Surface electronic structure of fullerides
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Chapter 1

An introduction to fullerides*

The phenomenology of $C_{60}$ both as isolated molecule and in condensed phases is reviewed. $C_{60}$ compounds (fullerides) display a wide range of electronic ground states ranging from magnetic insulators to superconductors. The fundamental properties and interactions (electron correlation, electron-phonon coupling, crystal fields, polymerization, intermolecular screening) which are responsible for the behaviour of these salts are discussed extensively, with an emphasis on the issues which remain open and which will be addressed in this thesis.

1.1 Organic quantum materials

Carbon is the main character in the microscopic act of life and a building block for new materials and technologies. The ability of forming two, three or four $\sigma$ bonds (that is, the possibility of hybridizing $sp$, $sp^2$ and $sp^3$) is the key property which makes carbon capable of constituting the backbone chain of biopolymers and macromolecules, and at the same time enables the rich chemistry of carbon in living beings and the synthetic reactions which are used to transform fossil fuels into artificial polymers such as plastics and rubbers.

In the solid state, carbon exists in two main forms, graphite and diamond, where the carbon atoms hybridize $sp^2$ and $sp^3$ respectively. In 1991 new allotropic forms of carbon were discovered which somehow represent the bridge between the carbon known to solid-state physicists and that familiar to biochemists and polymer scientists. Many all-carbon $\pi$-conjugated structures exist: they range from single or double graphene sheets to multi- or single-wall nanotubes, to carbon onions, to closed hollow molecules known as fullerenes. The most famous of these is Buckminsterfullerene ($C_{60}$), a highly symmetric molecule made out of 60 carbon atoms.

$C_{60}$ crystallizes in a close-packed structure. Due to the molecule's high electron affinity, solid state intercalation compounds (fullerides) are readily obtained with donor atoms. Owing to the almost spherical shape of the molecule, $C_{60}$ fullerides do not exhibit polymorphic domains as other organics, and crystalline phases are more easily obtained. The simple chemical formula and high molecular symmetry makes theoretical calculations and the interpretation of experimental data easier than for other organics with similar molecular weights.

For these reasons, $C_{60}$-derived solids are ideal model systems to investigate the physics of carbon-based $\pi$-conjugated molecular materials. The interest in organic molecular materials is not only academic, for organic solids have a high potential for application as cheap materials in electronic and optical devices, sensors, and as photovoltaic systems.

1.2 The $C_{60}$ ID card

Buckminster fullerene consists of 60 carbon atoms arranged to form a truncated icosahedron, with 20 hexagonal faces and 12 pentagonal faces. Each atom has a $sp^2$-like hybridization (though the curvature of the molecule leads to a small admixture of $sp^3$ character) and occupies a vertex common to two hexagons and one pentagon. Of the 360 electrons (6 per C atom), 120 are core electrons,
leaving 240 electrons for the valence molecular orbitals (MO’s) delocalized over the almost spherical cage.

Of the four valence electrons of each C atoms, three occupy lower lying MO’s forming the σ bonds that constitute the cage, and the forth participates in the formation of the outermost MO’s, which have mainly π character. The charge distribution inside these orbitals is such that two types of C-C bonds arise, 30 shorter “double bonds” (1.38Å) that fuse two hexagons and 60 longer “single bonds” (1.45Å) that fuse a hexagon to a pentagon. This results in an effective alternation of single and double bonds, that is, to conjugation.

The C_{60} molecule, with its 120 symmetry operations, belongs to the highest possible point-group symmetry, the icosahedral group (I_h). The high symmetry of the molecule leads to a high degree of degeneracy of the molecular orbitals: the highest occupied molecular orbital, HOMO, with symmetry h_u, is 5-fold degenerate, the HOMO-1 (symmetry: h_g+g_u) is 9-fold degenerate, and both the lowest unoccupied molecular orbital, LUMO, with t_{1u} symmetry and the LUMO+1 (symmetry: t_{1g}) have a threefold degeneracy. While the diameter of a fullerene measured through the C nuclei is 7.1Å, the size of the π-electron cloud as estimated from the distance between two layers in graphite is 3.35Å, giving an outer (HOMO) diameter of the isolated molecule of approximately 10.3Å.

