^2 \theta \\
  0 & 0 & \frac{\sqrt{3}}{2} \sin 2\theta & \cos 2\theta & -\frac{1}{2} \sin 2\theta \\
  0 & 0 & \frac{\sqrt{3}}{2} \sin^2 \theta & \frac{1}{2} \sin 2\theta & \frac{1}{2} \cos^2 \theta + \frac{1}{2}
\end{pmatrix}. \]
Appendix C

Asymptotic limit of \( |P_0(q)\rangle \) for \( q \to \infty \)

In this appendix it is shown that the variational wavefunction \( |P_0(q)\rangle \) is asymptotically equal to the wavefunction obtained from the semiclassical approximation \([64, 65]\) in the limit \( q \to \infty \). In Ref. \([64]\), the asymptotic wavefunction is given in first quantization with respect to phonon degrees of freedom. Therefore we will write the variational wavefunction \( |P(q)\rangle \) in first quantization and explore its asymptotic behavior for \( q \to \infty \). In order to do this we introduce states \( |Q, \text{fq}\rangle_p \) which have the property \( \langle Q, \text{fq}|\phi\rangle_p = \phi(Q) \). The letters "fq" stand for first quantization. In the case of a coherent state as defined in (3.29), the wavefunction in first quantization is just a displaced gaussian

\[
\langle Q, \text{fq}|q\rangle_p = \pi^{-\frac{\xi}{2}} \exp \left(-\frac{\xi}{2} |Q - q|^2 \right). \tag{C.1}
\]

The wavefunction \( |P_0(q)\rangle \) represented in first quantization with respect to the phonon degrees of freedom is given by the functions

\[
\Psi_n^P(Q, q) = \frac{\langle Q, \text{fq}|c_{n\uparrow}^T| P_0(q) \rangle}{\langle P_0(q)|P_0(q) \rangle^\frac{1}{2}} \tag{C.2}
\]

The asymptotic behavior of \( \langle P_0(q)|P_0(q) \rangle \approx 2/q^2 \) was discussed above. Here we only use the lowest order in \( 1/q \). To expand the nominator above is more involved. We start by using the definitions of \( |P_0(q)\rangle \) and the projection operator \( P_0 \).

\[
\Psi_n^P(Q, q) = \frac{3q}{8\pi^2} \int d\Theta' D_{00}^1(\Theta') \langle Q, \text{fq}|c_{n\uparrow}^T U(\Theta') c_{01}^T |q_{e_0}\rangle \tag{C.3}
\]

\[
= \frac{3q}{8\pi^2} \int d\Theta' D_{00}^1(\Theta') D_{0n}^1(\Theta') \langle [D^2(\Theta')]^{-1} |\text{fq}, q_{e_0}\rangle \exp \left(-\frac{1}{2} |[D^2(\Theta')]^{-1} Q - q_{e_0}|^2 \right).
\]

137
In the second equality, the rotation operator was applied on the bra-side of the vector product and the third equality made use of property (C.1). To continue the calculation, the vector $Q$ is written in the form (3.34), i.e., in terms of the Euler angles $\Theta$ and the parameters $Q, \alpha$: $Q = QD^2(\Theta)q_0(\alpha)$. Using this form, the matrix product $[D^2(\Theta')]^{-1}D^2(\Theta) = D^2(\Theta)D^2(\Theta')$. (C.4)

This is nothing else than a change of variable $\Theta' \rightarrow \Theta''$ in the integral. In order to rewrite the Wigner D-functions $D^1(\Theta')$ in terms of the variables $\Theta$ and $\Theta''$, the addition rules for Wigner D-functions have to be used [46]. This yields

$$\Psi^P_n(Q, q) = \frac{3q\pi^{-\frac{3}{2}}}{8\pi^2\sqrt{2}} \sum_{n'mn} D^1_{nm}(\Theta) D^1_{n'm}(\Theta') \int d\Theta'' D^1_{nm}(\Theta'') D^1_{n'm}(\Theta'') \int d\Theta'' \exp\left(-\frac{1}{2}Q[D^2(\Theta'')]^{-1}q_0(\alpha) - q_0^2\right).$$

(C.5)

