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# ELECTRONIC AND STRUCTURAL PROPERTIES OF ATOMIC CLUSTERS

By

YANG WANG

## A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the Degree of

### DOCTOR OF PHILOSOPHY

Department of Physics and Astronomy

1993

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### ABSTRACT

# ELECTRONIC AND STRUCTURAL PROPERTIES OF ATOMIC CLUSTERS

#### BY

#### YANG WANG

In this Thesis I have studied the electronic and structural properties of small atomic clusters, namely alkali metal clusters and the  $C_{60}$  carbon fullerene cluster. In my research, I addressed the possibility of collective excitations in small clusters, and found similarities between the excitation spectra of these two type of systems.

In alkali metal clusters, specifically  $Na_n$  and  $Li_n$ , I calculated the equilibrium structure and electronic excitations, as well as their damping, using *ab initio* methods. I used the Local Density Approximation (LDA) to describe the ground state properties of these systems, and the Random Phase Approximation (RPA) for the electronic excitations. Results for the excitation spectra of clusters with the "magic number" of n = 2,8 atoms are in good agreement with experimental data. I found that even in small clusters, one single excitation exhausts most of the total oscillator strength, which has also been observed experimentally. My calculations indicate that the coupling of electronic levels to vibrational degrees of freedom accounts quantitatively for the observed width of the collective electronic excitations in alkali dimers.

In the  $C_{60}$  system, my main interest has been devoted to the dielectric response of isolated clusters, and elastic properties and stability of the  $C_{60}$  fullerite solid in its pristine and intercalated phases.

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In the  $C_{60}$  solid, I found a very low value of the bulk modulus at zero pressure while at high pressures the bulk modulus of fullerite exceeds that of diamond and a phase transformation to diamond is likely. My calculations for the stability of potential  $C_{60}$  based superconductors indicate that alkali and some alkaline earth elements form stable fullerite intercalation compounds.

My calculations on the static polarizability and hyperpolarizability of the isolated  $C_{60}$  cluster have shown that the valence electrons are quite delocalized. Our RPA calculations of the dynamical response indicate a strong screening of low-lying excitations, which transfer their oscillator strength to a giant collective mode at  $\hbar\omega \approx 20$  eV. This mode has been subsequently observed experimentally. This high energy collective excitation which is very similar to a Mie plasmon results from a large electron delocalization across the fullerene and a large charge density in the C<sub>60</sub> cluster.

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### **Publications**

- "Stiffness of a Solid Composed of C<sub>60</sub> Clusters", Yang Wang, David Tománek, and George F. Bertsch, Phys. Rev. BR 44, 6562 (1991).
- "Collective Plasmon Excitations in C<sub>60</sub> clusters",
   George F. Bertsch, Aurel Bulgac, David Tománek, and Yang Wang,
   Phys. Rev. Lett. 67, 2690 (1991).
- "Hyperpolarizability of the C<sub>60</sub> Fullerene Cluster", Yang Wang, George F. Bertsch, and David Tománek, Z. Phys. D (1993).
- 4. "Stability of C<sub>60</sub> Fullerite Intercalation Compounds",
  Yang Wang, David Tománek, George F. Bertsch, and Rodney S. Ruoff,
  Phys. Rev. B (1993).
- 5. "Lanthanide and Actinide Based Fullerite Compounds: Potential A<sub>x</sub>C<sub>60</sub> Superconductors?" Rodney S. Ruoff, Yang Wang, and David Tománek, Chem. Phys. Lett. (1993).
- "Fullereneynes: A New Form of Porous Fullerenes",
   Ray H. Baughman, Douglas S. Galvao, Changxing Cui,
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# Chapter 1 Introduction

A cluster is a stable aggregate of atoms or molecules, the size of which can range from few atoms to a vaguely defined limit of thousands of atoms or molecules. Clusters seem to be the bridge connecting the discrete atomic and molecular limit and the continuum crystal limit. These systems have many unique and interesting properties, such as unconventional atomic packing [1], electronic shell structure [2], collective electronic excitations [3], magnetic properties vastly different from the bulk [4]. Clusters have attracted many researchers from different disciplines, and a great effort has been devoted to understand their physical properties [5, 6, 7, 8, 9, 10]. Cluster science is a fascinating new field and one of the fastest growing fields in the past ten years. For a long time, cluster research concentrated on alkali metal clusters exhibiting a rich variety of phenomena, many of which have been explained by an electronic shell model taken from nuclear physics [2, 6, 11]. A more timely and exciting example of cluster research is the  $C_{60}$  molecule, which aroused a tremendous research activity and many speculations about potential applications in the past two years. Five years after it was first proposed in 1985 [1], it was crowned "molecule of the year" in 1991 by the Science magazine.  $C_{60}$  is the first existing example of a homonuclear molecule that has the icosahedral symmetry [12]. These moleculars, packed into a crystal,

have established a third form of crystalline carbon, based on the  $C_{60}$  cluster, which is called "fullerite" [13].

Atomic clusters can be composed of a single atomic species, as homonuclear clusters, or a mixture of elements, composing a heteronuclear aggregate. Many different types of clusters have been investigated. Among them, the structural and thermal properties of noble gas clusters, such as argon clusters [14], have been studied. Clusters composed of metallic elements, such as alkali and alkaline earth elements, have attracted great attention, and many theoretical [10] and experimental [6] studies have been devoted to understand their behavior. Clusters with nonmetallic elements, such as silicon and carbon, have many interesting properties and potential applications [1, 15], in the semiconductor technology and in novel materials based on carbon clusters.

As mentioned before, clusters exhibit properties of both molecules with a discrete spectrum and the bulk with a continuum spectrum. These properties include the electronic structure [10], response to an external electromagnetic field [3], magnetic [4] and thermal properties [16]. In this work I will discuss the atomic packing and electronic properties of clusters, as well as their response to external perturbations (pressure, external field, temperature).

The stacking of atoms in a cluster is crucial for the stability of the cluster. Since clusters have a large fraction of surface atoms, and the environments of the bulk and surface atoms are quite different, one cannot simply consider them as a piece of the crystalline structure. The structure of a cluster will determine the formation process, the thermal properties of the cluster [16], the evaporation and dissociation patterns [17]. It will also have an effect on the electronic structure [18].

The electronic structure plays a major role in the bonding between the atoms.

Hence it affects the cluster stability, the interaction of the cluster with other atoms or the embedding matrix, its electromagnetic response, and other properties. Since one is dealing with finite Fermi systems, quantum size effects, such as shell structure of the electrons, can be seen. The character of electronic excitations in a cluster will be reminiscent of both the discrete single-particle excitation spectrum in the atomic limit and the collective plasmon behavior of the electron gas in the bulk limit.

In this Thesis, I will focus on describing the equilibrium atomic structure and optical response of small alkali metal clusters, namely Li<sub>2</sub>, Na<sub>2</sub>, and Na<sub>8</sub>, and a prominent carbon cluster, namely the C<sub>60</sub> molecule. The Thesis is organized as follows. In the remaining part of this Chapter, I will present the basic concepts used in this field, which will provide the background for further discussions. In Chapter 2, I present the theoretical tools I used in this study. The equilibrium structure of metal clusters will be studied by state-of-the-art *ab initio* LDA calculations. The optical response, mainly due to the collective motion of the delocalized electrons, will be described using the Random Phase Approximation (RPA). The corresponding results are presented in Chapter 3. In Chapter 4, I will present results for the structural properties of fullerite, a novel bulk material based on the C<sub>60</sub> cluster, and will also address the stability of fullerite intercalation compounds. Finally, in Chapter 5, I will present results on the static polarizability, hyperpolarizability, and the optical response of C<sub>60</sub>, obtained using a tight-binding Hamiltonian.

# 1.1 Alkali Metal Clusters

In this Section, I will discuss some basic concepts related to alkali metal clusters which will be useful for subsequent discussions in Chapter 3.

Alkali metal clusters are one of the best studied types of clusters so far, both

theoretically and experimentally [6]. Among the alkali metal clusters, the sodium systems have been most thoroughly investigated [2]. Sodium is heavier than lithium which may exhibit nuclear quantum effects [19]. The heavier potassium has many stable isotopes, which makes the interpretation of mass abundance spectra difficult. Knight and coworkers [2, 20] found that the shell structure in sodium clusters is more pronounced than in potassium clusters, due to the larger Fermi energy (Fermi energy in the free electron model is inversely proportional to the squared Wigner-Seitz free electron radius  $r_s$ ). This fact implies unique features for the stability of Na clusters. In Li clusters, the electronic shell structure is also not well pronounced for the following reason. The large optical electronic mass in bulk lithium  $m^* = 1.56m_e$  [21] indicates a strong electron-phonon coupling, which would make a static model of the ion lattice questionable for the lithium clusters. Therefore, sodium clusters are the simplest object to study if one wants to understand the collectivity of electronic excitations and, at a later stage, the coupling of electronic excitations to nuclear degrees of freedom.

### **1.1.1** Cluster synthesis and experimental techniques

A major experimental achievement in cluster physics is that now one can generate and investigate free clusters. This comes as a significant advantage when compared to the previous experimental setup, where clusters were investigated in a supporting matrix [22]. The latter experimental setup does not allow for a clear distinction of cluster features from those of the matrix [23]. More important, the cluster-matrix interaction can modify cluster properties significantly. With the development of molecular beam techniques, one is able to produce and detect free clusters over a large range of size and to analyze their basic properties [2, 24]. Alkali clusters can be produced in



Figure 1.1: Typical experimental setup for cluster spectroscopy: Cluster source and time-of-flight spectrometer [From de Heer et al, Solid State Physics 40, 128 (1987)].

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sufficiently large numbers to obtain statistically relevant information.

In Figure 1.1, I show a typical experimental setup for generating and analyzing cluster beams. At the far left is a supersonic nozzle source, in which the bulk metal is evaporated and the metal vapor mixes and condenses in a cold inert carrier gas. At the exit of the source, the mixture is ejected into the vacuum via a pinhole nozzle. The metal vapor undergoes an adiabatically rapid cooling, and condenses into clusters. Following the source, the cluster beam goes through a series of collimating slits and mechanic choppers. A laser light is used to ionize the cluster. Cluster ions are subsequently accelerated to generate a time-of-flight mass spectrum.

### 1.1.2 Structural properties

The equilibrium geometry is an important property of a cluster. Because of the significant fraction of low coordinated surface atoms, the cluster is not just a piece of the bulk lattice. The ground state geometry is crucial for the stability of the cluster and will also determine the other properties of the cluster, such as the polarizability [18], frequency of the collective electronic response [25], and the fission patterns [17], just to name a few.

Since present experimental tools cannot tell us directly where the nuclei are located in the free clusters, we have no direct information on regarding equilibrium structure of a cluster. Thus, the knowledge of the equilibrium structure of a cluster relies on theoretical calculations. Many investigations have addressed this question mostly using *ab initio* methods. Considerable progress has been made despite the substantial difficulties associated with this approach [18, 26, 27, 28].

Among the *ab initio* techniques, one can list the HF-CI calculations (Hartree-Fock plus configuration interaction) [27], pseudopotential DFT (Density Functional



Figure 1.2: Equilibrium geometries of small sodium clusters [From Bonacic et al, Phys. Rev. B 37, 4369 (1988) and Moullet et al, Phys. Rev. Lett. 65, 476 (1990)].

Theory) calculations based on the LDA (Local Density Approximation) [29], LSD (Local Spin Density) calculations [18], and calculations based on the Car-Parrinello method (unified density-functional theory and molecular dynamics) [28]. It has been found that there are generally many different geometries with a very similar total energy. Therefore each cluster has possibly several coexisting isomers. In general, most of the calculations agree with each other as far as the equilibrium geometry is concerned. Minor disagreements are found typically in some details such as the exact bond length.

In Figure 1.2, geometries of different small sodium clusters are shown. From Na<sub>2</sub> to Na<sub>6</sub>, the clusters have a planar structure. Na<sub>4</sub> has a rhombic equilibrium geometry. Na<sub>5</sub> has an almost trapezoidal shape. Na<sub>6</sub> is a relatively flat pentagonal pyramid, as stable as a planar structure with the D<sub>3h</sub> symmetry. Na<sub>7</sub> exhibits the first 3–D structure in the sequence, a pentagonal bipyramid. For Na<sub>8</sub>, the energetical lowest geometry is the  $T_d$  geometry with four caps attached to the four faces of an inner tetrahedron.

#### **1.1.3 Electronic shell structure**

The mass abundance spectrum of sodium clusters, shown in Figure 1.3(a), revealed interesting new physics. Clusters with a certain number of atoms (N=2, 8, 20, 40, 58, 92, ...), are much more abundant than their neighbours, indicating a remarkable stability of these clusters. The above mentioned numbers are called "magic numbers", in analogy to the magic numbers of nucleus associated with very stable nuclei. This observation shows that one is dealing with finite spherical Fermi systems, similar to nuclei. The magic numbers are determined mainly by the number of valence electrons in the clusters [11], corresponding to the closure of an electronic shell. This is con-



Figure 1.3: Mass abundance spectrum of Na<sub>N</sub> clusters. (a)Mass abundance spectrum of Na<sub>N</sub> clusters, N=4-75. The inset corresponds to N=75-100. (b) The calculated second derivative  $\Delta_2(N)$  of the total energy E(N) of jellium clusters, defined in Eq. (1.1), as a function of cluster size [From Knight et al, Phys. Rev. Lett. 52, 2141 (1984)].



firmed in the abundance spectrum of the positively charged potassium clusters [30]. In all alkali clusters, the magic numbers N=2, 8, 20, 40, 58, 92, ..., are common. For other elements, the magic numbers can be substantially different.

The shell structure underlying the abundancies in the mass spectra, results from quantum size effect in these systems. To understand the shell structure of clusters, detailed quantum calculations are necessary. Calculations of the electronic structure of a cluster are a challenging subject. The quantum chemistry approach typically starts with the Hartree–Fock (HF) method, which is based on the independent electron approximations and neglects the correlation between spin–up and spin–down electrons. A more sophisticated approach is based on configuration interaction (CI) calculations, which is exact and includes all correlation effects if the full CI expansion is included. HF can be done routinely for small clusters, but CI calculations can only be performed only for few fixed geometries due to the large number of configurations necessary for a converged calculation. HF-CI calculations are feasible only for small clusters (less than 10 atoms with the nowadays available computational resources).

On the other hand, physicists developed the Local Density Approximation (LDA) which is based on the Density Functional Theory (DFT) (the details will be discussed in Chapter 2). The Local Density Approximation to the DFT involves a local potential which mimics correlation effects in a mean-field framework, i. e., it is superior to HF. Compared to CI calculations, LDA calculations are easier but still give accurate ground state geometries. LDA is a powerful tool to calculate the total energy of a quantum system with a given atomic geometry, but is computationally intensive.

The simplest theoretical approach is the so-called jellium model, which has been used in solid state physics and nuclear physics for a long time. In the jellium model, the ions are smeared out to form a jellium of positive charges. The electrons move in
a potential of spherical symmetry generated by the jellium background. The jellium model is especially useful for large clusters, where the symmetry lowering due to the ions makes full *ab initio* calculations computationally prohibitively demanding. This simple model provides a good semi-quantitative understanding of different aspects of the physics governing the stability and electronic excitation spectra [11].

The requirements for a meaningful applicability of the jellium model are that the electrons be delocalized and the positions of the ions do not play an important role. It is generally agreed that this is the case in most alkali metal clusters [6].

Jellium calculations assume that electrons are moving in a spherical potential well. All the energy levels are obtained by solving the Kohn-Sham equations (see Chapter 2) self-consistently. The electrons fill the levels in ascending order with the constraint of satisfying the Pauli principle. Clusters with fully occupied shells of electrons will have a lower total energy than neighbouring clusters, and are therefore more stable. A quantity  $\Delta_2$  has been defined to measure the relative stability of the clusters,

$$\Delta_2 = E(N+1) + E(N-1) - 2E(N) \tag{1.1}$$

where E(N) is the total energy of electrons in spherical jellium with N electrons.  $\Delta_2(N)$  is the second derivative of the total energy E(N), and represents the relative binding energy change for clusters with N atoms compared to clusters with N+1 and N-1 atoms. A peak in  $\Delta_2(N)$  indicate that the cluster with N atoms is relatively stable than its neighbors. In Figure 1.3(b),  $\Delta_2$  is shown for sodium clusters as a function of the cluster size. As we can see, the trends clearly match the observed mass abundance spectrum of sodium clusters, shown in Figure 1.3(a).

#### **1.1.4 Optical response**

The response of a system to an external time dependent electromagnetic field is called optical response. There are essentially two experimental techniques to measure the optical response of free clusters. Namely the depletion technique and the resonant two-photon ionization technique. In addition to the setup for the generation and detection of clusters, shown in Figure 1.1, the depletion technique uses a pulsed laser which propagates collinearly against the molecular beam. At resonance, the cluster beam is depleted due to the dissociation of the excited clusters which have absorbed a photon from the pulsed laser beam. The resonant two-photon ionization uses the first laser (pump) to pump the cluster and the second laser (probe) to further ionize it, before the cluster beam enters the time-of-flight mass spectrometer (in a typical experimental setup, only one laser is used to pump and probe the clusters at the same energy). The mass spectrum provides a direct measure of the cross section as a function of the laser beam energy.

In Figure 1.4, I show the observed optical response of the Na<sub>8</sub> cluster using the depletion technique [31]. In this spectrum we can see a single prominent peak at 490 nm (2.53 eV). This peak is due to a collective excitation of the valence electrons. Its oscillator strength exhausts almost the entire Thomas-Reiche-Kuhn (TRK) sum rule (f-sum rule), which indicates that essentially all the valence electrons participate in the resonance. As I will discuss below, the physics of this transition is very similar to the dielectric response of a classical metal sphere.