In C_{60}-derived solids the fullerene molecular orbitals give rise to narrow bands. The nearly spherical C_{60} molecules form a close-packed fcc solid (fullerite) at room temperature {Fleming '91}, kept together by van der Waals interactions {Saito '91}. The lattice constant of the conventional cell is a_0 =14.2Å, with a nearest neighbour distance of approximately 10Å, close to the diameter of the isolated molecule.

As the HOMO-derived band is totally filled, fullerite is a band insulator, with a theoretical band-gap of 2.15 eV {Shirley '93}. At room temperature the molecules are free to spin on the picosecond timescale {Tycko '91}, which is a quite unique feature among solid systems and is obviously related to the almost spherical shape of C_{60}. At 249 K fcc fullerite undergoes an orientational phase transition in which the orientation of the molecule relative to the crystallographic axes becomes important and the symmetry reduces to simple cubic {Heiney '91}.*

* The icosahedral point group symmetry of the molecule is incompatible with a orientationally ordered fcc lattice: the four molecules in the conventional cell of the fcc phase are equivalent only due to the spinning and “ratcheting” motions.
1.3 $C_{60}$ fullerides

$C_{60}$ has a very high electron affinity (2.8 eV) and can support many different valence states due to the high orbital degeneracy. In fact, $C_{60}$ compounds are easily obtained with many electron donors, especially alkali, alkaline-earth and rare earth elements, but also with donor molecules. $C_{60}$ fullerides display a plethora of interesting and potentially useful physical properties, ranging from photoactive behaviour in solar cells \cite{Yu95} to superconductivity at moderately high critical temperature \cite{Hebard91}, to ferromagnetism without the presence of $d$ or $f$ electrons \cite{Prassides99, Takenobu00, Allemand91, Chauvet94}, to non-linear optical response \cite{Kajzar94, Kajzar01}.

In the fcc structure of pristine fullerite there are three interstitial sites per $C_{60}$ molecule, one with octahedral symmetry and two with tetrahedral symmetry. Owing to the large diameter of the $C_{60}$ molecules, the interstitial cavities are large enough to accommodate several species of dopant atoms without distortion of the close-packed lattice. If there is no hybridization between the electronic states of $C_{60}$ and dopant (which is often the case), stable compounds are obtained at integer doping, that is, at integer filling of the LUMO or LUMO+1 orbital.

For low stoichiometries these $C_{60}$ salts have, at least at high temperature, the same fcc structure as pristine $C_{60}$. When trying to fit more than three interstitial atoms per buckyball into the lattice, or if the size of the intercalant is too large, the structure distorts to body-centred tetragonal (bct) as in $A_4C_{60}$ stoichiometries or to a bcc as for $A_6C_{60}$ fullerides. These structures are less close-packed than the fcc lattice, hence providing more room for interstitial atoms.

While only few stable stoichiometries up to $x=6$ are formed with K, Rb and Cs, an abundance of higher stoichiometries can be obtained when $C_{60}$ is doped with Na and Li. This is only partially due to the reduced radius of the dopant, which allows multiple-filling of the larger intercalation sites and diffusion into smaller interstices \cite{Dresselhaus96}. Stoichiometries up to $x=28$ have been observed in Li-doped $C_{60}$. The fcc structure is usually retained, with the Li atoms forming clusters in the largest interstices between the fullerene molecules \cite{Cristofolini99}. Such high concentrations are clearly not compatible with a total charge transfer from the alkali species.