Note that the integral now only depends on the variable $Q, \alpha, q$. Using the explicit form of $q_0(\alpha)$ and the Wigner D-functions as given in appendix B.2 one finds

$$\Psi^P_n(Q, q) = \frac{3q\pi^{-\frac{3}{2}}}{8\pi^2\sqrt{2}} \sum_{n'k} D^1_{n0}(\Theta) D^1_{n0}(\Theta') \int d\Theta'' D^1_{n''0}(\Theta'') D^1_{n''0}(\Theta'') \int d\Theta'' \exp\left(Qq \left[\cos\alpha \left(\frac{3}{2} \cos^2 \theta'' - \frac{1}{2}\right) + \frac{\sqrt{3}}{2} \sin\alpha \sin^2 \theta'' \cos 2\phi''\right]\right).$$

(C.6)

As stated before, the limit $q \rightarrow \infty$ is considered. Hence, the main contributions to the integral come from the points which maximize the square bracket in the exponential function. There are two such points given by $\alpha = 0$ and $\theta'' = 0, \pi$. In the region of these points, $D^1_{n0}(\Theta') \approx 0$ for $n' = 1, 2$ whereas $D^1_{00}(\Theta') \approx \pm 1$. Therefore we can replace the two Wigner D-functions $D^1_{n0}(\Theta')$ in the integral by $\delta_{n0}$ (note that two minus signs cancel in the case $\theta = \pi$). Hence, the sums drop and one obtains

$$\Psi^P_n(Q, q) = \frac{q\pi^{-\frac{3}{2}}}{\sqrt{2}} e^{-\frac{3}{2}(\theta^2 + Q^2)} D^1_{00}(\Theta) D^1_{n0}(\Theta) I(Q, q),$$

where

$$I(Q, q) = \frac{3}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \exp\left(Qq \left[\cos\alpha \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2}\right) + \frac{\sqrt{3}}{2} \sin\alpha \sin^2 \theta \cos 2\phi\right]\right).$$

(C.7)
The integrand is symmetric around $\theta = \pi/2$ and the contributions from the two points $\theta = 0, \pi$ are equal. Hence, we calculate only the contribution from $\theta = 0$. This is done by expanding the exponent in second order of $\theta$, which allows than to do the integral analytically by taking the integration region to infinity ($0 \leq \theta < \infty$).

\[ I(Q, q) \approx 2 e^{Q q \cos \alpha} \frac{3}{4\pi} \int_0^{2\pi} d\phi \int_0^\infty d\theta \theta \exp \left[ -\theta^2 Q q \left( \frac{3}{2} \cos \alpha - \frac{\sqrt{3}}{2} \sin \alpha \cos 2\phi \right) \right] = \frac{e^{Q q \cos \alpha}}{Q q} \frac{3}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \sin \alpha \sin 3\alpha \exp \left[ -\frac{\sin^2 \alpha \cos \phi}{2Q q \sin 3\alpha} \left( \frac{3}{2} \cos \alpha - \frac{\sqrt{3}}{2} \sin \alpha \cos 2\phi \right) \right]

Collecting the various results yields

\[
\begin{pmatrix}
\Psi_1^P \\
\Psi_0^P \\
\Psi_1^P
\end{pmatrix} = \pi^{-\frac{3}{2}} \frac{\sqrt{3}}{2Q q \sin 3\alpha} e^{-\frac{1}{2} (q^2 + Q^2 - 2Q q \cos \alpha)} \cos \theta \begin{pmatrix}
\sin \theta \sin \phi \\
\cos \theta \\
\sin \theta \cos \phi
\end{pmatrix}
\]

which is exactly the asymptotic wavefunction as found in Ref. [64]. Finally we can check whether the normalization of this wavefunction in first quantization is 1. The Jacobian of the coordinates $(Q, \alpha, \phi, \theta, \gamma)$ is $2Q^4 \sin \theta \sin 3\alpha$ as given in Ref. [61] (there is no factor 2 in this reference because the coordinate $\beta = 2\gamma$ is used). The norm in the first quantization is then

\[
2 \int_0^\infty dQ \int_0^\frac{\pi}{2} d\alpha \sin 3\alpha \int_0^{2\pi} d\phi \int_0^{\frac{\pi}{2}} d\theta \sin \theta \int_0^\pi d\gamma \sum_{n=-1}^1 \left| \Psi_n^P (Q, \alpha, \Theta) \right|^2 = 2 \sqrt{\pi} \int_0^\infty dQ \int_0^{\pi/2} d\alpha \sin \alpha e^{-\frac{1}{2} (q^2 + Q^2 - 2Q q \cos \alpha)}
\]