In 1908, Mie [32] studied the optical response of small systems. In particular, he studied the optical response of a metal sphere to an external electric field with a wavelength much larger than the sphere radius. Under the influence of an external field, the negative charges move back and forth with respect to the positive charge



Figure 1.4: Optical response of the Na<sub>6</sub> cluster using the depletion technique. [From Wang et al, Chem. Phys. Lett. 166, 26 (1990)]

background, as illustrated in Figure 1.5. Mie established that the collective motion of the electrons, the so-called "Mie plasmon", solely depends on the density of the electrons n, as

$$\omega_{Mie}^2 = \frac{4\pi n e^2}{3m_e} \,. \tag{1.2}$$

Here,  $m_e$  is the mass of the electrons and e the electron charge. The factor 3 in the denominator occurs due to the spherical geometry. Since the rigid displacement of the electronic charge on a constant spherical ionic background results in a nonvanishing charge density only close to the surface, this collective motion is sometimes called the surface plasmon of the cluster.

In applying this classical model to clusters, two questions arise immediately. The first one is how large should the cluster be to support a collective electronic motion. As I will discuss later, even very small clusters can exhibit collective excitations. The second one arises from the fact that in this simple classical description the energy of the plasmon is independent of the cluster size and is totally determined by the free electron density of the cluster. Will the optical response of a cluster be peaked at the same energy, independent of cluster size? The answer is no. The energy of the collective excitation has a size dependence. In Figure 1.6, I show the experimental data showing the dependence of the excitation energy on the size of sodium clusters [33]. The frequency shifts from 2.4 eV in small clusters of about 10 atoms to the value 3.4 eV near the bulk limit. The energy of the collective mode obtained from the Mie formula overestimates the plasmon energy in small clusters. The discrepancy cannot be explained without a detailed calculation. Its origin is speculated to be partly due to the inadequacy of the spherical jellium model, partly due to the quantum effects, such as the spill-out of electrons which is neglected in the Mie theory, and finally the electronic structure of the cluster which can be significantly different from jellium



Figure 1.5: A classical picture of the Mie plasmon. (a) If no electrical field is applied, the positive and negative charge background coincide with each other. (b) Under an external electrical field with a particular frequency, the negative charge background will move back and forth with respect to the positive background. Since the collective motion results in a nonvanishing total charge density only near the surface, it is often called the surface plasmon of the cluster.

spheres.

The first improvement over the classical Mie description are RPA calculations for spherical jellium [34, 35, 36, 37]. Assuming that the position of the ions can be neglected, the electrons are assumed to move in a spherical potential well. Particlehole interactions in the excited states are considered in RPA. LDA-RPA results for spherical jellium show a weak size dependence of the excitation energy [36].

Within the *ab initio* approach, CI calculations of electronic excitations have been carried out for small sodium clusters [38, 39]. Due to the large number of electrons, the calculations have been done with empirical core potentials. Since the computational load is large, the CI calculations have been performed only for several selected geometries, and the expansion space has been limited to low energy states. Therefore, the results can only give semiquantitive answers [38].

To overcome these difficulties and to get a quantitative understanding of the experimental results, we adopted the *ab initio* LDA-RPA approach. We describe the ground state and the single particle spectrum using LDA, and calculate the electronic excitations using RPA. As I have mentioned in Section 1.1.2, LDA has the advantage of a local exchange-correlation potential, hence it includes some correlation effects. It has been shown that LDA gives reliable results for the structure of sodium clusters [18]. RPA is a linear response theory, and is the small amplitude limit of the time-dependent LDA. It considers the one-particle one-hole interactions and is most suitable for a large number of active electrons. Our *ab initio* results for electronic excitations in alkali clusters will be presented in Chapter 3.

According to the simple Mie classical picture discussed above, the optical response spectrum of a cluster exhibits only one single sharp peak. But due to different damping mechanisms, a broad peak is observed in the experiment. For example, in the



Figure 1.6: Dependence of the collective electronic excitation energy on the cluster size in  $Na_N$  clusters. Energies derived from reflectivity change spectra (solid circles) and energies calculated via sum rule from experimental static polarizabilities (open circles) are compared with jellium calculations (crosses) [From Parks et al, Phys. Rev. Lett. 62, 2301 (1989)].

case of  $Na_8$ , the observed width of the plasmon peak is about 0.25 eV, as shown in Figure 1.4.

There are three different known mechanisms which give rise to a fragmentation of the plasmon, namely: fragmentation due to a static shape deformation, Landau damping, and the coupling of electronic excitations to the vibration modes.

The static fragmentation due to shape deformations, illustrated in Figure 1.7(a), occurs simply due to the fact that the cluster is asymmetric. For a cluster with a magic number of electrons, the shape is spherical in the jellium model. Non-magic clusters are likely to be prolate or even oblate ellipsoids in the jellium approximation in analogy to nuclei. According to the Mie theory, for a non-spherical geometry, a single resonance frequency will be split into two or three distinct peaks [25]. The oscillator strengths will also be divided into the corresponding parts. If the splitting is small and the levels are indistinguishable, the absorption will be observed as a single broad peak.

If there is a large density of electronic states near the highest occupied molecular orbital (HOMO) (close to the Fermi energy), damping can also be caused by particle-hole excitations which can build up a collective state. This will smear out the spectrum, as shown in Figure 1.7(b). This mechanism is called Landau damping [40]. Landau damping is not important for the small clusters since the energy levels are well separated in energy and particle-hole excitations unlikely. For large clusters, however, Landau damping is the major plasmon fragmentation mechanism, since the energy levels are very dense.

There is also damping due to the coupling of electronic excitations to vibration modes. This mechanism is very similar to the Frank-Condon effect in molecular physics. This effect is illustrated in Figure 1.7(c), where I plot the electronic levels



Figure 1.7: Damping mechanisms for collective electronic excitations. (a) Static fragmentation due to aspherical shape. (b) Landau damping. (c) Electron-vibration coupling.

as a function of the generalized coordinate. The lowest curve represents the ground state total energy  $E_{tot}$ , which can be obtained by LDA. The other curves are given by  $E_{tot} + \epsilon_{RPA}$ , where  $\epsilon_{RPA}$  is the electronic excitation energy. In the Frank-Condon model, the configuration coordinate remains unchanged during the transition, since the electronic excitation is much faster than the motion of the ions; we can speak of an adiabatic process. The probability density distribution of the nuclear coordinates due to the ionic zero point motion will spread the energies of the electronic excitations.

This latter mechanism can also give rise to thermal line broadening of the plasmon. As we discussed above, the vibrational zero point motion couples to the electronic excitations and hence broadens a given transition even at T = 0 K. At higher temperatures, the thermal energy can activate higher vibration modes, which increase the shape fluctuations of the cluster. This is the so-called thermal line broadening. The line width resulting from this mechanism has been estimated for the jellium model, and the temperature dependence of the broadening has been found to be proportional to  $\sqrt{T}$  [25], where T is the temperature of the cluster. At zero temperature, the linewidth will be due to zero-point motion only.

In Chapter 2, I will address these mechanisms again for the interpretation of the results for the equilibrium structure, collective electronic excitations, and their damping in  $Na_2$  and  $Na_8$ .

# **1.2 Carbon Clusters**

In the last years, carbon clusters have been investigated extensively both experimentally and theoretically, by chemists and physicists alike [8]. The importance of carbon clusters in chemistry is evident, since the whole organic chemistry is based on carbon compounds. A good understanding of carbon composites is a prerequisite for gaining insight into chemical reactions involving organic compounds. In physics, one of the original motivation for an investigation of carbon clusters is the still unanswered question regarding the absorption spectrum of the interstellar dust. An unexplained absorption line is believed to be caused by carbon and its clusters [50]. The study of carbon clusters and their interaction with other elements in the laboratory could provide us with a unique tool to gain further understanding of the universe.

One family of carbon clusters is represented by the fullerenes [41]. Fullerenes designate a group of carbon clusters with a hollow cage structure and only pentagons and hexagons on the surface. From Euler's rule for closed polyhedra (C - E + F=2,where C, E, and F are the number of corners, edges, and faces, respectively), one can deduce that the number of pentagons in any fullerene is 12. The best known member of this family, which has been identified so far, is the C<sub>60</sub> cluster [1], the so-called buckminsterfullerene. This name was inspired by the well known architect Buckminster Fuller, who designed geodesic dome structures.

The study of  $C_{60}$  clusters lead also to the discovery of a novel crystalline material fullerite [13], a crystal composed of  $C_{60}$  clusters. Fullerite is the third pure crystalline form of carbon, in addition to diamond and graphite.

One of the aims of this work is to study in detail the structural and electronic properties of the  $C_{60}$  cluster and the  $C_{60}$  solid. In the following sections I will review the basic properties of the  $C_{60}$  molecule and of fullerite; these concepts will be necessary for the discussion that follows in Chapters 4 and 5.

### **1.2.1** Synthesis of $C_{60}$ and the $C_{60}$ crystal

 $C_{60}$  was first synthesized using laser vaporization of graphite [1]. The experimental setup is shown in Figure 1.8. The method can be summarized as follows: graphite is

vaporized by a laser, the generated carbon plasma is carried to a nozzle by helium gas which provides the environment to cool the gas. The cooled carbon gas aggregates into clusters, which are ejected from the nozzle in a supersonic molecular beam. The molecular beam is analyzed using the time-of-flight mass spectrometer. The outstanding characteristic of the mass abundance spectrum, shown in Figure 1.9, was that a single cluster with 60 atoms was observed to be far more abundant than any other cluster size. The high stability of this cluster with 60 atoms has been postulated to result from a closed cage structure, shown in Figure 1.10. In the mass abundance spectrum, the  $C_{70}$  cluster turned out to be very abundant as well, hence probably more stable than the neighboring clusters.

The above graphite vaporization method produces only free  $C_{60}$  clusters which are hard to analyze in any detail. In 1990, however, a new method [13] was developed, which is able not only to produce  $C_{60}$  clusters in bulk quantities but can also produce the crystalline fullerite solid.

The experimental setup is depicted in Figure 1.11. Graphite rods are butted together and a high current passes through. Carbon vaporizes in the vicinity of the contact and in the helium gas the carbon plasma condenses into soot. The soot contains a large fraction of  $C_{60}$  clusters and also a sizable amount of  $C_{70}$  clusters. Since  $C_{60}$  and  $C_{70}$  can be dissolved in benzene, they can be separated from the soot.  $C_{60}$  can be separated from  $C_{70}$  by high-pressure liquid chromatography. Drying the solvent, one obtains the  $C_{60}$  fullerite crystal.

### **1.2.2** Structural properties of $C_{60}$ and the $C_{60}$ crystal

Since a single crystal consisting of pure  $C_{60}$  clusters can be produced, crystalgraphic techniques can be used to determine not only the lattice structure but also the struc-



Figure 1.8: Schematic diagram of the pulsed supersonic nozzle used to generate carbon cluster beams [From Kroto et al, Nature 318, 162 (1985)].



Figure 1.9: Experimental mass spectrum of carbon clusters. [From Kroto et al, Nature 318, 162 (1985)]



Figure 1.10: Structure of the  $C_{60}$  "buckyball" cluster.



Figure 1.11: Mass production technique for fullerite. [From Huffman, Physics Today, 44, 22 (1991)]

ture of the cluster itself. Based on X-ray diffraction data [13], fullerite has been shown to be a close-packed molecular solid with a face-centered cubic structure and with a nearest neighbor distance D = 10.04 Å. Raman and infrared (IR) spectroscopy data [42, 43] confirm that the "soccer ball" structure of C<sub>60</sub> is preserved in the solid.

The  $C_{60}$  cluster has an uncommon hollow cage structure, resembling a soccer ball, composed of 12 pentagons and 20 hexagons. It is a truncated icosahedron and hence has  $I_h$  symmetry. Nuclear-magnetic-resonance (NMR) experiments [44] show a single peak in the absorption spectrum at room temperature, which indicates that all the carbon atoms in the cluster are equivalent and that the clusters rotate in the lattice. C<sub>60</sub> is a low strain structure; it is nearly spherical, and all pentagons are separated by hexagons. Because of this geometry, carbon atoms have neither pure  $sp^2$  nor  $sp^3$  bonding, which are typical of graphite and diamond, respectively. In the hexagonal bonds the  $p_{\perp}$  electrons, which are locally perpendicular to the surface, form a resonant  $\pi$  bond, while in the pentagons, an anti-resonant  $\pi$  bond is formed. The result is that the bond length in the hexagons is shorter than that in the pentagons. The chemical bonds in the pentagons are called "single" bonds and those remaining in the hexagons "double" bonds. Extended-X-Ray-Absorption-Fine-Structure (EXAFS) data [42] indicate that the single bond length is 1.45 Å and the double bond length is 1.40 Å. The average carbon-carbon nearest-neighbour distance in C<sub>60</sub>  $d_{C-C} = 1.42$  Å, the same as in graphite. This bond length corresponds to a radius R = 3.55 Å of the C<sub>60</sub> fullerene cluster.

Because of the large lattice constant of the fullerite crystal, the closest distance between the two surfaces of adjacent clusters is d = 2.9 Å at zero pressure, somewhat smaller than the interlayer spacing in graphite, d = 3.35 Å. Due to this large equilibrium separation between C<sub>60</sub> clusters, their mutual interaction is mainly via Van der Waals forces, which are weak. However, the  $C_{60}$  cluster itself is a rigid object, due to the covalent bonding between the atoms. Pressure dependent X-ray diffraction data, obtained in a diamond-anvil cell, indicate a large change of the bulk modulus of fullerite as a function of pressure [45]. Speculations that the stiffness of fullerite might exceed that of diamond, the hardest material known, will be addressed in Chapter 4.

Perhaps the most exciting property of  $C_{60}$  fullerite is superconductivity which occurs when the crystal is doped. Following the discovery of superconductivity in  $K_3C_{60}$  with a critical temperature  $T_c = 18$  K [46], new compounds have been synthesized using a large variety of intercalants [47], yielding critical temperatures as high as 33 K in  $Cs_2RbC_{60}$  [48]. While  $T_c$  values of doped fullerite are still below those found in high- $T_c$  cuprate perovskite superconductors, intercalated fullerite shows superior material properties and hence bears a higher potential for applicability. The intercalation process and the rigid-band behavior of intercalated fullerite resembles in many ways the extensively studied graphite intercalation compounds. The crucial property of fullerite intercalation compounds  $A_xC_{60}$  is their stability against decomposition into the components in the standard state, i.e.  $C_{60}$ (solid) and A(solid). The formation enthalpy is of interest not only for the donor compounds mentioned above, but also for potential acceptor compounds. The stability of intercalated fullerite will be addressed in Section 4.2.

## **1.2.3** Electronic properties of $C_{60}$ and the $C_{60}$ crystal

In Figure 1.12, I show the energy spectrum of the  $C_{60}$  cluster. A large energy gap of 2.2 eV contributes to the extraordinary stability of the  $C_{60}$  cluster. The highest occupied molecular orbital (HOMO) is five fold degenerate and the lowest unoccupied molecular orbital (LUMO) is three fold degenerate. The levels near the Fermi level are



Figure 1.12: (a) Single-particle energy level spectrum of a  $C_{60}$  cluster, as obtained using the tight-binding Hamiltonian described in Section 2.3. The levels have been sorted by symmetry. (b) Expanded region of the energy level spectrum near the Fermi level. Allowed dipole transitions between states with gerade (g) and ungerade (u) parity are shown by arrows [From G. F.Bertsch, A. Bulgac, D. Tománek, and Y. Wang, Phys. Rev. Lett. 67, 2690 (1991)].

all formed by the  $\pi$  system of electrons. The electronic states of C<sub>60</sub> have a definite parity, and optical excitations follow dipole selection rules. As a consequence, the HOMO to LUMO dipole transition is parity forbidden.

An interesting feature of the energy level spectrum is that the levels can be grouped into rotational bands characterized by the angular momentum L. Due to the  $I_h$ symmetry of the cluster, the 2L + 1 fold degeneracy of energy levels in the rotational band with angular momentum L is broken. The representations of the  $I_h$  group give as possible degeneracies 1(a), 3(t), 4(g), and 5(h).

A recent photoemission experiment [49] shows that the spectrum of the  $C_{60}$  solid contains remarkably sharp lines, indicating a small band dispersion. This small band dispersion results from the large separation between the clusters. The energy bands are derived from the  $C_{60}$  orbitals. Their isolated molecular character is most pronounced for the deeply bound states. Solid  $C_{60}$  is a semiconductor with an indirect energy gap of 1.9 eV. The cubic symmetry of the crystal field splits the molecular orbitals of isolated  $C_{60}$ . For example, the  $h_u$  HOMO level is split into a three-fold and a doubly degenerate band.

Because of the three dimensional resonant  $\pi$  system of the C<sub>60</sub> cluster, which is very similar to that of conjugated polymers, a nonlinear behavior of the electromagnetic response is expected. This topic is the subject of Section 5.1.

### **1.2.4** Optical response of $C_{60}$ and the $C_{60}$ crystal

The interest in the optical response of  $C_{60}$  originates in certain unexplained features of the absorption and emission spectra of interstellar dust [50]. The spectrum can be used as a unique tool to identify the components of the interstellar matter, which have not been accounted for so far; this will greatly improve our knowledge of the



Figure 1.13: Optical response of the  $C_{60}$  cluster [From H. Ajie et al, J. Phys. Chem. 94, 8630 (1990)].

outer space.

After the hollow cage structures for  $C_{60}$  was proposed, many theoretical studies predicted the energy spectrum and optical response of  $C_{60}$ . The HOMO to LUMO dipole transition is forbidden by symmetry and the lowest dipole allowed transition is a HOMO to LUMO+1 excitation. This has been first suggested in a semiempirical CI calculation [51], which has shown that the first allowed transition occurs at 3.6 eV, with an oscillator strength of 0.08. This motivated the experimental work of Heath et al [52]. They found the lowest transition to occur at 3.22 eV with a much smaller oscillator strength 0.004, more than one order of magnitude smaller than the theoretical results. This discrepancy is one of the subjects of our study presented in Chapter 5.