As in other molecular crystals, the phonon spectrum of $C_{60}$-derived solids may be divided in two groups. At high frequency there are the intramolecular phonons, with energies in the range 30-200 meV. The low frequency range up to 30 meV comprises the soft intermolecular modes, intercalant-related phonons, and the librational modes at energies of about 4 to 5 meV. Due to symmetry, the LUMO $t_{1u}$ electrons can only couple to the two modes with $A_g$ and the eight
phonons with \( H_g \) symmetry, which are Jahn-Teller active. The coupling to the \( H_g \) phonons is believed to be the one relevant for the superconductivity of \( A_3C_{60} \) compounds (\( A = K, Rb, \) and \( Cs \)).

A crucial point for the electronic properties of fullerides, true for most organics, is that the intermolecular electronic hopping is much smaller than the intramolecular one, so that the bands which stem from the molecular orbitals are fairly narrow. As a consequence, it does not pay for an electron to be delocalized over many molecular units; instead, the high polarizability of the molecules entails that a localized electron is stabilized by a large polarization energy contribution due to dipoles forming on neighbouring molecules (Silinsh ‘94). This localization of electrons on single molecules, which also implies a strong on-site inter-electron repulsion and correlation effects, is a common feature of many \( C_{60} \) compounds (see section 1.4).

The presence of pseudo-double bonds in the \( C_{60} \) molecule allows for covalent bonds to be formed between molecules. A tendency to oligo- and polymerization is indeed reported in pure and doped \( C_{60} \). In these structures the molecules adopt well-defined orientations with respect to one another, which can lead to the formation of one or two \( \sigma \)-bonds (sp\(^3\)) connecting neighbouring molecules. The intermolecular distances in polymer phases are shorter than between those observed in monomer phases. While in monomer phases the electronic bands and phonon modes derive from corresponding features of the \( C_{60} \) molecule, in oligomer and polymer phases these features are characteristic of the new structure.

1.4 Correlation, molecular polarizability, Jahn-Teller coupling, polymerization, and surface effects

If the valence electrons in a solid are not delocalized wave packets of Bloch waves as in simple metals, but are largely localized on single atoms or molecules, the electron-electron repulsion can no longer be considered a weak perturbation on the non-interacting electronic band structure, but must instead be treated on equal footing together with the electron-ion interaction. Systems in which the inter-electron repulsion is important are called strongly correlated electron systems.

The simplest and most widely used model for the theoretical description of correlated solids is the Hubbard model, which contains both the electron tendency to delocalization in the form of a hopping parameter \( t \) between nearest-neighbour sites (as in the tight binding approach), and the intra-site Coulomb repulsion \( U \) (called the “Hubbard \( U \)”) between two electrons on the same site.
The Hubbard $U$ is more properly defined as the Coulomb energy lost in creating a charge fluctuation in the system, and implicitly contains the energy gained due to the polarization of the lattice induced by the local excess of charge. The effect of such polarization screening in fullerides will be treated in more detail in Chapter 5.

For vanishing $U$, the Hubbard model reduces to the independent-electron tight binding model, resulting in a metallic band of width $W$ which is a function of $t$ and of the lattice geometry. The relative strength of the parameters $U$ and $W$ measures the degree of localization of the electrons of a solid, and determines the insulating or conducting nature of the ground state. For $U \gg W$, the ground state of the system at half filling is an insulator, due to the large energy cost $U$ of charge fluctuations (double site-occupancy). The hopping term in the Hubbard Hamiltonian leads to inter-site hybridization (band formation) and thereby to magnetic correlations between neighbouring sites. The insulating state of the Hubbard model is thus a magnetic state. The magnetic free energy gain plays a role in determining the nature (order) of the transition from the metallic to the insulating state (the so-called Mott transition), and should be included in the Hubbard Hamiltonian if the details of the transition are to be described.