The main contributions to the integral com from points where the exponent is maximal. This is the case for $Q = 2q \cos \alpha > 0$. Hence, expanding the integration boundary of $Q$ to $-\infty$ adds only contributions that are exponentially suppressed in the limit $q \to \infty$. The integral can then be calculated analytically:

\[
\frac{2}{\sqrt{\pi}} \int_{-\infty}^\infty dQ Q^2 \int_0^{\pi/2} d\alpha \sin \alpha e^{-\frac{1}{2} (q^2 + Q^2 - 2Q q \cos \alpha)} = 1 - \frac{1}{2} e^{-\frac{1}{2}q^2}.
\]

Indeed the normalization becomes 1 as $q \to \infty$. 
Bibliography


Acknowledgments

I am very grateful to my PhD father, Manfred Sigrist, who gave me the opportunity to do this PhD which was a wonderful period in my life. I most appreciated the freedom he gave me to do whatever I liked and I'm thankful for the confidence he had in me. Despite his numerous duties as a researcher, teacher and leader of the institute he was always open to discussions and enthusiastically supported my ideas. I'm also very grateful to Maurice Rice who accepted me years ago as his diploma student which was the beginning of my stay in Zurich. Maurice always cared about my work and I'm happy that the collaboration with him continued throughout my whole PhD. I greatly appreciated the important stimulations he gave and his clear judgements about physics.

Another important man is Igor Milat. It was a pleasure to share office E4 with him. We moved in at the beginning of our PhD's and I always felt comfortable there – also because of our Revox sound system. We not always shared the same music taste but we certainly agreed on our enthusiasm and commitment to physics. Another member of the institute I want to thank is Christian Helm with whom I published my third paper. I could step by at his office at every time and with whatever confused idea about physics – things usually cleared up during a relaxed chat with Christian.

Of course, I thank all the other members of the institute, in particular all my PhD colleagues, which are equally responsible for the good professional as well as social life I had during my PhD. Special thanks goes to Martin & Martin (great climbers), Jérôme (fabulous horn player), Paolo (Italian chef), Slavo, Michele, Sebi (incredible climber), Alvise, Simon etc.

I thank a lot Jürg Osterwald and Erik Koch for taking the time to work themselves trough the 140 preceding pages and for co-examination of my thesis. I owe special thanks to Erik for spontaneously accepting the collaboration I suggested to him. I also thank Erik for inviting me to Stuttgart, more precisely to Olle Gunnarsson's group, which did so much great work on C_{60}.

... and I thank Barbara for sharing life with me.
List of publications

• S. Wehrli, T. M. Rice, M. Sigrist
  Theory of the different photoemission spectra of metallic and insulating C60 compounds

• S. Wehrli, C. Helm
  Interface steps in field effect devices

• S. Wehrli, E. Koch, M. Sigrist
  Limits to field-doping of C60 crystals: Polarization and Stark splitting

• E. Koch, O. Gunnarsson, S. Wehrli, and M. Sigrist
  Field-doping of C60 crystals: A view from theory
  Published in: H.Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.):
  Electronic Properties of Novel Materials

• S. Wehrli, D. Poilblanc, T. M. Rice, M. Sigrist
  Electronic Structure and Charge Distribution in the C60-FET
  Published in: H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.):
  Structural and Electronic Properties of Molecular Nanostructures

• S. Wehrli, D. Poilblanc, T. M. Rice
  Charge profile of surface doped C60
Seite Leer / Blank leaf
Curriculum Vitae

Personalien

Name: Samuel Wehrli
Geburtsdatum: 11. April 1975
Nationalität: Schweizer

Ausbildung

1991-1995 Alte Kantonsschule Aarau, Matura Typus C
1996-2001 Physikstudium an der EPF Lausanne
   3. Studienjahr an der CMU, Pittsburgh PA., USA
   Diplomarbeit an der ETH Zürich bei Prof. Rice
2001-2004 Doktoratsstudium im Institut für theoretische Physik
   an der ETH Zürich bei Prof. Sigrist