 $C_{60}$  is a resonant  $\pi$  bonding system, in analogy to graphite. Each atom has three neighbouring atoms. In Figure 1.13, we show the low-frequency optical response of  $C_{60}$  in solution [53]. Several broad peaks have been observed in the energy region between 3-6 eV. In this energy region, the excitations involve mostly  $\pi$  electrons. I will discuss the optical spectrum in Section 5.2. There, I not only find a satisfactory explanation of the experimental results in the low energy region, but also predict an unusual high energy collective mode, due to the collective excitation of the valence electrons. This massively high-energy collective electronic excitation in a small covalently bonded cluster comes as a surprise.

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# Chapter 2

# **Computational Techniques**

In the past twenty years, the rapid development of computational facilities has provided us with the ability to predict the equilibrium structure and electronic properties of materials. Eventually it will be possible to design novel materials with the desired properties. This progress is made possible not only by the development of computer technology, but especially by new computational methods. Many computational techniques, such as Hartree-Fock configuration interaction (HF-CI), Local Density Approximation (LDA) [1], the Car-Parrinello method [2], the embeddedatom method [3], and the quantum Monte Carlo technique [4] have been developed and have the power to accurately predict structural, electronic, and other properties of clusters.

Ab initio HF-CI calculations with Gaussian orbitals (such as implemented in the GAUSSIAN code) have been used extensively, and have become a basic research tool in chemistry. Due to the large amount of computer resources required by *ab initio* calculations, many semi-empirical methods appropriate for different purposes have been developed in the meantime, such as CNDO (complete neglect of differential overlap), INDO (intermediate neglect of differential overlap), NDDO (neglect of diatomic differential overlap) and MNDO (minimum neglect of differential overlap). Today, these

names have become common jargon in the chemistry literature.

Physicists also developed many computational methods to obtain a clear physical picture of different phenomena. In this Chapter I will review the *ab initio* and other computational methods used in our calculations.

# 2.1 Density Functional Theory (DFT)

In 1964, Hohenberg and Kohn [5] showed that the total energy of a system in a nondegenerate ground state is a unique functional of the total charge density  $\rho(r)$ . This theorem forms the basis of the Density Functional Theory (DFT).

Moreover, from the point view of the variational principle, the correct charge density has been shown to minimize the total energy of the system in the ground state, i.e.,

$$E[\rho] = T[\rho] + \int d\vec{r} \ \rho(\vec{r}) V_{ext}(\vec{r}) + E_H[\rho] + E_{xc}[\rho] = min.$$
(2.1)

Here,  $T[\rho]$  stands for the kinetic energy functional,  $V_{ext}(\vec{r})$  stays for the external field (e.g., the Coulomb field of the ion cores).  $E_H[\rho]$  gives the Hartree energy, which is the electrostatic energy of the electrons, and  $E_{xc}[\rho]$  is the exchange and correlation energy functional.

Since especially the general form of  $E_{xc}[\rho]$  is unknown, Kohn and Sham proposed the Local Density Approximation (LDA) to DFT as a workable scheme to determine  $\rho$  and the total energy [1].

## 2.1.1 Local Density Approximation (LDA)

Starting from the variational principle of the DFT, given in Equation (2.1), Kohn and Sham [1] developed a set of self-consistent equations which use the concept of

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the quasiparticles in the spirit of mean field theory:

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}[\rho] + V_H[\rho] + V_{xc}[\rho]\right]\psi_i = \epsilon_i\psi_i , \qquad (2.2)$$

where the total charge density is given by

$$\rho(\vec{r}) = \sum_{i}^{occ} |\psi_i(\vec{r})|^2.$$
(2.3)

In the first Kohn-Sham Equation (2.2),

$$V_H(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$$
(2.4)

is the Hartree potential, and

$$V_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})}$$
(2.5)

is the exchange-correlation "potential". The Kohn-Sham equations are typically solved iteratively, until self-consistency is achieved. The total energy of the system is given by

$$E_{tot} = \sum_{i} \epsilon_{i} - \frac{1}{2} \int \frac{\rho(\vec{r})\rho(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r} d\vec{r'} + E_{xc}[\rho] - \int V_{xc}(\rho)\rho(\vec{r})d\vec{r} .$$
(2.6)

In the Local Density Approximation (LDA), the nonlocal functional  $E_{xc}[\rho]$  is replaced by a local function  $E_{xc}(\rho)$ , given by

$$E_{xc}[\rho] \approx \int \epsilon_{xc}(\rho(\vec{r}))\rho(\vec{r})d\vec{r} . \qquad (2.7)$$

The form of  $E_{xc}(\rho)$  is assumed to be universal, given by the homogeneous electron gas [6]. The local exchange-correlation potential is then given by

$$V_{xc}(\rho(\vec{r})) = \frac{d}{d\rho} (\epsilon_{xc}(\rho(\vec{r}))\rho(\vec{r})) . \qquad (2.8)$$

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Several parametrized forms of the exchange-correlation energy have been proposed [6]. A simple expression for the local exchange has been given by Slater [7] and the correlation energy, as parametrized by Ceperley and Alder [4, 8] based on a quantum Monte Carlo calculation, reads in atomic units

$$\epsilon_{exchange} = -\frac{0.916}{r_s} \tag{2.9}$$

and

$$\epsilon_{correlation} = \begin{cases} -0.2846/(1+1.0529r_s^{1/2}+0.3334r_s) & \text{for } r_s > 1\\ 0.0622 \ ln(r_s) - 0.096 + (0.004 \ ln(r_s) - 0.0232)r_s & \text{for } r_s < 1 \end{cases}$$
(2.10)

Here,  $r_s$  is the Wigner-Seitz radius given by

$$\frac{4\pi}{3}r_{\bullet}^{3} = \rho^{-1}.$$
 (2.11)

### 2.1.2 Norm conserving pseudopotentials

A sodium atom has eleven electrons, ten of them in the core. A full calculation of Na<sub>2</sub>, therefore, has to consider 22 electrons, and a calculation of Na<sub>8</sub> will deal with 88 electrons. This represents a very large configurational space. Moreover, the determination of multi-center integrals between the valence wave functions is difficult due to the many nodes in the core region, imposed by the orthogonality between the valence and the core wave functions.

It is well known that the localized core electrons do not contribute to bonding between the atoms in a cluster. Cohesion is mainly due to the valence electrons in the region of large valence wave function overlap, which is smooth outside the core region. It would appear as desirable to discuss cohesion in atomic clusters by smooth pseudo wave functions, the eigenstates of a conveniently defined atomic pseudopotential.

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The optimum pseudopotential yields wave functions which resemble the valence wave functions in the interesting region outside the core, and which are smooth and nodeless inside the core. A further requirement on the pseudo wave function is that it has the the same eigenvalue as the all-electron wave function. A pseudopotential is typically generated to describe best a specific electronic configuration of an atom. Transferability of a pseudopotential, i.e., its ability to describe different electronic configurations with adequate accuracy, is crucial when addressing inhomogeneous systems such as atomic clusters.

In this work, I use the so-called Hamann-Schlüter-Chiang (HSC) norm-conserving ab initio pseudopotential [9]. It satisfies the following four criteria:

(1) Eigenvalues associated with the all-electron and pseudo wave functions agree for a chosen "prototype" electronic configuration.

(2) All-electron and pseudo wave functions agree beyond a chosen core radius  $r_c$ .

(3) The integrated total charge between r = 0 and a given radius r for the allelectron and the pseudo wave functions agree for  $r > r_c$  for each valence state. This property is called norm conservation, and will guarantee that the electrostatic potential produced outside  $r_c$  is identical for the true and the pseudo charge distributions.

(4) The logarithmic spatial derivatives of the all-electron and the pseudo wave function and their first energy derivatives agree for  $r > r_c$ . This will make the scattering properties of the true ion cores to be reproduced by the pseudopotential with minimum error. Additional shifts of the eigenstates with respect to the atomic situation occur due to orbital hybridization mainly outside the core region, which is described correctly by the pseudopotential.

In this formalism the interaction between the valence electrons and the ion cores


Figure 2.1: The 3s, 3p and 3d pseudo wave functions and the corresponding allelectron wave functions of the sodium atom. Outside the core radius  $r_c$ , the pseudo wave functions and the all-electron wave functions are the same. Inside the core, the pseudo wave functions are nodeless and smooth. At  $r_c$ , the spatial derivative of the all-electron and the pseudo wave functions, as well as their first energy derivatives, agree with each other. The eigenvalues associated with the pseudo wave function agree with those of the all-electron wave function. The bottom panel shows the pseudopotentials for the s, p and d states. Inside the core radius, the pseudopotentials are finite, and at large radii, the pseudopotentials approach  $-e^2/r$ .

is represented by a pseudopotential. The pseudopotentials can also be angular momentum dependent, and this type of pseudopotentials are called "nonlocal pseudopotentials". The residual interaction between the electrons is described by the Hartree term plus a local density-dependent interaction which accounts for exchange and correlation effects. The latter are described using the parameterization of Ref. [8], which is based on electron-gas correlation energies calculated in Ref. [4]. The pseudo wave functions in a cluster are obtained using these potentials in the Kohn-Sham Equations (2.2). Then, the total energy of the atomic cluster is given by Eq. (2.6).

Figure 2.1 displays the radial part of the all-electron wave functions (from an allelectron LDA calculation) and the pseudo wave functions of the sodium atom, along with the nonlocal pseudopotentials. For r larger than the core radius  $r_c$ , both wave function are identical. For r smaller than  $r_c$ , the pseudo wave function is nodeless and smooth. The bottom panel of Figure 2.1 displays the pseudopotential. Inside the core radius  $r_c$ , the pseudopotential is finite and always less attractive than the full LDA potential. Far away from the core, the ionic pseudopotential takes on the  $-e^2/r$  form.

#### **2.2** Jellium model

As I mentioned in Chapter 1, the simplest theoretical approach to describe the electronic structure of a metallic cluster is the jellium model, which has been used in solid state physics and nuclear physics for a long time. The spherical jellium background model addresses the behavior of a free electron gas in a finite system. The basic assumption is that the ionic positions do not play an important role. In the jellium model, the positive ions are smeared out as a homogeneous jelly across a finite volume, and the electrons adjust to the confining potential [10].



Figure 2.2: Energy spectrum and self-consistent potential of the Na<sub>8</sub> cluster obtained from the spherical jellium model.

The experimentally observed mass abundancies associated with the shell structure of sodium clusters by Knight *et al.* [11] can be explained by the jellium model [10]. The jellium model is especially suitable for large clusters, for which the computations are beyond the capacity of quantum chemistry methods. In this case, the jellium model proved to be very powerful and has provided us with a good understanding of quantum finite size effects [10].

Conventionally, we take the density of the jellium background as the density  $\rho$  of the valence electrons in the corresponding bulk material. The radius R of the spherical jellium background, similar to the nuclear radius, is given by

$$R = r_s Z^{1/3} . (2.12)$$

Here,  $r_{\bullet}$  is the Wigner-Seitz radius of the bulk, given by Eq. (2.11), and Z is the total number of valence electrons in the cluster. In the case of neutral (monovalent) alkali metals, Z is equal to the number of atoms. A self-consistent solution of the Kohn-Sham equations yields the electronic structure of the cluster.

The first closed-shell configuration in  $Na_n$  clusters occurs for  $Na_2$ .  $Na_8$  has the second closed shell configuration, which also means that it is more stable than its neighbouring clusters. Since  $Na_8$  has a closed shell structure, we do not expect energy lowering upon symmetry reduction, due to Jahn-Teller effect. The cluster keeps spherical symmetry, so the spherical jellium model will be appropriate to use. In Figure 2.2, I show the self consistent potential and the energy spectrum of the  $Na_8$  cluster, based on the spherical jellium background model [12].

The self consistent potential is very similar to the Woods-Saxon potential of nuclei. The 1s and 1p levels are fully occupied. The first unoccupied level is the 1d state, separated from the 1p level by 1.52 eV. Clusters with fully occupied electron shells

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have a higher binding energy per atom than neighbouring clusters. They are relatively more stable and occur more abundantly in the mass spectra.

### 2.3 Tight-binding Hamiltonian

The jellium model is best applicable to alkali metal clusters, where the electrons are delocalized. This assumption does not apply in nonmetallic clusters. In this Section, I will discuss the tight-binding Hamiltonian, which is suitable for nonmetal clusters with strong covalent, directional bonds. The usage of this semiempirical Hamiltonian for carbon clusters is motivated by the fact that *ab initio* techniques become enormously cumbersome when applied to anything but very small systems, such as small molecules, or infinitely large crystals. It is far from trivial to apply *ab initio* methods to very large but finite systems, such as the carbon fullerenes, with an adequate accuracy.

In order to determine the single-particle wavefunctions and energy levels in  $C_{60}$ , I use a tight-binding model which has been recently developed [13] to study the relative stability of different carbon cluster structures. The tight-binding Hamiltonian, which considers only the *s* and *p* valence electrons of C, is given by

$$H = \sum_{\alpha,i} \epsilon_{\alpha} a^{\dagger}_{\alpha,i} a_{\alpha,i} + \sum_{\alpha,\beta,i,j} t_{\alpha\beta}(r_{ij}) a^{\dagger}_{\alpha,i} a_{\beta,j} .$$
(2.13)

Here, *i* labels the atomic sites and  $\alpha = s, p_x, p_y, p_z$  labels the atomic orbitals.  $\epsilon_{\alpha}$  is the orbital energy, and  $t_{\alpha\beta}$  are the hopping matrix elements between different sites. The parameters have been obtained from a global fit to Local Density Approximation (LDA) [1, 5] calculations of the electronic structure of C<sub>2</sub>, a graphite monolayer, and bulk diamond, for different nearest-neighbor distances [13], similar to what had been done previously to describe silicon clusters [14]. The diagonal elements of this

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Hamiltonian are the energy levels  $\epsilon_s = -7.3$  eV and  $\epsilon_p = 0.0$  eV. The off-diagonal matrix elements  $t_{\alpha\beta}(r)$  are assumed to have a distance dependence  $\sim r^{-2}$ . Their values for r = 1.546 Å, which is the equilibrium nearest-neighbor distance in diamond, are  $V_{ss\sigma} = -3.63$  eV,  $V_{sp\sigma} = 4.20$  eV,  $V_{pp\sigma} = 5.38$  eV, and  $V_{pp\pi} = -2.24$  eV in the Slater-Koster parametrization [15]. In this Hamiltonian, we consider those atoms as nearest neighbors which are closer than the cutoff distance  $r_c = 1.67$  Å. This is the average of the nearest- and second nearest-neighbor distances in bulk diamond, and hence near the minimum of the radial distribution function.

The total energy of a carbon cluster has been given as a sum of four terms,

$$E_{tot} = \sum_{\alpha} n_{\alpha} \epsilon_{\alpha} + \sum_{i < j} E_r(d_{ij}) + \sum_i \psi(Z_i) + U \sum_{i=1}^n (q_i - q_i^0)^2.$$
(2.14)

The first term in Eq. (2.14) is the one-electron energy of the cluster, obtained using the tight-binding Hamiltonian. The second term consists of pairwise repulsive energies  $E_r(d)$  arising from nuclear repulsion and the overlap of the ion cores.  $E_r$  is defined as the difference of the "exact" calculated *ab initio* binding energy and the tight-binding one-electron energy of C<sub>2</sub>. The third term represents corrections to the binding energy during the transition to higher (bulk-like) coordination numbers  $Z_i$ . The parameters in this term are chosen to reproduce binding energies of selected bulk-like structures. The final fourth term is an intra-atomic Coulomb repulsion arising from possible charge transfers between inequivalent sites. Zero point vibrational energies are neglected. A more detailed discussion of this Hamiltonian is given in Ref. [13].

The binding energy of a  $C_n$  cluster (with respect to isolated atoms) is then given by

$$E_{coh} = n \ E_{tot}(C \ atom) - E_{tot}(C_n). \tag{2.15}$$

This tight-binding energy formula contains the essential physics which governs bonding in carbon structures. It addresses directionality of bonding and the electronic shell structure. It is easily applicable to very large carbon clusters, which are inaccessible to *ab initio* techniques, at the expense of avoiding an explicit treatment of multicenter integrals which can be important in small structures. It is expected to give a reasonably accurate interpolation between the dimer and selected bulk structures [13].

In Chapters 4 and 5, I will use this Hamiltonian to study carbon clusters. This is done in two steps. First, the equilibrium geometry of the free  $C_{60}$  cluster and  $C_{60}$ under "hydrostatic pressure" is determined. Once the geometry is given, I address the nonlinear optical properties of the  $C_{60}$  clusters and collectivity of electronic excitations in this system.

#### 2.4 Random Phase Approximation (RPA)

In this Section I will outline our approach to study the optical response spectrum of clusters. This approach will be used in Chapters 3 and 5.

The single particle energy spectrum of a system is the basis for calculating its optical response to an external electromagnetic field. In the crudest approximation, the allowed excitations can be estimated as the energy differences in the single-particle spectrum, and their transition strength from the Fermi's golden rule, using the dipole matrix element between the initial state and the final state. In this approximation, the configuration of all but the one electron to be excited is frozen, and only this electron is allowed to change its quantum state. This is the so-called free response of a system, and only considers single-particle transitions.

This approximation completely ignores the important effect of collective dynamical screening of electronic excitations by the other electrons in the system. This collective

response modifies the transition energy, transition strength, hence the entire response function as compared to that obtained assuming free response. I will use the linear response theory to address the response of clusters to small perturbations.

In order to describe the dynamical response to external fields, I use the Random Phase Approximation (RPA) which has been developed by Bohm and Pines [16]. RPA is equivalent to the time-dependent Hartree-Fock theory in the limit of small amplitudes. It considers one particle-one hole interactions, and hence presents more realistic results than free response.