A rough estimate can be easily found for the critical ratio $(U/W)_c$ at which the Mott metal-insulator transition occurs. In the presence of correlation, the non-interacting electronic band is effectively split into two so-called “Hubbard sub-bands”, of which the lower one (corresponding to single occupancy of sites) is completely filled while the upper one (double occupancy) is empty. In the case of a non-degenerate band, the critical ratio is simply $(U/W)_c \approx 1$, which stems from the fact that for $U < W$ the two Hubbard sub-bands overlap, while for $U > W$ they are completely separated. In the case of fullerene compounds with electron donor atoms, since the LUMO and LUMO+1 orbitals are both threefold degenerate, a degenerate Hubbard model must be considered. For orbital degeneracy $n$, the critical $U/W$ ratio has been shown to increase from 1 to roughly $\sqrt{n}$ \{Lu ’94, Gunnarsson ’96, ’97b; Koch ’99b\}. Qualitatively, this comes about because the possibilities for hopping between nearest neighbours are enhanced by the orbital degeneracy.

The theoretical width $W$ for the $C_{60}$ LUMO-derived band is expected to be around 0.5 eV \{Erwin ’91\}. The value of $U$ for the isolated molecule (in the gas phase) is above 3 eV \{Rudolf ’99\}, but screening in the solid state reduces it to roughly 1.5 in pristine fullerite \{Lof ’92a, Antropov ’92, Pederson ’92, Brühwiler ’93, Maxwell ’96\}, and to values between 0.5 and 1.5 eV in doped samples, depending on the compound, as will be shown in Chapter 5. This puts fulleride salts on the verge of the Mott metal-insulator transition, where the
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effective orbital degeneracy is crucial for metallic behaviour.

The effect of electron correlation (Hubbard $U$) is to suppress charge delocalization, thus determining an effective narrowing of the bandwidth from its uncorrelated value. In organic molecular solids, localization is also favoured by the strong intra-molecular electron-phonon coupling, and by the high molecular polarizability which results in a large polarization screening energy associated with localized charges, as discussed in the previous section. These effects in concert lead to a strong renormalization of the bandwidth $W$ by a factor $\zeta << 1$. Hence, even small interactions and perturbations (of the order of $\zeta W$) can have a large impact on the electronic properties. Effects which are usually too weak to break the effective degeneracy of the ground state of a system, such as Jahn-Teller molecular distortions, weak crystal fields or orientational ordering, become crucial in determining the metallic or insulating nature of a phase.

In fact, the Hubbard model is not sufficient to explain the phenomenology of alkali fullerides. In the Mott-Hubbard picture all integer-stoichiometry compounds $A_nC_{60}$ ($1 \leq n \leq 5$) should be either magnetic Mott insulators or correlated metals; instead, $A_2C_{60}$ and $A_4C_{60}$ compounds are non-magnetic insulators, while $A_3C_{60}$ compounds are metallic and even superconductors at low $T$ ($A_6C_{60}$ is a band insulator). The proximity of the Mott transition is evidenced by the fact that a lattice expansion by ammoniation in odd stoichiometries results in a Mott insulating state \{Rosseinsky '93, Iwasa '96, Allen '96\} (and this even for cubic systems where the effective LUMO degeneracy is retained \{Durand '03\}), while e.g. Rb$_4$C$_{60}$ becomes metallic under pressure \{Kerkoud '96\}.

Other interactions need therefore be taken explicitly into account. A very important coupling in C$_{60}$ fullerides, as mentioned above, is the vibronic interaction between the valence electrons (HOMO, LUMO) and the intra-molecular phonons. In the solid state, the electron-phonon coupling is responsible in general for a number of properties and phenomena, such as electrical resistivity and superconductivity. In a highly symmetric solid or molecule, the electron-phonon interaction may lead to a so-called Jahn-Teller distortion. This occurs when a degenerate valence orbital is only partially filled: upon distortion, the degeneracy is lifted, with the resulting electronic levels having a higher or lower energy than the degenerate ones. If only the lower energy orbitals are filled, there is a corresponding electronic energy gain to the distortion; if this is larger than the elastic energy loss, the Jahn-Teller distortion is favourable.

Many Jahn-Teller distorted states of the C$_{60}$ molecule exist, with different energies. It should be noted that these molecular distortions are not necessarily static: due to the high molecular symmetry, distortions with respect to different
molecular axes have the same energies, which leads to a so-called “dynamical” Jahn-Teller energy gain. The lowest energy Jahn-Teller state of a \((\text{C}_{60})^{1-}\) or \((\text{C}_{60})^{2-}\) anion (that is, anions of even charge) is a diamagnetic gapped state, due to the splitting of the LUMO orbital. One can envisage that the Jahn-Teller coupling may compete with the on-ball exchange which tends to favour high spin states; several studies have however shown that the Jahn-Teller energy gain for \(\text{C}_{60}\) anions is larger than that derived from the on-ball Coulomb exchange \{Auerbach '94, Manini '94, Lüders '03\}, and indeed the phenomenology of alkali fullerides shows that the Jahn-Teller state is favoured.

The net energy gain associated with molecular Jahn-Teller distortions is largest for even-charge anions, as can be expected intuitively. It is convenient to define a Jahn-Teller pairing energy \(E_{\text{JT}}\) as a function of the anionic charge \(n\) as

\[
E_{\text{JT}}(n) = E(n+1) + E(n-1) - 2E(n),
\]

where \(E(n)\) is the energy gain associated with the Jahn-Teller distortion of the isolated \((\text{C}_{60})^n\) anion. It turns out that this pairing energy is positive for odd \(n\), which favours charge fluctuations, while it is negative for even \(n\), which means that in phases of even stoichiometry the Jahn-Teller effect reinforces the effect of electron correlation and further suppresses fluctuations. Monomeric \(A_2\text{C}_{60}\) and \(A_4\text{C}_{60}\) phases are in fact diamagnetic insulators, and are described as Mott-Jahn-Teller insulators \{Fabrizio '97\}.

As mentioned previously, the Jahn-Teller coupling of LUMO electrons to the \(H_g\) phonons is responsible for superconductivity in \(A_3\text{C}_{60}\) and \(A\bar{A}_2\text{C}_{60}\) fullerides (where \(A\) and \(\bar{A}\) indicate two different alkali metals). This can be understood as the Jahn-Teller pairing energy stabilizes charge fluctuations involving \((\text{C}_{60})^{1-}\) and \((\text{C}_{60})^{2-}\) charge states, thus effectively acting as a local inter-electron pairing in \(A_3\text{C}_{60}\) superconductors. How such local (molecular) coupling can overcome the supposedly strong on-site Coulomb repulsion, is still a controversial issue. Since the Jahn-Teller active modes have energies between 0.15 and 0.2 eV, which is comparable with the Fermi energy (bandwidth), the validity of the Migdal-Eliashberg theory for \(\text{C}_{60}\)-derived solids is questionable and non-adiabatic effects might play a role \{Yang '03\}.

Another option is that charge correlation is weaker in metallic fullerides. The value of \(U\) at low temperatures in conducting phases cannot be easily determined experimentally, and on the theoretical side it is not clear how effective electronic screening should be in suppressing correlation effects \{Lammert '95, Koch '99a\}. We will discuss the interplay between the Jahn-Teller coupling and electron correlation in fullerides when presenting our results on the cubic phases of \(\text{RbC}_{60}\) in chapter 4. A detailed discussion of correlation in fullerides, and on how the Hubbard \(U\) can be determined experimentally in these salts, is given in chapter 5.

In non-cubic phases the crystal field splitting can be a crucial factor in
determining an insulating character of the ground state. In the ammoniated compound NH$_3$K$_3$C$_{60}$, for example, the formation of an insulating antiferromagnetic (Mott) phase is observed at low temperature \{Prassides '99\}. The suppression of metallicity and superconductivity has been related to the symmetry reduction from fcc K$_3$C$_{60}$ to orthorhombic NH$_3$K$_3$C$_{60}$, which entails a crystal field splitting of 0.15 eV (which is only one fourth of the non-renormalized bandwidth $W$) \{Gunnarsson '04\}.