The independent-particle polarization propagator (particle-hole Green's function)  $\Pi^0$  defined as

$$\Pi^{0}(\vec{r},\vec{r},\omega) = \sum_{i}^{occ} \psi_{i}^{0*}(\vec{r}) \left(\frac{1}{H-\epsilon_{i}-w} + \frac{1}{H-\epsilon_{i}+w}\right) \psi_{i}^{0}(\vec{r},\omega) , \qquad (2.16)$$

where  $\psi^0$  is the independent-particle wave function,  $\epsilon_i$  is the single particle energy, and  $\omega$  is the energy of the photon ( $\hbar = 1$ ). The RPA polarization propagator is given by [12]

$$\Pi^{RPA}(\vec{r},\vec{r}\prime) = \Pi^{0}(\vec{r},\vec{r}\prime) + \int \int d\vec{r_{2}}d\vec{r_{3}}\Pi^{0}(\vec{r},\vec{r_{2}}) \frac{\delta V(\vec{r_{2}})}{\delta\rho(\vec{r_{3}})} \Pi^{RPA}(\vec{r_{3}},\vec{r}\prime) , \qquad (2.17)$$

where V is composed of a Coulomb and an exchange-correlation term, and it is given by a local potential, and  $\rho$  is the charge density.  $v = \delta V/\delta \rho$  is called the residual interaction. In matrix form, Equation (2.17) can be expressed as

$$\Pi^{RPA} = (1 + \Pi^0 \frac{\delta V}{\delta \rho})^{-1} \Pi^0.$$
(2.18)

The free response spectrum to an external potential  $V_{ext}$  is relative to the imaginary part of the free polarization propagator and is given by

$$S(V_{ext}, \omega) = \sum_{f} \langle i | V_{ext} | f \rangle^{2} \, \delta(\omega - E_{i} - E_{f}) \,.$$
(2.19)

The RPA response spectrum can be obtained using the imaginary part of the RPA polarization propagator from

$$S(V_{ext},\omega) = \frac{1}{\pi} \int d\vec{r} d\vec{r'} V_{ext}(\vec{r},\omega) V_{ext}(\vec{r'},\omega) \operatorname{Im}\Pi(\vec{r},\vec{r'},\omega).$$
(2.20)

 $S(V_{ext}, \omega)$  obeys the energy weighted sum rule [12]

$$\int S(\omega)\omega d\omega = \int d\vec{r} \frac{(\nabla V_{ext})^2}{2m_e} \rho_0 , \qquad (2.21)$$

where  $m_e$  stands for the electron mass and  $\rho_0$  stands for the ground state charge density.

In the case of an external electromagnetic dipole field with the electric field component aligned along the z axis,  $V_{ext} = -eEz$ . The sum rule for the dipole operator is the Thomas-Reiche-Kuhn (TRK) (or f-) sum rule [17],

$$\sum \langle i|z|f \rangle^2 \omega = N \frac{\hbar^2}{2m_e} , \qquad (2.22)$$

which relates the integrated oscillator strength to the number of active electrons.

The dynamic polarizability of the system is given by

$$\alpha(\omega) = -e^2 \int d\vec{r} d\vec{r'} \, z \Pi(\vec{r}, \vec{r'}, \omega) z' , \qquad (2.23)$$

which can be also applied to the static case  $\omega = 0$ .

If we assume that all the oscillator strength is collected in a single mode, namely the Mie plasmon, the f-sum rule can be used to relate the plasmon frequency  $\omega$  to the static polarizability  $\alpha$  by

$$\omega_p^2 = \frac{Ne^2}{m_e \alpha} . \tag{2.24}$$

The above equations give the RPA formulation in coordinate space. If the interaction is taken as a local function, the above outlined formulation is the best choice for calculating optical response. This is the case in the jellium model, where the single-particle spectrum and the exchange interaction is obtained using LDA [12].

In the case of non-local potentials, the AB matrix representation of RPA is more appropriate. In matrix RPA, the system response to perturbations is given by [18]

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} X \\ -Y \end{pmatrix}.$$
 (2.25)

A and B are (sub-) matrices, given by

$$A_{ph,p'h'} = (e_p - e_h)\delta_{p,p'}\delta_{h,h'} + v_{ph',hp'},$$
(2.26)

and

$$B_{ph,p'h'} = v_{pp',hh'} \quad . \tag{2.27}$$

The matrix elements  $v_{mi,nj}$  of the residual interaction v can be expressed as

$$v_{mi,jn} = \int \psi_m^*(\vec{r}) \psi_i^*(\vec{r'}) v(\vec{r},\vec{r'}) \psi_j(\vec{r'}) \psi_n(\vec{r'}) d\vec{r} d\vec{r'} , \qquad (2.28)$$

using the convention that m, n represent the unoccupied (particle) states and i, jthe occupied (hole) states.  $X_{ph}$  stands for particle-hole amplitudes and  $Y_{ph}$  for holeparticle amplitudes.

Eq. (2.25) is a nonhermitian eigenvalue equation, but it can be replaced by the following Hermitian problem:

$$\omega_{\alpha}^{2}u^{\alpha} = (A - B)^{1/2}(A + B)(A - B)^{1/2}u^{\alpha}$$
(2.29)

where  $u^{\alpha} \equiv X^{\alpha} + Y^{\alpha}$  is the eigenvector. In the case of local potentials,

$$v_{ph',hp'} = v_{pp',hh'} \tag{2.30}$$

and the equation can be expressed in terms of the single-particle energy matrix  $\epsilon_{ph,p'h'} = (e_p - e_h)\delta_{p,p'}\delta_{h,h'}$  as

$$\omega_{\alpha}^2 u^{\alpha} = \epsilon^{1/2} (\epsilon + 2v) \epsilon^{1/2} u^{\alpha}.$$
(2.31)

where the vector and matrix indices have been omitted for simplicity and  $u_{ph}^{\alpha}$  represents the amplitude of the particle-hole configuration  $|ph^{-1}\rangle$  in the collective mode  $\alpha$ .

Finally, the transition strength associated with an external field F(r) is given by

$$<\alpha|F|0>^{2} = \frac{|\sum_{ph} u_{ph}^{\alpha} < p|F|h>|^{2}}{\omega_{\alpha} \sum_{ph} |u_{ph}^{\alpha}|^{2}}.$$
(2.32)

Thus, the oscillator strength associated with the vibration is

$$\omega_{\alpha} < \alpha |F|0\rangle^{2} = \frac{|\sum_{ph} u_{ph}^{\alpha} < p|F|h\rangle|^{2}}{\sum_{ph} |u_{ph}^{\alpha}|^{2}}.$$
(2.33)

From this it may be seen that the total (or integrated) oscillator strength is the same as for the free response. In other words, the f-sum rule is automatically satisfied.

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# Chapter 3 Alkali Clusters

Alkali metal clusters are very interesting systems which bridge the gap between isolated atoms and bulk metals. The large degree of delocalization of valence electrons, characteristic of the simple metals, is an important property of these clusters. This delocalization shows up most dramatically in the appearance of magic numbers corresponding to shell orbitals encompassing the entire cluster [1, 2]. The electronic response of these systems is particularly interesting in that it shows one of the characteristics of a macroscopic plasmon, namely a large fraction of the oscillator strength concentrated in a narrow frequency range [3]. In the following, we will address this collective mode as the cluster plasmon mode [3]. In contrast to the prediction of the classical Mie theory as applied to metal spheres, this collective mode is typically 30% lower in frequency for small clusters, and does show a pronounced size dependence [4]. The results of this study will also be published elsewhere [5].

Of especial interest to us is the width of the collective excitation. The observed width of the plasmon peak is 0.11 eV in Na<sub>2</sub> [6] and 0.25 eV in Na<sub>8</sub> [7], much larger than the natural line width for the photoexcitation which is due to the life time of the excitation. In large clusters with a high density of states near the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO), particle-hole excitations

(Landau damping) and multiparticle-hole excitations will dominate the fragmentation of the plasmon [8, 9]. In the small clusters with  $n \leq 8 - 40$  atoms, however, Landau damping is considered to be negligible due to the low level density near the HOMO. As we will show below, the dominant plasmon damping mechanism in these systems results from the coupling of electronic excitations to cluster vibrations. The quantum motion of nuclei gives a broadening which is described more precisely as a distribution of states with a variable number of vibrational quanta excited together with the plasmon. An increased nuclear motion in the ground state has been estimated to account for a line broadening with increasing temperature [10, 11].

Because of the large number of vibrational modes and the small value of the vibrational energy, it hardly makes sense to study this effect by explicit calculation of the vibrational wave functions and the associated Franck-Condon factors for the transitions. Instead, we shall apply an approximation that directly gives the width of the strength distribution irrespective of the quantization of the vibrational final state.

We determine the ground state structural and electronic properties of small alkali clusters using the Local Density Approximation (LDA) [12]. Electronic excitations are calculated using the Random Phase Approximation (RPA) [13], using LDA singleparticle wave functions and energies. In this Chapter, we apply this formalism to  $Li_2$ ,  $Na_2$  and  $Li_8$ ,  $Na_8$  clusters. The complete spectroscopy of the dimers is well established [14]. Consequently, these systems are ideally suitable for testing the accuracy of our methods in the ground state, and the power of our predictions in the excited state. For the larger clusters, the scenario is not so clear, since even their exact ground state geometry is uncertain [15, 16, 17, 18]. We proceed as follows. We first demonstrate the precision of our method by calculating the ground state properties of the bulk metals and comparing them to experimental data. We do the same for the ground state of the addressed clusters. Next, we use the LDA-RPA to determine the excitation spectra. Finally, we determine the coupling of electronic excitations to cluster vibrations and compare the results with experiment.

#### 3.1 Equilibrium geometry of small alkali clusters

In our LDA calculations, we consider the valence electrons only, and describe the effect of the core electrons by *ab initio* norm-conserving nonlocal pseudopotentials. Our pseudopotentials have been generated using the Hamann-Schlüter-Chiang scheme [19]. The electronic configurations which we used to generate the pseudopotentials, Li  $2s^{0.8}2p^{0.1}$  [with the core radii  $r_c(2s) = 0.915$  Å and  $r_c(2p) = 0.788$  Å] and Na  $3s^{0.7}3p^{0.1}3d^{0.05}$  [ $r_c(3s) = 1.005$  Å,  $r_c(3p) = 1.323$  Å,  $r_c(3d) = 1.746$  Å], provide very good transferability especially towards the excited states. A partial core correction has been used in the LDA calculations [20]. We use the Ceperley-Alder parametrization of the exchange-correlation potential [21] in the Kohn-Sham equations.

In order to minimize the influence of a finite basis on our results, we decide to place our clusters on a face-centered cubic superlattice with a large lattice constant. This minimizes the volume associated with each cluster for a constant inter-cluster separation. Plane waves are the natural basis in this case which can be improved systematically. We find this approach more reliable for alkali clusters with delocalized electron states than an atom-centered Gaussian basis. Treatment of an isolated cluster in real space on a radial grid turns out numerically as involved as our approach. We used an energy cutoff in the Fourier expansion of the charge density  $E_{max} = 6.9$  Ry for the solid and  $E_{max} = 4.0$  Ry for the clusters. Symmetry has been used to reduce the computational effort. The lattice constant a = 15 Å for the superlattice guarantees negligible overlap between the clusters and hence vanishing crystal field splitting, as verified by comparing the band structure at different points in the Brillouin zone.

The calculated ground state properties of bulk Li are the lattice constant  $a_{LDA} =$  3.42 Å ( $a_{expt} = 3.49$  Å [22]), the bulk cohesive energy (with respect to an isolated spin-polarized atom)  $E_{LDA}^{coh} = 1.64$  eV ( $E_{expt}^{coh} = 1.63$  eV [22]), and the bulk modulus  $B_{LDA} = 0.112 \times 10^{11}$  Pa ( $B_{expt} = 0.116 \times 10^{11}$  Pa [22]). The corresponding values for Na are  $a_{LDA} = 4.04$ Å ( $a_{expt} = 4.23$ Å [22]),  $E_{LDA}^{coh} = 1.23$  eV ( $E_{expt}^{coh} = 1.11$  eV [22]), and  $B_{LDA} = 0.089 \times 10^{11}$  Pa ( $B_{expt} = 0.068 \times 10^{11}$  Pa [22]). As expected from converged LDA calculations, the bulk is somewhat overbound. The larger difference between the calculated and the observed bulk moduli is presumably due to the pseudopotential approximation which suppresses exchange and correlation between valence and core orbitals. This effect is expected to be much smaller in atomic clusters where long-range exchange and correlation is absent.

The smallest system we aim to describe are the dimers, the first closed-shell system within the spherical jellium background model. The large stability of alkali dimers is explained within the jellium model by a large separation between the fully occupied 1s state and the empty 1p state of the cluster. The dimer geometry deforms the charge density along the molecular axis, and splits the threefold degenerate 1p level into one  $\sigma$  and two  $\pi$  states. The dimer has only one nuclear degree of freedom, the dimer stretch mode, which simplifies the calculation of electron-vibration coupling significantly.

In Figure 3.1, we show the total energy of the system as a function of the interatomic distance. LDA results for dissociation energies, bond lengths and vibrational energies of  $Li_2$  and  $Na_2$ , shown in Table 3.1, are in striking agreement with the experimental values [14].



Figure 3.1: Franck-Condon broadening of the collective electronic excitations in (a) Na<sub>2</sub> and (b) Li<sub>2</sub>. The lowest levels are the LDA dissociation energies D(d) of the dimers as a function of the bond length d. The higher levels give the excitations energies, which are presented as  $D(d) + E_{RPA}(d)$  [From Y. Wang et al, (submitted for publication)].

System	$d_e(A)$		$D_e(eV)$		$\hbar\omega_e(\mathrm{meV})$	
	expt.ª	theory	expt. <sup>a</sup>	theory	expt.ª	theory
Li <sub>2</sub>	2.672	2.730	1.03	1.01	43.572	46.0
$Na_2$	3.078	3.032	0.72	0.91	19.742	20.0

Table 3.1: Ground state properties of sodium and lithium dimers: Equilibrium bond length  $d_e$ , dissociation energy  $D_e$ , and vibration frequency  $\omega_e$ .

See G. Herzberg, "Molecular Spectra and Molecular Structure. I Spectra of Diatomic Molecules", second edition, (D. Van Nostrand Company, Inc.), New York, 1950.

The next closed shell configuration in alkali clusters occurs for 8 atoms. The physics of these systems is much more complex due to their 18 nuclear degrees of freedom and many different isomers which lie close in energy. As mentioned before, not even the equilibrium geometry is well established [15, 16, 17, 18], although calculations [16, 17, 18] suggest the  $T_d$  symmetry for the ground state. Consequently, we base our calculations on this geometry. The LDA superlattice calculations are essentially the same as for the dimers, but we increase the fcc lattice constant to a =50 A in order to minimize the interaction between clusters. The latter was checked by observing the calculated band dispersion  $\Delta \epsilon$  across the Brillouin zone. Our value  $\Delta \epsilon \approx 0.01$  eV, gives an estimate for the upper bound of cluster-cluster interaction. We use again an energy cutoff of 4.0 Ry, corresponding to a plane wave basis with 4279 components. The equilibrium structure of these clusters in the  $T_d$  geometry is uniquely defined by the radial distance  $d_i$  of the "inner tetrahedron" atoms from the cluster center, and the corresponding distance  $d_o$  of the outer tetrahedron atoms. The calculated atomization energy per atom for the Na<sub>8</sub> cluster in equilibrium geometry with  $d_i = 2.11$  Å and  $d_o = 3.51$  Å is 0.77 eV, in reasonable agreement with the value of 0.86 eV, obtained in a previous LSDA calculation [15].

# **3.2** Collective electronic excitations (Mie plasmon) in small alkali clusters

Once the equilibrium geometries are known, we proceed to calculate the response to external electric fields. The static response is a ground state property of the system and can be obtained directly from LDA. We use the above described superlattice geometry<sup>1</sup> to determine the static dielectric response of these systems to a field which is parallel or perpendicular to the dimer axis. For an isolated Na atom we find  $\alpha_{LDA}(Na) = 22.0 \text{ Å}^3$ , in good agreement with the experimental value of  $\alpha_{expt}(Na) = 23.6 \text{ Å}^3$  [23]. The polarizability of a negatively charged sodium ion  $\alpha_{LDA}(Na^-)$  is 63.0 Å<sup>3</sup>, much larger than that of the atom, caused by the weak binding of the outermost electron. The polarizability of the Na<sub>2</sub> along the axis is  $\alpha_{LDA}^{\parallel}(Na_2) = 63.5 \text{ Å}^3$ , while the value perpendicular to the axis is  $\alpha_{LDA}(Na_2) = 22.1 \text{ Å}^3$ . The average over all directions of the polarizability gives  $\langle \alpha_{LDA}(Na_2) \rangle = \frac{1}{3} \sum_{i=1}^{3} \alpha_i = 35.9 \text{ Å}^3$ , which can be measured experimentally. This value agrees well with Local Spin Density Approximation (LSDA) calculations of Moullet *et al.* [18], who obtained  $\alpha^{\parallel}(Na_2) = 53 \text{ Å}^3$  and  $\alpha^{\perp}(Na_2) = 30 \text{ Å}^3$ , leading to  $\langle \alpha_{LDA}(Na_2) \rangle = 37.7 \text{ Å}^3$ .

Once the static dielectric response is established, we proceed to calculate the electronic excitation spectrum within the linear response framework. We use the RPA which is based on an electronic ground state described by LDA. RPA automatically satisfies energy-weighted sum rules, and has the correct physical limits, namely independent-particle transitions at high momentum transfer, where the interaction is weak, and strong collective excitations at low momentum transfer, where the in-

<sup>&</sup>lt;sup>1</sup>In a cluster superlattice, the external field is generally modified by the field of the induced dipoles on the other sites. Since our system has inversion symmetry, the corresponding correction vanishes exactly at each lattice point, and is very small over the cluster volume. The polarizabilities of atoms and dimers can then be obtained directly using second order perturbation theory.

teraction is strong. It is customary in condensed matter physics to implement RPA by choosing the potential field as the basic object of computation. In this case, the wave function enters indirectly via the dynamic polarizability. However, if only a few electron states participate in the excitation, the most efficient approach is to set up the RPA equations for the wave function directly [24]. We shall use this method in the present work.

We start with the single-electron wave functions  $\phi_i(\mathbf{r})$  and energies  $\epsilon_i$ , obtained from the LDA calculation. We shall need both occupied and unoccupied orbitals, from which we construct the particle-hole states. We designate the particle-hole state as  $|ij^{-1}\rangle$ , where *i* designates an unoccupied (particle) state and *j* an occupied (hole) state. The Hamiltonian matrix may be separated into a diagonal part that gives the energy of the particle-hole state, and an off-diagonal part that describes the coupling to other particle-hole excitations. The diagonal part includes the kinetic energy operator and the self-consistent Hartree and exchange-correlation field. We write this part of the Hamiltonian matrix as

$$\langle ij^{-1}|\epsilon|i'j'^{-1}\rangle = \delta_{ii'}\delta_{jj'}(\epsilon_i - \epsilon_j).$$
(3.1)

The residual interaction contributes matrix elements of the form

$$\langle ij^{-1}|v|i'j'^{-1}\rangle = \int d\mathbf{r} d\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}') v(\mathbf{r},\mathbf{r}') \phi_{i'}(\mathbf{r}) \phi_{j'}^*(\mathbf{r}'), \qquad (3.2)$$

where v includes the residual Coulomb interaction and exchange correlation. The RPA eigenvectors  $u^{\alpha}$  and their associated frequencies  $\omega_{\alpha}$  are given by the eigenvalue Equation (2.31).

Let us first discuss the application of the above formalism to the dimers,  $Li_2$  and  $Na_2$ . The results of our calculations for these systems, obtained using different approximations, are summarized in Figure 3.1 and Table 3.2.

Table 3.2: Collective electronic excitations in small sodium and lithium clusters. Our results for the plasmon frequency  $\hbar\omega_{Plasmon}$  and its width  $\Gamma$  are listed together with results based on spherical jellium [25],  $\hbar\omega_{JELLYRPA}$ , and results of the classical Mie theory,  $\hbar\omega_{Mie}$ .

System	$\hbar \omega_{Plasmon} (eV)$		$\Gamma$ (eV)		$\hbar \omega_{JELLYRPA}$ (eV)	$\hbar\omega_{Mie} (eV)$
	expt.	theory	expt.	theory	theory	theory
Li <sub>2</sub>		2.23		0.063	3.6	4.6
Na <sub>2</sub>	1.92ª	2.43	0.11ª	0.095	2.8	3.5
Li <sub>8</sub>					3.6	4.6
Na <sub>8</sub>	2.53 <sup>b</sup>	3.10	0.25 <sup>b</sup>	0.03	2.8	3.5

<sup>a</sup> See A. Herrmann et al, Chem. Phys. Lett. **52**, 418 (1977).

<sup>b</sup> See C. R. C. Wang et al, Chem. Phys. Lett. 166, 26 (1990).

In Figure 3.1, we plot the energy of the dimers for a given electronic configuration as a function of the bond length d. The lowest curve gives LDA results for the  ${}^{1}\Sigma_{g}^{+}$ ground state. The  ${}^{1}\Sigma_{u}^{+}$  curve is obtained by adding the RPA excitation energy to the energy of the  ${}^{1}\Sigma_{g}^{+}$  state. In the adiabatic approximation, we determine the transitions from the energy difference between the vibrational ground state and the excited state in the same geometry, as indicated by arrows in Figure 3.1. From Figure 3.1 we notice that the potential energy surface and equilibrium geometry of the excited state are different from those of the ground state. The equilibrium bond length  $d_{e,RPA}^{*}(Na_{2}) =$ 3.50 Å compares well with the experimental value  $d_{e,expt}^{*}(Na_{2}) = 3.63$  Å [14]. The corresponding value for Li<sub>2</sub> is  $d_{e,RPA}^{*}(Li_{2}) = 3.17$  Å, which again compares well with the observed value  $d_{e,expt}^{*}(Li_{2}) = 3.10$  Å [14]. Experimental data [14] indicate that the energy difference between the  ${}^{1}\Sigma_{g}^{+}$  ground state at  $d_{e}$  and the  ${}^{1}\Sigma_{u}^{+}$  excited state at  $d_{e}^{*}$ is 1.76 eV for Li<sub>2</sub> and 1.82 eV for Na<sub>2</sub>. These energies compare reasonably well with our LDA-RPA results of 2.20 eV for Li<sub>2</sub> and 2.33 eV for Na<sub>2</sub>. However, a comparison between calculated and observed adiabatic (vertical) excitation energies in Table 3.2 shows that the calculated plasmon energy is blue-shifted by 0.5 eV (see Figure 3.2) with respect to the observed value. This blue shift is characteristic of LDA-RPA calculations, and reflects the incorrect asymptotic behavior of the effective potential which is exponential decay instead of  $\frac{1}{r}$  potential [9].

As we will discuss below, the difference between the potential energy surfaces in the ground and the excited state is responsible for vibrational broadening of electronic excitations. Of particular importance in this respect is the shape of the excited potential energy surface. We find our calculated values for the vibrational frequencies in the  ${}^{1}\Sigma_{u}^{+}$  state  $\omega_{e}^{*}(\text{Li}_{2}) = 31.7$  meV and  $\omega_{e}^{*}(\text{Na}_{2}) = 17.8$  meV to compare very well with the experimental data [14]  $\omega_{e,expt}^{*}(\text{Li}_{2}) = 31.7$  meV and  $\omega_{e,expt}^{*}(\text{Na}_{2}) = 14.6$  meV.

As expected and discussed in the following, these results are superior to calculations for spherical jellium representing Na<sub>2</sub> and Li<sub>2</sub> clusters. Our corresponding LDA-RPA results, obtained using the JELLY-RPA program [25], are shown in Table 3.2. In the jellium model scenario, the *single-particle* ground state has a 1s character, and the lowest unoccupied states have 1p, 1d and the 2s character. The spherical potential clearly cannot describe the splitting of the first two excited states which is substantial in the dimers. Among the above jellium states, there is only one dipole-allowed transition from the ground state, namely the  $1s \rightarrow 1p$  transition. Other allowed transitions have a much larger excitation energy, and are essentially single-particle transitions. Our numerical results, shown in Table 3.2, yield values for the collective excitations in jellium which lie up to 60% above the LDA-RPA results for the realistic geometry, mainly due to the spherical approximation in the jellium model. Another important disadvantage of spherical jellium is that it cannot address vibrational damping of electronic excitations, which we shall discuss below.

Next, we turn to the  $Li_8$  and  $Na_8$  clusters. The results for the collective excitation



Figure 3.2: Calculated spectral function of Na<sub>2</sub> (in arbitrary units) and its broadening due to nuclear zero-point motion (dashed line), as compared to the observed photoionization spectrum of Ref. [6] (solid line). The width of the Gaussian envelop is 0.10 eV and the displayed theoretical data are red-shifted by 0.5 eV with respect to the calculated results [From Y. Wang et al, (submitted for publication)].

energies in these systems, obtained using different approximations, are summarized in Table 3.2. The LDA calculation for spherical jellium gives the occupied ground state levels at  $\epsilon(1s) = -4.46$  eV and  $\epsilon(1p) = -3.19$  eV. The lowest unoccupied states lie at  $\epsilon(1d) = -1.65$  eV and  $\epsilon(2s) = -1.15$  eV. The relatively large HOMO-LUMO gap of 1.54 eV contributes substantially to the stabilization of this magic cluster size. The LDA-RPA calculations for this system predicts a plasmon energy of  $\hbar \omega_{JELLYRPA} = 2.8$  eV.

Our LDA calculation for Na<sub>8</sub> in  $T_d$  geometry shows that the lowest nondegenerate unoccupied level, corresponding to the jellium 2s level, lies at  $\epsilon = -0.82$  eV and is lower in energy than the manifold of levels originating from the jellium 1*d* level. This manifold results from symmetry breaking of the fivefold degenerate 1*d* type level of the spherical jellium into a threefold degenerate level at  $\epsilon = -0.73$  eV (consisting of orbitals with xy, yz, zx character) and a doubly degenerate level at at  $\epsilon = -0.35$  eV (consisting of orbitals with  $2z^2 - x^2 - y^2, x^2 - y^2$  character).

The RPA spectrum of  $Na_8$  in the realistic geometry discussed above is given in Figure 3.3. The spectrum shows three distinct peaks, but is dominated by a single resonance at  $\hbar \omega_{Plasmon} = 3.1$  eV. This is in agreement with experimental results which show three distinctive resonance [7], but disagrees with previously calculated photoabsorption spectra which has five excitations [26]. The strong resonance exhausts 87.4% of the *f*-sum rule, which is indicative of its strong collective character. As in Na<sub>2</sub>, this value is blue-shifted with respect to the experimental value  $\hbar \omega_{Plasmon,expt} = 2.53$  eV [7].



Figure 3.3: Calculated oscillator strength distribution in the excitation spectrum of Na<sub>8</sub> [From Y. Wang et al, (submitted for publication)].

### **3.3** Damping of the Mie plasmon in small alkali clusters

Our above results indicate that the present scheme is able to determine collective electronic excitations reasonably well, especially when compared to the jellium model. We now turn to the fragmentation of this collective mode. Due to the low level density near the HOMO, Landau damping is improbable in these systems [9]. The dominant broadening mechanism at T = 0 K is the coupling of the electronic excitations to nuclear zero-point motion, as described by the Franck-Condon effect. With increasing temperature, higher vibration modes and possibly transformations between different isomers are likely to further broaden the plasmon linewidth. This thermal broadening mechanism is expected to play a more pronounced role in the larger n = 8 atom clusters with soft vibrational modes.

A Hamiltonian which describes the coupling between the electronic excited state  $\epsilon_c$  and the vibrational normal modes  $\mu$  with energy  $\hbar \omega_{\mu}$  is [27]

$$H = c^{\dagger}c\left(\epsilon_{c} + \sum_{\mu} M_{\mu}(a^{\dagger}_{\mu} + a_{\mu})\right) + \sum_{\mu} \hbar\omega_{\mu}a^{\dagger}_{\mu}a_{\mu}.$$
(3.3)

Here,  $c^{\dagger}$  and  $a^{\dagger}$  are the creation operators for electronic and vibrational states, respectively. In the case of dimers, Eq.(3.3) is simplified due to the presence of a single ground state vibration mode with energy  $\hbar\omega_0$ . The coupling of electrons to nuclear motion is described by the term  $M(a^{\dagger}+a) \equiv Fx$ , where F is the slope of the potential energy surface for the excited state at the transition point. As a result, the exact solution for the spectral density distribution  $A(\hbar\omega)$  at zero temperature is given by the Poisson distribution [27]

$$A(\hbar\omega) = 2\pi e^{-g} \sum_{n=0}^{\infty} \frac{g^n}{n!} \delta(\hbar\omega - \epsilon_c + g\hbar\omega_0 - \hbar\omega_1 n), \qquad (3.4)$$

where  $\omega_1$  is the vibrational frequency of the excited state. In this equation, g is related to the slope F and the ground state vibration energy  $\hbar\omega_0$  by  $g = F^2/(2m\hbar\omega_0^3)$ , and n gives the corresponding quantum level.  $A(\hbar\omega)$  is hence a sum of equally spaced delta functions (as shown in Figure 3.2), with separation energy  $\hbar\omega_0$  and a Poisson peak height distribution. In the limit of large g, the Poisson distribution can be approximated by a Gaussian distribution, as

$$A(\hbar\omega) = \sum_{n=0}^{\infty} \frac{1}{\sqrt{2\pi n}} e^{-\frac{(n-g)^2}{2n}} \delta(\hbar\omega - \epsilon_c + g\hbar\omega_0 - \hbar\omega_1 n).$$
(3.5)

The resulting line shape has a full-width at half maximum (FWHM)  $\Gamma$ , which is given by

$$\Gamma = 2F\sqrt{\frac{\hbar\ln 2}{m\omega_0}} \tag{3.6}$$

for the vibrational ground state corresponding to T = 0 K. An intuitive way to understand this formula is the following. The probability distribution for a harmonic oscillator in the ground state is a Gaussian with a width  $(\Delta x)^2 = \hbar/(m\omega_0)$ . Assuming that the dependency of the excitation energy on x is given by  $\Delta E = F\Delta x$ , one obtains for the distribution of excitation energies  $f(E) = \exp\{-m\omega_0(E - E_0)^2/(\hbar F^2)\}$ . This is essentially the same result as in Eq. (3.6).

Our results for the plasmon damping in Na<sub>2</sub> and Li<sub>2</sub> are summarized in Table 3.2 and Figure 3.2. For Li<sub>2</sub>, no such experimental data are available to the best of our knowledge. For Na<sub>2</sub>, we obtain for the  ${}^{1}\Sigma_{g}^{+} \rightarrow {}^{1}\Sigma_{u}^{+}$  transition a FWHM of 0.10 eV, in very good agreement with the experimental value  $\Gamma = 0.11$  eV [6]. The perfect agreement of the envelope functions in Figure 3.2 indicates that in this case, the coupling between electronic and vibrational degrees of freedom dominates the plasmon fragmentation. For the  ${}^{1}\Sigma_{g}^{+} \rightarrow {}^{1}\Pi_{u}$  transition, we predict a line width of 0.06 eV. No experimental data for the line width are presently available for this transition.

Investigations of the vibrational broadening of collective electronic excitations are in progress for Li<sub>8</sub> and Na<sub>8</sub>. The calculation is more complex not only due to the larger cluster size, but also due to the significantly larger number of nuclear degrees of freedom in these systems. In order to obtain a rough estimate of the plasmon line broadening in these systems, we proceed as follows. We assume that the broadening is dominated by a single low-frequency mode with a large quadrupolar component. We restrict our calculations of the clusters with assumed  $T_d$  geometry to the lowest vibration mode with  $D_{2d}$  symmetry, which is obtained using the parametrized Many-Body Alloy Hamiltonian [28]. The LDA-RPA calculation for this distortion indicates only a very small line broadening in Na<sub>8</sub> of  $\Gamma \approx 0.03$  eV, much smaller than the observed value  $\Gamma_{expt} = 0.25$  eV [7]. The discrepancy between the calculated and the observed value may be due to our neglect of the other vibrational degrees of freedom, or a large temperature of the observed clusters. For a thermally excited cluster,  $\Gamma$ can be estimated in analogy to Ref. [11] as  $\Gamma = 2F\{(k_BT\ln 2)/(m\omega_0^2)\}^{1/2}$ . Using this expression, and relying on the validity of the harmonic approximation, we find a line broadening of 0.25 eV to correspond to a temperature  $T \approx 4000$  K for the vibrational mode above. Even though this temperature is likely to be overestimated by the harmonic approximation, our result suggests that other vibrational modes contribute significantly to the line broadening. Moreover, substantial line broadening could result from structural transitions between different isomers of the n = 8 atom structures which are very close in energy [15, 16, 17, 18].

#### **3.4 Conclusions**

In conclusion, I have presented results for the equilibrium structure and collective electronic excitations and their damping in small  $Na_n$  and  $Li_n$  clusters. In the calcu-

lations, we have used the Local Density Approximation to describe the ground state properties of these systems, and the Random Phase Approximation for the electronic excitations. We have discussed the collective excitations in the first two closed-shell clusters with n = 2, 8 atoms in detail. Our results indicate that the coupling of electronic levels to vibrational degrees of freedom accounts quantitatively for the observed width of the collective electronic excitations in alkali dimers. More calculations are necessary to address the damping mechanism of the collective electronic excitations in Li<sub>8</sub> and Na<sub>8</sub>.

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### Chapter 4

# Structural Properties of $C_{60}$ and Solid $C_{60}$

The carbon atom has two 2s electrons and two 2p electrons in the valence shell. These four valence electrons can hybridize in various ways, leading to sp,  $sp^2$  and  $sp^3$  bonding in carbon. Carbon crystallines either in the layered graphite structure with  $sp^2$  bonding, or in the diamond structure with  $sp^3$  bonding, the hardest material in nature. Recently [1], a third form of solid carbon has been synthesized: fullerite, a crystal based on the C<sub>60</sub> clusters.

In this Chapter, I will investigate the structural properties of the  $C_{60}$  crystal and the stability of fullerite intercalation compounds. The results pertinent to the elastic behaviors of solid  $C_{60}$  have been published in the meantime as Ref. [2] and those related to  $C_{60}$  intercalation compounds as Ref. [3].

## 4.1 Structural and elastic properties of the $C_{60}$ based solid

When crystallized,  $C_{60}$  clusters [4] form a solid with a face-centered cubic structure which has been given the name "fullerite" [1]. In spite of the considerable effort
invested in understanding the equilibrium properties of  $C_{60}$  clusters [5, 6, 7, 8], many questions regarding the material properties of fullerite remain open. So far, based on X-ray diffraction data [1], fullerite has been shown to be a close-packed molecular solid with a face-centered cubic structure and a nearest distance between neighboring  $C_{60}$ clusters D = 10.04 Å. Extended-X-Ray-Absorption-Fine-Structure (EXAFS) data [9] indicate an average carbon-carbon nearest-neighbour distance  $d_{C-C} = 1.42$  Å which is the same as in graphite. This bond length corresponds to a radius R = 3.55 Å of the fullerene cluster. In other words, the closest distance between two surfaces of adjacent clusters is d = 2.9 Å at zero pressure. Raman and infrared (IR) spectroscopy data [9, 10, 11, 12] confirm that the "soccer ball" structure of  $C_{60}$  is preserved in the solid. Pressure dependent X-ray diffraction data, obtained in a diamond anvil cell, indicate a large change of the bulk modulus of fullerite as a function of pressure [13].