In phases where the molecules are bridged by covalent bonds, the Jahn-Teller effect is less important and the modification of the electronic structure brought about by the polymerization may change the impact of electron correlation on the electronic properties. Furthermore, polymerization can also affect the transport properties. Many different structures and bonding motifs are observed in fullerides. Polymerization can also occur in pristine fullerite upon application of high pressure or irradiation with visible or UV light. Singly or doubly bonded dimers \{Oszlánya '95, Zhu '95, Thier '97, Wang '97\} and polymer chains \{Stephens '94, Chauvet '94, Pekker '94, Bendele '98\}, as well as two-dimensional \{Nunez-Regueiro '95, Oszlánya '97, Okotrub '01\} and even three-dimensional networks \{Blank '98, Marques '99, Yamanaka '06\} of C$_{60}$ molecules have been reported.

The thermodynamically stable phase of AC$_{60}$ compounds at room temperature is an orthorhombic or monoclinic phase of linear polymer chains where the C$_{60}$ monomers are linked via two $\sigma$-bonds. The monomers are oriented in such a way that the edge which fuses two adjacent hexagonal phases on a given molecule is facing an analogous edge on the next molecule in the chain. The double-like ($\pi$) bond at these edges is broken and two new $\sigma$-bonds are formed as visible in Fig. 1.1(c). This type of polymeric bonding is called “[2+2] cycloaddition”.

In the case of two-dimensional (2D) polymerization different geometries and bonding motifs exist. The 2D polymer structure obtained from undoped C$_{60}$ has either rhombohedral or tetragonal symmetry, with the molecules linked via [2+2] cycloaddition \{Nunez-Regueiro '95\}. Mg fullerides form a 2D rhombohedral polymer phase \{Borondics '03\}.

2D polymerization in alkali fullerides is only observed for the smallest alkalis Li and Na. The polymer phase of Na$_4$C$_{60}$ is based on planar rectangular networks where each molecule forms four single bonds within the plane \{Oszlánya '97\}. In the rectangular polymer phase of Li-doped C$_{60}$, whose electronic properties will be addressed in Chapter 3, the bonding motif is mixed, with [2+2] cycloaddition bonds in one direction and single bonds in the orthogonal direction (see figure 1.1(a)) \{Margadonna '04, Riccò '05, Wagberg '06\}. Linear polymer and dimer
structures are observed in alkali fullerides of odd stoichiometry such as $A\text{C}_{60}$ or $AB_2\text{C}_{60}$ ($A=$Rb, K, Cs; $B=$Li, Na) (figures 1.1(c) and (f)) {Stephens ’94, Bendele ’98}.

The impact of polymerization on the electronic properties of fullerides will be addressed in the discussion of the polymer phases of Li$_4$C$_{60}$ and RbC$_{60}$ in chapters 3 and 4, respectively.

It should also be noted that the electronic character of the surface of fulleride salts can be different than that of the bulk – a general phenomenon that arises due to the peculiar electrostatics at the truncation of ionic crystals. This will be discussed in detail for all compounds studied in this thesis.

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**Figure 1.1** Some of the bond types and structures encountered in fullerene structures. (a) the structure of the 2D polymeric planes observed in Li$_4$C$_{60}$; (b) the rhombohedral 2D polymer structure; (c) structure of the linear polymer chains observed present at room temperature in AC$_{60}$ compounds; (d) the C$_{60}$ molecule; (e) the C$_{70}$ molecule; (f) the azafullerene dimer (C$_{59}$N)$_2$ (if the N atoms are substituted with C atoms, the structure becomes that of the charged (C$_{60}$)$_2$ dimer observed in AC$_{60}$ compounds).