In this Section, I will address the static and elastic properties of fullerite as a function of pressure. I will present a physical model, based on first principles calculations, for the cohesion of the solid. In this investigation, I will focus on the interesting question, whether fullerite can become less compressible than diamond.

When fullerite is compressed, part of the volume reduction comes from squeezing the clusters closer together, and part from the compression of the clusters themselves. Our model exploits this distinction to make a tractable calculation without the fullscale apparatus of the Local Density Approximation (LDA) theory [14]. While the LDA is computationally feasible with present computers [5], it does not provide the insight possible with a simplified treatment. Also, the LDA does not have any fundamental significance for purely Van der Waals forces which dominate the interaction at separations between the  $C_{60}$  clusters which are much larger than their equilibrium distance. A schematic picture of the model is shown in Figure 4.1. Effectively, there

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are two spring constants,  $c_1$  associated with the interaction between clusters and  $c_2$  associated with the compression of the clusters themselves.

Under external pressure, we expect  $C_{60}$  clusters not to deviate much from a spherical shape due to the close-packed structure of the crystal with twelve-fold coordination of the lattice sites. Also, the symmetry of the lattice is incompatible with the icosahedral symmetry of  $C_{60}$ , which would make distortions towards a cubooctahedral shape difficult. This is supported by the low activation energy of only  $\approx 0.15$  eV (per cluster) for molecular rotation [15]. We shall therefore treat the clusters in the spherical approximation.

The C<sub>60</sub> surface is similar to a curved piece of graphite, with predominantly  $sp^2$ bonding and a nearest neighbor distance of  $d_{C-C} = 1.42$  Å. Owing to the large equilibrium separation of d = 2.9Å between C<sub>60</sub> clusters, their mutual interaction is mainly due to a Van der Waals force which should be very similar to the interaction between layers of graphite. We shall base this part of our model on the LDA results for interactions between graphite layers [16]. Our expectation, confirmed by the analysis, is that the individual clusters are highly incompressible compared to the interaction between clusters. Thus, for low pressures at least, there is a close relationship between the compressibility of fullerite and the *c*-axis compressibility of graphite.

We shall model the Van der Waals interaction assuming that atoms in the neighboring graphite layers interact pairwise [17], as

$$E = \sum_{i} \sum_{j} U(r_{ij}) . \tag{4.1}$$

The pair interaction is constructed to reproduce the *ab initio* LDA calculations for the binding energy of graphite [16]. We use a modified Morse potential of the



Figure 4.1: Schematic drawing of the the elastic parameters describing the interaction between neighboring  $C_{60}$  clusters in fullerite. The weak Van der Waals bond between these clusters can be mapped onto an anharmonic soft spring (spring constant  $c_1$ ). The compressibility of the stiff  $C_{60}$  fullerene cluster itself can be described by a stiff anharmonic spring (spring constant  $c_2$ ) [From Y. Wang, D. Tománek, and G. F. Bertsch, Phys. Rev. **BR 44**, 6562 (1991)].

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$$U(r) = D_e[(1 - e^{-\beta(r - r_e)})^2 - 1] + E_r e^{-\beta' r}.$$
(4.2)

Here, i, j denote atoms in adjacent graphite layers,  $D_e$  is the equilibrium binding energy of these atoms,  $r_e$  is the equilibrium distance between these atoms, and  $E_r$  describes an additional hard-core repulsion.  $\beta$  and  $\beta'$  describe the distance dependence of these interactions. The binding energy of graphite as a function of the interlayer distance d, obtained using Eqs. (4.1) and (4.2), is shown in Figure 4.2(a) together with the LDA data. The corresponding interlayer force is shown in Figure 4.2(b). The parameters used in Eq. (4.2) are listed below<sup>1</sup>.

Since the Van der Waals interaction is long-ranged, it is convenient to replace the double sum in Eq. (4.1) by a double integral which averages over the atomic sites. The interatomic binding energy U is then replaced by the energy  $\tilde{U}$  corresponding to the interaction energy between two small areas  $\Delta A$  in adjacent graphite layers. Then,

$$E = \int_{A_1} d\mathbf{r_1} \int_{A_2} d\mathbf{r_2} \tilde{U}(|\mathbf{r_1} - \mathbf{r_2}|) , \qquad (4.3)$$

$$\tilde{U}(r) = \tilde{D}_{e}[(1 - e^{-\beta(r-r_{e})})^{2} - 1] + \tilde{E}_{r}e^{-\beta' r} . \qquad (4.4)$$

We use Eqs. (4.3) and (4.4) to determine the interaction energy  $E_{VdW}$  between neighboring C<sub>60</sub> clusters and note that the double integral extends over the surface areas of both clusters. In case that the direct line connecting the area elements at  $\mathbf{r_1}$  and  $\mathbf{r_2}$  contains a part of any cluster, we neglect the corresponding contribution to the double integral due to screening. The resulting pairwise interaction energy

<sup>&</sup>lt;sup>1</sup>In Eq. (4.2), we use  $D_e = 6.50 \times 10^{-3}$  eV,  $r_e = 4.05$  Å,  $E_r = 6.94 \times 10^{-3}$  eV,  $\beta = 1.00$  Å<sup>-1</sup> and  $\beta' = 4.0$  Å<sup>-1</sup>. In Eq. (4.4), we use  $\tilde{D}_e = 9.47 \times 10^{-4}$  eVÅ<sup>-4</sup> and  $E_r = 9.915 \times 10^{-4}$  eVÅ<sup>-4</sup>. The parameters in Eqs. (4.2) and (4.4) are related by the fact that the area per C atom in graphite is 2.619 Å<sup>2</sup>.



Figure 4.2: (a) Binding energy of hexagonal graphite (with respect to isolated layers, per carbon atom) as a function of the interlayer spacing d. The solid line represents a modified Morse fit [Eqs. (4.1) and (4.2)] to ab initio LDA results of Overney et al, J. Phys. C 4, 4233 (1992). (b) Negative gradient of the energy given in (a), corresponding to the interlayer force [From Y. Wang, D. Tománek, and G. F. Bertsch, Phys. Rev. BR 44, 6562 (1991)].

between neighboring clusters is shown in Figure 4.3(a). The corresponding force, given in Figure 4.3(b), indicates that at zero pressure, the distance of closest approach between neighboring C<sub>60</sub> clusters is d = 2.65 Å.

We calculate the binding energy  $E_{60}$  of an isolated  $C_{60}$  cluster using a modified tight-binding Hamiltonian [18], which had been tested successfully in previous studies of the equilibrium structure and vibration modes of small Si<sub>n</sub> clusters [19]. The breathing mode of the  $C_{60}$  cluster is described by the dependence of the binding energy on the cluster radius R, as shown in Figure 4.3(c). The restoring force, shown in Figure 4.3(d), is zero at the equilibrium radius  $R_{eq} = 3.25$  Å.

With all force constants at hand, we can now proceed to calculate the equation of state of fullerite. The solid can now be viewed as an fcc lattice of fullerenes represented by mass points and connected with strongly anharmonic nearest neighbor springs, shown in Figure 4.1. In compressed fullerite, the equilibrium geometry minimizes the binding energy per  $C_{60}$  cluster in the fcc structure

$$E_{coh}(D) = 6E_{VdW}(d) + E_{60}(R)$$
(4.5)

with fixed D = d + 2R, corresponding to a unit cell volume  $V = D^3/\sqrt{2}$ . The first term in this equation correctly avoids double counting the nearest neighbor Van der Waals bonds, and the second term is the energy of an isolated C<sub>60</sub>. The binding energy of fullerite  $E_{coh}(V)$  is shown in Figure 4.4(a). At T = 0, one obtains the pressure from  $p = -dE_{coh}/dV$  and the bulk modulus from  $B = -V(\partial p/\partial V)$ .

In Figs. 4.4(b) and 4.4(c), we show the dependence of the cell volume and the bulk modulus on the external pressure. From these results it is obvious that the elastic behavior of fullerite resembles closely that of an inert gas solid. At very small pressures, the interactions between clusters are dominated by the compressible Van



Figure 4.3: (a) Interaction energy between two  $C_{60}$  fullerene clusters as a function of the closest approach distance d. (b) Negative gradient of the interaction energy in (a), corresponding to the pairwise force between neighboring  $C_{60}$  clusters. (c) Binding energy of an isolated  $C_{60}$  fullerene cluster as a function of the cluster radius R. (d) Negative gradient of the binding energy given in (c). Note the difference in scales between (b) and (d) [From Y. Wang, D. Tománek, and G. F. Bertsch, Phys. Rev. **BR 44**, 6562 (1991)].



Figure 4.4: (a) Binding energy of fcc-fullerite (per  $C_{60}$  cluster, with respect to isolated carbon atoms) as a function of cell volume V. (b) Pressure dependence of the equilibrium cell volume V of fullerite. (c) Pressure dependence of the bulk modulus B of fullerite (solid line), as compared to diamond (dashed line, from Yin et al, Phys. Rev. Lett. 50, 2006 (1983)) [From Y. Wang, D. Tománek, and G. F. Bertsch, Phys. Rev. BR 44, 6562 (1991)].

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der Waals bonds causing a very low bulk modulus  $B \approx 0.2$  Mbar. With increasing external pressure, the clusters themselves are compressed at a high cost in energy, causing a large increase in the bulk modulus. We found it instructive to compare the bulk modulus of fullerite at high pressures to diamond. The diamond data of Ref. [20], obtained using LDA calculations, are shown in Figure 4.4(c) by a dashed line. From our calculation, we conclude that the compressibility of fullerite exceeds that of diamond only at pressures exceeding  $\approx 70$  GPa.

As discussed earlier, fullerite can be viewed as an fcc solid consisting of heavy mass points representing  $C_{60}$  clusters, with nearest neighbor interactions. In Figure 4.5, we show the phonon band structure of this lattice. The relatively low vibration frequencies result from the heavy mass of the clusters and the weak Van der Waals interactions at p = 0.

It should be possible to turn fullerite locally into diamond under very large pressures. The mechanism is very similar to that discussed by Fahy et al. for the conversion of rhombohedral graphite with  $sp^2$  bonding to diamond with  $sp^3$  bonding [21]. This transition is initiated in graphite by a strong interlayer coupling occurring when inter- and intralayer carbon nearest-neighbor bonds are comparable. In fullerite, this transition should occur when the distance of closest approach between adjacent fullerene clusters d is close to 1.5 Å. This occurs at the upper end of the pressure scale in Figs. 4.3(b) and 4.3(c) and should be more easily achieved in fullerite than in graphite. Following this prediction, a transformation from fullerite to diamond has indeed been achieved experimentally [22].

In this study, we used Eqs. (4.3) and (4.4) to calculate the interaction between neighboring clusters which have been approximated by spherical shells. As mentioned earlier, the atomic granularity of the clusters is averaged out to a large degree. Based



Figure 4.5: Phonon dispersion relation  $\nu(\mathbf{k})$  of bulk fullerite with fcc structure [From Y. Wang, D. Tománek, and G. F. Bertsch, Phys. Rev. **BR** 44, 6562 (1991)].

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T. Ьy on our expression in Eqs. (4.1) and (4.2), we find a residual activation energy for cluster rotation of the order of 0.1 eV (per cluster), in fair agreement with experimental data [15].

# 4.2 Stability of donor and acceptor intercalated $C_{60}$ solid

Perhaps the most exciting property of  $C_{60}$  fullerite is superconductivity which occurs in the doped compound. Following the discovery of superconductivity in  $K_3C_{60}$  with a transition temperature  $T_c = 18$  K [23], new compounds have been synthesized using a variety of intercalants [24, 25, 26, 27, 28], yielding critical temperatures as high as 33 K in  $Cs_2RbC_{60}$  [29]. While  $T_c$  values of doped fullerite are still below those found in high- $T_c$  perovskite superconductors [30], intercalated fullerite shows superior materials properties and hence bears the higher potential for applicability. The intercalation process and the rigid-band behavior of intercalated fullerite resembles in many ways the extensively studied graphite intercalation compounds [31].

The crucial property of fullerite intercalation compounds  $A_xC_{60}$  is their stability against decomposition into the components in the standard state, i.e.  $C_{60}$ (solid) and A(solid). The formation enthalpy is of interest not only for the donor compounds mentioned above, but also for potential acceptor compounds. This quantity is hard to calculate, since cohesion in these ionic compounds is dominated by a large Madelung energy [32, 33]. Still, even a rough estimate of the formation enthalpies across the periodic table is useful when considering the synthesis of novel  $C_{60}$  based materials. The difficulty to obtain a reliable value for the formation enthalpy is best illustrated by the spread of *ab initio* values for the formation enthalpy of  $K_3C_{60}$  from K metal and bulk C<sub>60</sub>, ranging from  $\Delta H_f^0 = -1.7$  eV per K atom [34] to  $\Delta H_f^0 = -6.6$  eV [35]<sup>2</sup>, indicative of an extremely exothermic intercalation process.

We decompose the formation process of fullerite intercalation compounds into well-defined steps and estimate the energy involved in each step across the periodic table. These steps are combined into a thermodynamic Born-Haber cycle which determines the formation enthalpy. The prerequisite for this calculation is a detailed knowledge of the structure, lattice constant and compressibility. Since this information is not available for most of the systems discussed here, we calculate these properties, together with the phonon structure, for the compounds of interest first. This is interesting information on its own merit and will be presented together with the calculated formation energies.

## 4.2.1 Born–Haber cycle

The formation enthalpy  $\Delta H_f^0$  at T = 0 K of  $A_n C_{60}$  is defined by

$$nA(solid) + C_{60}(solid) \xrightarrow{n \Delta H_f^0} A_n C_{60}(solid)$$
. (4.6)

If  $\Delta H_f^0$  is negative, the compound  $A_n C_{60}$  is stable against decomposition into the pure components, namely the intercalant A in its solid form, A(solid), and pure fullerite,  $C_{60}(\text{solid})$ . We determine  $\Delta H_f^0$  by formally decomposing the formation process of a fullerite intercalation compound into several physically well defined steps and evaluating the energies involved in the individual steps. This procedure, known as the Born-Haber cycle, has been used to determine reaction enthalpies of complex multi-stage reactions. The cycle for the formation of the donor compound  $A_3C_{60}$  is illustrated in Figure 4.6(a).

<sup>&</sup>lt;sup>2</sup>The value quoted has been obtained using the experimental cohesive energy of metallic K,  $E_{coh}(K) = 0.934 \text{ eV}$ , and of fullerite,  $E_{coh}(C_{60}) = 1.6 \text{ eV}$ . The latter value is a theoretical result obtained in the same reference.



Figure 4.6: Born-Haber cycle used to predict the formation enthalpy  $\Delta H_f^0$  of (a) donor and (b) acceptor C<sub>60</sub> fullerite intercalation compounds [From Y. Wang, D. Tománek, G. F. Bertsch, and R. S. Ruoff, Phys. Rev. B (1993)].

The first step involves the separation of the reference system into individual A atoms and C<sub>60</sub> molecules, taking into account that 3 A atoms occur in the formula unit of the doped solid. The energy involved in this step is the cohesive energy of A,  $3E_{coh}(A)$ , and the binding energy of a C<sub>60</sub> molecule in C<sub>60</sub> (solid),  $E_{coh}(C_{60}$  solid). In the next step, we consider the ionization of the three A atoms and the charge transfer to the C<sub>60</sub> molecule. Here we have implied that C<sub>60</sub> can act as electron acceptor; the electron affinity of the C<sub>60</sub> molecule will be discussed later. This step requires the energy 3 I(A), I(A) being the the ionization energy of the A atom. The three electrons are transferred from the donor atoms to the C<sub>60</sub> molecule and release the energy  $A_{tot} = A(C_{60}) + A(C_{60}^{-}) + A(C_{60}^{-})$ , where A is the electron affinity. In the last step, the A<sup>+</sup> and  $C_{60}^{3-}$  ions are combined to form the solid, thereby releasing the formation energy  $E_{coh}(A_3^+C_{60}^{3-})$ . Hence, the total energy gain during the formation of the  $A_3^+C_{60}^{3-}$  system is

$$\Delta H_f^0 = 3E_{coh}(A) + E_{coh}(C_{60}) + 3I(A) - A(C_{60}) - A(C_{60}^-) - A(C_{60}^{--}) - E_{coh}(A_3^+ C_{60}^{3--}).$$

$$(4.7)$$

The relatively low ionization potential of  $C_{60}$  makes it a potential electron donor, raising the question about the stability of acceptor intercalated fullerite. The Born-Haber cycle for the formation of the acceptor compound  $A_3C_{60}$  is illustrated in Figure 4.6(b). It differs from the former one in the direction of charge transfer between the intercalant and the matrix. The electron affinity A(A) of the intercalant and the ionization potentials of multiply charged  $C_{60}$  clusters,  $I(C_{60}^{n+})$ , are required in this step. The formation energy of the compound from the ions,  $E_{coh}(A_3^-C_{60}^{3+})$ , is defined with respect to the appropriately charged ions, and is given by

$$\Delta H_f^0 = 3E_{coh}(A) + E_{coh}(C_{60}) - 3A(A) + I(C_{60}) + I(C_{60}^+) + I(C_{60}^{2+}) - E_{coh}(A_3^- C_{60}^{3+}).$$
(4.8)

When evaluating the formation enthalpy using the Born-Haber cycle, we approximated each step by the corresponding energy and hence have neglected the contributions of nonzero temperature and pressure to  $\Delta H_f^0$ , which we estimate to be of the order of  $\leq 0.1$  eV. Precise experimental data exist for the cohesive energies  $E_{coh}(A)$  [36], the ionization potentials I(A) and electron affinities A(A) across the periodic table [37, 38]. Unfortunately, no reliable experimental values exist for the binding energy of a C<sub>60</sub> molecule in single crystals of C<sub>60</sub>, and *ab initio* techniques tend to underestimate the weak Van der Waals binding between the C<sub>60</sub> clusters [5]. Therefore, we estimate this quantity in the close-packed fullerite lattice using a pair bond model as  $E_{coh}(C_{60}$  solid) =  $6D(C_{60} - C_{60})$ . The distance dependence of the pair potential  $D(C_{60} - C_{60})$  is given by the Morse form

$$D(r) = D_e \left( \left( 1 - e^{-\beta(r-r_e)} \right)^2 - 1 \right) , \qquad (4.9)$$

where  $D_e$  is the the dissociation energy of a pair of  $C_{60}$  molecules and  $r_e$  is their nearest-neighbor distance, and where  $\beta$  describes the distance dependence of the  $C_{60}-C_{60}$  interaction. We use  $r_e = 10.04$  Å [6],  $\beta = 0.866$  Å<sup>-1</sup>, and  $D_e = 0.8$  eV based on a combination of our previous calculation for the  $C_{60}$  solid [39] and experimental data [13]. Recent experimental data suggest a smaller value  $E_{coh}(C_{60} \text{ solid}) = 1.76$  eV (at T = 0 K) for polycrystalline  $C_{60}$  films [40]. As we will show later on, an accurate value of the cohesive energy is not crucial for the stability of the compounds since it is partly or mostly compensated in the formation of the compound with the same fcc crystal structure. It only has a small influence on the formation energy of the  $A_6C_{60}$ phase with a bcc structure, and a small inaccuracy in  $E_{coh}(C_{60} \text{ solid})$  will not reverse the conclusions we draw.

We use the experimental results for the electron affinity of neutral C<sub>60</sub>,  $A(C_{60}) = 2.74 \text{ eV}$  [41], and the ionization potential  $I(C_{60}) = 7.54 \pm 0.04 \text{ eV}$  [42]. We note

that the electron affinity of  $C_{60}$  is only slightly smaller than that of the electronegative elements in group 7A, which makes the  $C_{60}$  molecule a good electron acceptor. On the other hand, the ionization potential of the  $C_{60}$  molecule lies close to that of electropositive Mg, which makes the  $C_{60}$  molecule a good electron donor as well. When calculating the higher electron affinities and ionization potentials, we modify the above values by the electrostatic energy which occurs during the attachment or detachment of electrons from a charged sphere with the  $C_{60}$  molecule radius R = 3.5 Å. The calculated total ionization potentials and electron affinities are summarized in Tables 4.1 and 4.2. These estimates are in good general agreement with available experimental data of Refs. [43, 44, 45, 46]. In particular, there is experimental evidence for a linear dependence of the ionization potentials and electron affinities on the final state charge [47].

The formation energy  $E_{coh}(A_n^+C_{60}^{n-})$  of the intercalation compound from the ions depends strongly on the structure. Here, we consider the AC<sub>60</sub> and A<sub>3</sub>C<sub>60</sub> solid with the fcc structure, and the A<sub>6</sub>C<sub>60</sub> solid with the bcc structure [32].  $E_{coh}(A_n^+C_{60}^{n-})$  can be decomposed into three terms,

$$-E_{coh}(A_n^+C_{60}^{n-}) = E_{Madelung} + E_{BM} - \frac{Z}{2}D(C_{60}^{n-} - C_{60}^{n-}) .$$
(4.10)

The factor Z in the pair potential term denotes the coordination number of the  $C_{60}$  molecules, which is 12 in the close-packed fcc structure and 8 in the bcc structure.

The formation of intercalation compounds is driven by a large gain in Madelung energy. We consider a complete charge transfer between the intercalants and the  $C_{60}$ clusters, in agreement with *ab initio* results of Refs. [34, 35] for the alkali compounds. We express the Madelung energy per unit cell as

$$E_{Madelung} = -\alpha q^2/a . \tag{4.11}$$

Table 4.1: Total ionization energy  $I_{tot}$  corresponding to the process  $C_{60} \longrightarrow C_{60}^{n+} + n e^{-}$ .

Final state configuration	$C_{60}^+$	$C_{60}^{2+}$	$C_{60}^{3+}$	$C_{60}^{6+}$	$C_{60}^{12+}$
$I_{tot} (eV)^a$	7.54	19.20	34.96	106.98	362.07
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- The first line contains data used in our calculation.
- <sup>b</sup> Experimental value of Hertel et al, Phys. Rev. Lett. **68**, 784 (1992), based on photoionization.
- <sup>c</sup> Experimental value of Steger et al, Chem. Phys. Lett. (1992), based on photoionization.

Table 4.2: Total electron affinity  $A_{tot}$  corresponding to the process  $C_{60}+n e^- \longrightarrow C_{60}^{n-}$ .

Final state configuration	$C_{60}^{-}$	$C_{60}^{2-}$	$C_{60}^{3-}$	$C_{60}^{6-}$	$C_{60}^{12-}$
$A_{tot} (eV)$	2.74ª	3.42	1.09	-24.65	-173.06

\* Experimental value of S. H. Yang et al, Chem. Phys. Lett. 139, 233 (1987).

Structure	α
$A^+C_{60}^-$	3.4951
$A_3^+ C_{60}^{3-}$	22.1220
$A_6^+C_{60}^{6-}$	56.2670

Table 4.3: Madelung constants  $\alpha$  for the structures considered in this work.

Here, q is the charge on the intercalant and a is the lattice constant of the conventional cubic unit cell. The Madelung constants for the different structures have been evaluated using the Ewald method. Our values are in agreement with previous results [32, 33] and are listed in Table 4.3. Note that the Madelung constants for  $A_3C_{60}$ and  $A_6C_{60}$  are extremely large when compared to the  $AC_{60}$  compound. This fact is mainly due to the large number of neighboring counter-ions for each  $C_{60}$  cluster.

The gain in Madelung energy is only partly compensated by the (mainly) closedshell repulsion between the  $A^+$  and the  $C_{60}^{3-}$  ions in the lattice. An accurate knowledge of this repulsive interaction is necessary since it affects not only the cohesive energy, but also the equilibrium structure and compressibility of the bulk compounds. We model this closed-shell repulsion energy  $E_{BM}$  by pairwise Born-Mayer type repulsive potentials  $V_{ij}^{BM}(r)$  [48] as

$$E_{BM} = \sum_{i < j} V_{ij}^{BM}(r) .$$
 (4.12)

The pairwise potentials have been parametrized as [48]

$$V_{ij}^{BM}(r) = a_{ij} e^{-\frac{r}{\rho}} , \qquad (4.13)$$

where

$$a_{ij} = b\left(1 + \frac{z_i}{n_i} + \frac{z_j}{n_j}\right) e^{\frac{r_i + r_j}{\rho}}.$$
(4.14)

Here,  $z_i$  and  $z_j$  are the valences of the two interacting ions,  $n_i$  and  $n_j$  are the numbers of valence electrons in the outer shells of the ions, and  $r_i$  and  $r_j$  are the ionic radii. The valences have negative signs for electronegative ions. We use n = 8 for all simple ions except for Li where we use n = 2. We neglect the z/n term at the  $C_{60}$  sites due to the large number of valence electrons on the  $C_{60}$  molecule. We use  $\rho = 0.345$  Å for the characteristic length of the Born-Mayer repulsion across the whole periodic table [48]. For ion pairs containing a  $C_{60}$  molecule, corresponding to the index j in Eq. (4.14), we use  $r_j = r(C_{60})$  and express b as  $b = \tilde{b} \exp[-r(C_{60})/\rho]$ . We determine the value of b using the observed structural and elastic properties of  $K_3C_{60}$  [49] and find  $\tilde{b} = 1.76 \times 10^5$  eV. We find that this value of b fits the properties of  $Rb_3C_{60}$  [49, 50], and use it for all other intercalation compounds as well. In Eq. (4.12) we only consider repulsive interactions between the  $C_{60}$  sites and the neighboring intercalant ions. We find that the non-Coulombic (mainly closed-shell) repulsion between the intercalant ions can be neglected due to their small ionic radii and large separations. We estimate the repulsive energy between two intercalant sites using the Many Body Alloy Hamiltonian [51]. At the closest interionic distance, which is found in  $A_6C_{60}$ , the pair interaction energy is  $\approx 0.02$  eV and can be safely neglected when compared to the other energy terms. Of course, the interionic Coulomb repulsion is taken care of in the Madelung energy.

Finally, the intercalated solid is further stabilized by attractive interactions between neighboring  $C_{60}^{3-}$  clusters, stemming from weakly overlapping valence orbitals and Van der Waals interactions. Again, we decompose these interactions energies into pairwise energies. In the A<sub>3</sub>C<sub>60</sub> compound, the energy gain associated with attractive C<sub>60</sub>-C<sub>60</sub> interactions is 6  $D(C_{60}^{3-} - C_{60}^{3-})$ . As discussed, the Coulomb repulsion part of this pairwise interaction is taken care of in the Madelung energy. In this context, we note that the inhomogeneity in the induced charge on the surface of the  $C_{60}$  molecules does not change the crystal energy, since the corresponding interactions average to zero in the crystal. On the other hand, the extra charge on a  $C_{60}$ molecule, which itself has 240 valence electrons, has a negligible effect on the non-Coulombic part of the interaction between a pair of  $C_{60}$  molecules. Consequently,  $D(C_{60}^{3-} - C_{60}^{3-}) \approx D(C_{60} - C_{60})$ . This fact explains why  $\Delta H_f^0$  is not sensitive to  $D(C_{60} - C_{60})$ , as mentioned above. In the case of AC<sub>60</sub> and A<sub>3</sub>C<sub>60</sub>, the pristine and the intercalated solids have the same structure. Then, the contribution of Van der Waals interactions between C<sub>60</sub> molecules to  $\Delta H_f^0$  stemming from the first and the last step of the Born-Haber cycle will nearly cancel.

# 4.2.2 Structural and cohesive properties of fullerite intercalation compounds

The energies associated with the individual steps in the Born-Haber cycle depend sensitively on the equilibrium structure of the corresponding compounds. Especially, the large Madelung energies which stabilize the intercalated compounds are balanced by repulsive interactions which in turn are closely related to the elastic properties of the compounds. In order to calculate these energies with adequate precision, we found it necessary to obtain accurate estimates of the equilibrium lattice constants and bulk moduli for all compounds of interest.

Pristine fullerite is a face-centered cubic solid at room temperature, with  $C_{60}$  occupying the Bravais lattice sites. The conventional cubic unit cell has a large lattice constant a = 14.20 Å [6]. The lattice contains two types of interstitial sites, namely the smaller tetrahedral and the larger octahedral sites, which can be occupied by intercalants. There are two tetrahedral sites and one octahedral site per  $C_{60}$  in the lattice. Using  $r_C = 0.92$  Å for the atomic radius of carbon [36] and 3.5 Å for the

radius of the C<sub>60</sub> molecule, we find that the diameter of the larger octahedral cavity is  $\approx 5.4$  Å and that of the smaller tetrahedral cavity is  $\approx 3.5$  Å. These large sizes guarantee that especially the octahedral cavity can host any element in the periodic table. In the alkali intercalated (and superconducting) A<sub>3</sub>C<sub>60</sub> compound [32], which is the most stable phase for the alkali systems, all octahedral and tetrahedral sites are filled. We found it instructive to compare formation energies in this compound to the AC<sub>60</sub> phase with the NaCl structure, where the intercalants occupy only the octahedral sites. Upon prolonged exposure of fullerite to the intercalant metal vapor, a transition from the fcc A<sub>3</sub>C<sub>60</sub> phase to the saturated phase A<sub>6</sub>C<sub>60</sub> with the bodycentered cubic structure is observed [52]. In this case, each C<sub>60</sub> molecule is surrounded by 24 intercalant ions.

As in graphite intercalation compounds, the stability of each of these phases is determined by the energetics of electron transfer between the intercalant and the  $C_{60}$ . For a given element, this energetics is given by the relationship between the ionization potential and electron affinity of the intercalant atom and the  $C_{60}$  molecule, respectively. As we discussed in Section II,  $C_{60}$  can act both as electron donor and electron acceptor. Consequently, both acceptor and donor elements can in principle be intercalated in fullerite. We investigate donor intercalants from groups 1A and 2A and acceptor intercalants from groups 6A and 7A and summarize our results in Figures 4.7, 4.8, and 4.9.

We determine the equilibrium lattice constant a of the compound by maximizing the cohesive energy of the intercalated solid with respect to the isolated ions,  $E_{coh}(A_n^+C_{60}^{n-})$  (or the corresponding acceptor compound), using the expression in Eq. (4.10). The bulk modulus B is obtained from the second derivative of  $E_{coh}(a)$ with respect to a in the equilibrium geometry. The distance dependence of  $D(C_{60}-$ 

	$A^+C_{60}^-$	$A^{2+}C^{2-}_{60}$	$A^{2-}C^{2+}_{60}$	$A^{-}C_{60}^{+}$
	Li	Be	0	F
	a=14.14Å	a=13.97Å	a=14.00Å	a=14.16Å
	B=0.20MBar	B=0.27MBar	B=0.26MBar	B=0.20MBar
	$\Delta H_f^0 = 0.74 \mathrm{eV}$	$\Delta H_f^0 = 13.14 \mathrm{eV}$	$\Delta H_f^0 = 4.68 \mathrm{eV}$	$\Delta H_f^0 = 1.50 \mathrm{eV}$
	Na	Mg	S	Cl
	a=14.14Å	a=13.97Å	a=14.07Å	a=14.23Å
	B=0.20MBar	B=0.27MBar	B=0.26MBar	B=0.19MBar
	$\Delta H_f^0 = -0.02 \mathrm{eV}$	$\Delta H_f^0 = 6.48 \mathrm{eV}$	$\Delta H_f^0 = 3.95 \mathrm{eV}$	$\Delta H_f^0 = 2.04 \mathrm{eV}$
I	K	Ca	Se	Br
	1	•••		
	a=14.16Å	a=13.98Å	a=14.12Å	a=14.28Å
	a=14.16Å B=0.20MBar	a=13.98Å B=0.27MBar	a=14.12Å B=0.25MBar	a=14.28Å B=0.19MBar
	$a=14.16\text{\AA}$ $B=0.20\text{MBar}$ $\Delta H_{f}^{0}=-0.95\text{eV}$	$a = 13.98 \text{\AA}$ B = 0.27 MBar $\Delta H_j^0 = 2.14 \text{eV}$	$a = 14.12 \text{\AA}$ B=0.25MBar $\Delta H_{f}^{0} = 3.85 \text{eV}$	a=14.28Å B=0.19MBar $\Delta H_{f}^{0} = 2.23$ eV
	a=14.16Å B=0.20MBar $\Delta H_{f}^{0} = -0.95eV$ Rb	$a=13.98\text{\AA}$ $B=0.27\text{MBar}$ $\Delta H_f^0 = 2.14\text{eV}$ Sr	$a=14.12Å$ $B=0.25MBar$ $\Delta H_f^0 = 3.85eV$ Te	$a=14.28 \text{\AA}$ $B=0.19 \text{MBar}$ $\Delta H_f^0 = 2.23 \text{eV}$ $I$
	a=14.16Å B=0.20MBar $\Delta H_{f}^{0} = -0.95eV$ Rb a=14.17Å	a=13.98Å B=0.27MBar $\Delta H_{f}^{0}=2.14eV$ Sr a=13.98Å	a=14.12Å B=0.25MBar $\Delta H_{f}^{0}=3.85eV$ Te a=14.24Å	$a=14.28 \text{\AA}$ B=0.19 MBar $\Delta H_f^0 = 2.23 \text{eV}$ I $a=14.38 \text{\AA}$
	a=14.16Å B=0.20MBar $\Delta H_{f}^{0} = -0.95eV$ Rb a=14.17Å B=0.20MBar	a=13.98Å B=0.27MBar $\Delta H_f^0 = 2.14eV$ Sr a=13.98Å B=0.27MBar	a=14.12Å B=0.25MBar $\Delta H_f^0 = 3.85 \text{eV}$ Te a=14.24Å B=0.24MBar	a=14.28Å B=0.19MBar $\Delta H_{f}^{0} = 2.23eV$ I a=14.38Å B=0.18MBar
	a=14.16Å B=0.20MBar $\Delta H_{f}^{0} = -0.95 \text{eV}$ Rb a=14.17Å B=0.20MBar $\Delta H_{f}^{0} = -1.16 \text{eV}$	a=13.98Å B=0.27MBar $\Delta H_{f}^{0} = 2.14eV$ Sr a=13.98Å B=0.27MBar $\Delta H_{f}^{0} = 0.78eV$	a=14.12Å B=0.25MBar $\Delta H_{f}^{0} = 3.85 \text{eV}$ Te a=14.24Å B=0.24MBar $\Delta H_{f}^{0} = 4.09 \text{eV}$	a=14.28Å B=0.19MBar $\Delta H_{f}^{0} = 2.23 \text{eV}$ I a=14.38Å B=0.18MBar $\Delta H_{f}^{0} = 2.70 \text{eV}$
	a=14.16Å B=0.20MBar $\Delta H_{f}^{0} = -0.95 \text{eV}$ Rb a=14.17Å B=0.20MBar $\Delta H_{f}^{0} = -1.16 \text{eV}$ CS	a=13.98Å B=0.27MBar $\Delta H_{f}^{0} = 2.14eV$ Sr a=13.98Å B=0.27MBar $\Delta H_{f}^{0} = 0.78eV$ Ba	a=14.12Å B=0.25MBar $\Delta H_{f}^{0} = 3.85 \text{eV}$ Te a=14.24Å B=0.24MBar $\Delta H_{f}^{0} = 4.09 \text{eV}$	a=14.28Å B=0.19MBar $\Delta H_{f}^{0} = 2.23 \text{eV}$ I a=14.38Å B=0.18MBar $\Delta H_{f}^{0} = 2.70 \text{eV}$
	a=14.16Å B=0.20MBar $\Delta H_{f}^{0} = -0.95 \text{eV}$ Rb a=14.17Å B=0.20MBar $\Delta H_{f}^{0} = -1.16 \text{eV}$ CS a=14.20Å	a=13.98Å B=0.27MBar $\Delta H_f^0 = 2.14eV$ Sr a=13.98Å B=0.27MBar $\Delta H_f^0 = 0.78eV$ Ba a=14.00Å	a=14.12Å B=0.25MBar $\Delta H_{f}^{0} = 3.85 \text{eV}$ Te a=14.24Å B=0.24MBar $\Delta H_{f}^{0} = 4.09 \text{eV}$	a=14.28Å B=0.19MBar $\Delta H_{f}^{0} = 2.23 \text{eV}$ I a=14.38Å B=0.18MBar $\Delta H_{f}^{0} = 2.70 \text{eV}$
	a=14.16Å B=0.20MBar $\Delta H_{f}^{0} = -0.95 \text{eV}$ Rb a=14.17Å B=0.20MBar $\Delta H_{f}^{0} = -1.16 \text{eV}$ CS a=14.20Å B=0.20MBar	a=13.98Å B=0.27MBar $\Delta H_f^0 = 2.14eV$ Sr a=13.98Å B=0.27MBar $\Delta H_f^0 = 0.78eV$ Ba a=14.00Å B=0.26MBar	a=14.12Å B=0.25MBar $\Delta H_{f}^{0} = 3.85 \text{eV}$ Te a=14.24Å B=0.24MBar $\Delta H_{f}^{0} = 4.09 \text{eV}$	a=14.28Å B=0.19MBar $\Delta H_{f}^{0} = 2.23 \text{eV}$ I a=14.38Å B=0.18MBar $\Delta H_{f}^{0} = 2.70 \text{eV}$

Figure 4.7: Predicted equilibrium lattice constant a, bulk modulus B, and formation enthalpy  $\Delta H_f^0$  for C<sub>60</sub> fullerite intercalation compounds AC<sub>60</sub>(fcc structure). Results are presented for elements A from the 1A, 2A, 6A and 7A groups of the periodic table [From Y. Wang, D. Tománek, G. F. Bertsch, and R. S. Ruoff, Phys. Rev. B (1993)].

$A_3^+ C_{60}^{3-}$	$A_3^{2+}C_{60}^{6-}$	$A_3^{2-}C_{60}^{6+}$	$A_3^- C_{60}^{3+}$
Li	Be	0	F
a=13.95Å	<b>a=13.34Å</b>	<b>a=</b> 13.72Å	<b>a</b> =14.27Å
B=0.30MBar	B=0.74MBar	B=0.64MBar	B=0.26MBar
$\Delta H_f^0 = -0.78 \mathrm{eV}$	$\Delta H_f^0 = 8.10 \mathrm{eV}$	$\Delta H_f^0 = 5.63 \mathrm{eV}$	$\Delta H_f^0 = 2.13 \mathrm{eV}$
Na	Mg	S	Cl
a=14.01Å	a=13.38Å	a=14.34Å	<b>a=</b> 14.96Å
B=0.30MBar	B=0.72MBar	B=0.51MBar	B=0.19MBar
$\Delta H_f^0 = -1.45 \mathrm{eV}$	$\Delta H_f^0 = 1.55 \mathrm{eV}$	$\Delta H_f^0 = 6.48 \mathrm{eV}$	$\Delta H_f^0 = 3.29 \mathrm{eV}$
K	Ca	Se	Br
a=14.24Å	a=13.47Å	a=14.62Å	a=15.26Å
B=0.26MBar	B=0.70MBar	B=0.46MBar	B=0.16MBar
$\Delta H_f^0 = -2.09 \mathrm{eV}$	$\Delta H_f^0 = -2.49 \mathrm{eV}$	$\Delta H_f^0 = 6.94 \mathrm{eV}$	$\Delta H_f^0 = 3.67 \mathrm{eV}$
Rb	Sr	Te	I
a=14.41Å	a=13.54Å	a=15.15Å	a=15.80Å
B=0.24MBar	B=0.68MBar	B=0.39MBar	B=0.13MBar
$\Delta H_f^0 = -2.12 \mathrm{eV}$	$\Delta H_f^0 = -3.63 \mathrm{eV}$	$\Delta H_f^0 = 8.01 \mathrm{eV}$	$\Delta H_f^0 = 4.31 \mathrm{eV}$
Cs	Ba		
a=14.69Å	a=13.70Å		
B=0.21MBar	B=0.64MBar		
$\Delta H_f^0 = -2.10 \mathrm{eV}$	$\Delta H_f^0 = -4.41 \mathrm{eV}$		

Figure 4.8: Predicted equilibrium lattice constant a, bulk modulus B, and formation enthalpy  $\Delta H_f^0$  for C<sub>60</sub> fullerite intercalation compounds A<sub>3</sub>C<sub>60</sub>(fcc structure). Results are presented for elements A from the 1A, 2A, 6A and 7A groups of the periodic table [From Y. Wang, D. Tománek, G. F. Bertsch, and R. S. Ruoff, Phys. Rev. B (1993)].

		· · · · · · · · · · · · · · · · · · ·	
$A_6^+ C_{60}^{6-}$	$A_6^{2+}C_{60}^{12-}$	$A_6^{2-}C_{60}^{12+}$	$A_6^- C_{60}^{6+}$
Li	Be	0	F
a=10.92Å	a=10.11Å	<b>a=</b> 10.57Å	a=11.28Å
B=0.49MBar	B=1.86MBar	<b>B=</b> 1.60MBar	B=0.43MBar
$\Delta H_f^0 = -0.62 \mathrm{eV}$	$\Delta H_f^0 = 8.76 \mathrm{eV}$	$\Delta H_f^0 = 11.46 \mathrm{eV}$	$\Delta H_f^0 = 4.06 \mathrm{eV}$
Na	Mg	S	Cl
a=11.00Å	<b>a=10.16Å</b>	<b>a=</b> 11.16Å	a=11.91Å
B=0.48MBar	<b>B</b> ≔1.83MBar	B=1.34MBar	B=0.33MBar
$\Delta H_f^0 = -1.28 \mathrm{eV}$	$\Delta H_f^0 = 2.34 \mathrm{eV}$	$\Delta H_f^0 = 13.25 \mathrm{eV}$	$\Delta H_f^0 = 5.19 \mathrm{eV}$
K	Ca	Se	Br
a=11.26Å	a=10.28Å	a=11.40Å	<b>a=</b> 12.16Å
B=0.43MBar	B=1.76MBar	B=1.24MBar	B=0.30MBar
$\Delta H_f^0 = -1.87 \mathrm{eV}$	$\Delta H_f^0 = -1.36 \mathrm{eV}$	$\Delta H_f^0 = 13.98 \mathrm{eV}$	$\Delta H_f^0 = 5.54 \mathrm{eV}$
Rb	Sr	Te	Ι
a=11.43Å	a=10.37Å	a=11.83Å	a=12.56Å
B=0.40MBar	B=1.72MBar	B=1.10MBar	B=0.26MBar
$\Delta H_f^0 = -1.89 \mathrm{eV}$	$\Delta H_f^0 = -2.29 \mathrm{eV}$	$\Delta H_f^0 = 15.48 \mathrm{eV}$	$\Delta H_f^0 = 6.15 \mathrm{eV}$
Cs	Ba		
a=11.69Å	a=10.56Å		
B=0.36MBar	B=1.61MBar		
$\Delta H_f^0 = -1.88 \mathrm{eV}$	$\Delta H_f^0 = -2.66 \mathrm{eV}$		

Figure 4.9: Predicted equilibrium lattice constant a, bulk modulus B, and formation enthalpy  $\Delta H_f^0$  for C<sub>60</sub> fullerite intercalation compounds A<sub>6</sub>C<sub>60</sub>(bcc structure). Results are presented for elements A from the 1A, 2A, 6A and 7A groups of the periodic table [From Y. Wang, D. Tománek, G. F. Bertsch, and R. S. Ruoff, Phys. Rev. B (1993)].



Figure 4.10: Phonon band structure of (a)  $KC_{60}$ , (b)  $K_3C_{60}$ , and (c)  $Rb_3C_{60}$  [From Y. Wang, D. Tománek, G. F. Bertsch, and R. S. Ruoff, Phys. Rev. B (1993)].

 $C_{60}$ ),  $E_{Madelung}$  and  $E_{BM}$  in the intercalated solid has been discussed in Eqs. (4.9), (4.11) and (4.12), respectively. Since both *a* and *B* are of intrinsic interest, they are also listed in Figures 4.7, 4.8, and 4.9 for all the intercalation compounds we investigated.

Once the equilibrium structure and the elastic behavior of the intercalated compounds are known, the phonon spectra can be calculated by constructing the dynamical matrix. These phonon spectra are important in the determination of relevant phonon modes which can couple conduction electrons and lead to superconductivity [53, 54, 55, 56, 57, 58]. In Figure 4.10 we present the phonon band structure of  $KC_{60}$ ,  $K_3C_{60}$ , and  $Rb_3C_{60}$  along the high symmetry lines in the Brillouin zone. The corresponding phonon density of states for the superconducting compound  $K_3C_{60}$  [23] is shown in Figure 4.11. The calculated phonon spectrum is characterized by low lying  $C_{60}$  derived acoustic modes which show little or no hybridization with high-frequency alkali derived optical modes, which can be understood as Einstein modes.

From our results in Figures 4.7, 4.8, and 4.9 we conclude that the lattice constant a increases with increasing atomic number of the intercalant within the same group. The decrease of a when comparing neighboring alkali and alkaline earth elements is due to the larger Madelung energy in the divalent donor based solid. A similar trend is found when comparing neighboring group 6A and group 7A elements, where group 6A based compounds have the smaller lattice constant. We find intercalant-induced changes of the lattice constant to be relatively moderate due to the large size of the interstitial sites in fullerite. Opposite and much more pronounced trends as for the lattice constant are found for the bulk modulus B. The main reason for this fact is the strongly anharmonic interionic repulsive interaction which leads to stiffer bonds at smaller values of the lattice constant.



Figure 4.11: Phonon density of states (solid line) and integrated density of states (dashed line) of  $K_3C_{60}$  [From Y. Wang, D. Tománek, G. F. Bertsch, and R. S. Ruoff, Phys. Rev. B (1993)].

The most important information which comes from our calculations is the formation energy  $\Delta H_f^0$  of intercalated fullerite. As seen from our results in Figures 4.7, 4.8, and 4.9, we expect only alkali and heavy alkaline earth elements to form stable fullerite intercalation compounds, indicated by the negative sign of  $\Delta H_f^0$ . As we discuss in the following Section, the trends across the periodic table can be understood from the delicate balance between the Madelung energy, ionization potentials and electron affinities of the intercalant atoms.

### 4.2.3 Discussion

The results for the formation enthalpies, presented in Figures 4.7, 4.8, and 4.9, can be interpreted as resulting from several trends across the periodic table. The heats of formation are dominated by the Madelung energy which, for a given group, does not change significantly due to only moderate changes of the lattice constant. More important are the changes of the ionization potential and electron affinity between elements in the same group which enter in the second step of the Born-Haber cycle, shown in Figure 4.6. Due to the decreasing ionization potential of group 1A and 2A elements with increasing atomic number, the heavier elements get ionized more easily. This is reflected in larger absolute values for the reaction enthalpies, which are indicative of a strongly exothermic intercalation process, in agreement with the experimental trends [23, 24, 25, 26, 27]. An analogous decrease of the electron affinity with increasing atomic number occurs in groups 6A and 7A. The heavier intercalants are less likely to accept electrons and are consequently less reactive. This leads to an increasingly endothermic behavior during the intercalation process of heavy group 6A and 7A elements.

We assume that group 2A elements are doubly ionized which is more difficult to

achieve than the single ionization of their alkali neighbors. This results in a smaller energy gain (or even a loss) during the intercalation process. For the acceptor elements, attachment of two electrons in the 6A group is much more difficult than of a single electron in the halide neighbor, resulting in larger energy *losses* predicted for the intercalation of group 6A elements as compared to group 7A elements.

A more detailed discussion of the formation enthalpies of fullerite intercalation compounds is presented, group by group, in the following subsections.

#### Group 1A

In the most dilute system with the  $AC_{60}$  stoichiometry, only Li does not form a compound, mainly due to the large cohesive energy of the Li metal and the high ionization potential of the Li atom. Na has a smaller cohesive energy and a lower ionization potential than Li which makes the compound with NaCl structure marginally stable. The Na atom is much smaller than the interstitial sites and is likely to be in off-center geometry. The additional gain in Madelung energy (with respect to the high-symmetry geometry) is likely to further stabilize this compound. The radii of group 1A intercalant elements never exceed the size of the octahedral cavity, resulting in very small changes of the lattice constant and bulk modulus. On the other hand, the cohesive energies and atomic ionization potentials of alkali metals steadily decrease from K to Rb and Cs, which is reflected in the increased stability of the intercalation compounds with the heavier elements.

In the  $A_3C_{60}$  phase, all the alkali elements form stable intercalation compounds due to large Madelung energies. The calculated energy gain per atom in this phase is larger than in the AC<sub>60</sub> phase, which is confirmed by the experimental observation that the  $A_3C_{60}$  phase does not decompose into AC<sub>60</sub> and the pure metal. The occupation of the smaller tetrahedral sites in the  $A_3C_{60}$  phase makes these structures stiffer, which is reflected in a significantly larger bulk modulus.  $K_3C_{60}$  and  $Rb_3C_{60}$  are the most thoroughly investigated fullerite intercalation compounds to date [23, 24, 25, 26, 27, 49, 50, 59, 60]. As we mentioned in Section II, the calculated repulsive interactions are based on the observed lattice constant and bulk modulus of  $K_3C_{60}$ . We test our predictions in  $Rb_3C_{60}$ , where we find our predicted lattice constant a = 14.41 Å to be in close agreement with the experimental value  $a_{expt} = 14.49$  Å [49, 50], and the predicted bulk modulus B = 0.24 MBar to be in similar agreement with the experimental value  $B_{expt} = 0.22$  MBar [49].

As shown in Figure 4.9, all alkali compounds  $A_6C_{60}$  with the bcc structure are stable. This has been confirmed by the successful synthesis of the  $A_6C_{60}$  compounds, where A = Li, Na, K, Rb and Cs [52, 60, 61, 62, 63]. The observed insulating behavior of these compounds is easily understood by the complete filling of the  $t_{1u}$ orbital of the  $C_{60}$  molecules by six donor electrons. The bcc structure of the  $A_6C_{60}$ phase has a smaller packing fraction than the fcc lattice. There are only octahedral interstitial sites in this structure, three per C<sub>60</sub> molecule, all of them filled by four alkali atoms (each alkali atom belongs to two neighboring octahedral sites). The intercalants are well separated from each other by a nearest neighbor distance which is  $\geq 1$  Å larger than the bond length in the alkali metal. As we mentioned before, the Born-Mayer repulsive energy between the intercalants is negligibly small in this geometry as we estimated. The electrostatic attraction between the  $C_{60}^{6-}$  molecules and the large number of alkali counter-ions reduces the distance between nearest neighbor C<sub>60</sub> molecules by  $\approx 0.2$  Å with respect to the value in pristine fullerite. We find the absolute value of the Madelung energy to be much larger in the  $A_6C_{60}$  than the  $A_3C_{60}$  phase, in spite of the strong Coulomb repulsion between four intercalant

ions at the same octahedral site. The energy gain per intercalant atom in the  $A_6C_{60}$ phase is only slightly smaller than in the  $A_3C_{60}$  phase. The negative sign of  $\Delta H_f^0$ shows that the  $A_6C_{60}$  phase can be formed by intercalating A into the  $A_3C_{60}$  phase; the slightly smaller value of  $\Delta H_f^0$  indicates that  $A_6C_{60}$  is the saturated phase. We find the reaction

$$A_3C_{60} + 3A(metal) \xrightarrow{\Delta E} A_6C_{60} \tag{4.15}$$

to be exothermic with  $\Delta E = -4.95$  eV in the case of K, which indicates that  $A_6C_{60}$ will not decompose into  $A_3C_{60}$  and the metal A. On the other hand, one can speculate about the possibility to synthesize the  $A_3C_{60}$  compound by mixing the pristine  $C_{60}$ solid and the saturated  $A_6C_{60}$  compound, as

$$C_{60}(solid) + A_6 C_{60} \xrightarrow{\Delta E} 2A_3 C_{60} . \tag{4.16}$$

In the case of K, we find this reaction to be exothermic with  $\Delta E = -1.32$  eV. This "back titration" is used as a well-defined synthesis process for K<sub>3</sub>C<sub>60</sub> [49] and Rb<sub>3</sub>C<sub>60</sub> [61]. The bulk modulus of the A<sub>6</sub>C<sub>60</sub> alkali compounds is considerably larger than in the other phases since all interstitial sites are occupied by four intercalant atoms. We find our theoretical value for the lattice constant of K<sub>6</sub>C<sub>60</sub>, a = 11.26 Å, to be in close agreement with the experimental value  $a_{expt} = 11.39$  Å [52].

#### Group 2A

We assume in our calculations that the group 2A elements transfer both of their valence electrons to  $C_{60}$  in the compound. We find that among these elements, only Ba is stable in the AC<sub>60</sub> phase. The lattice constant of alkaline earth intercalation compounds is smaller than that of the comparable alkali compounds, mainly due to

the larger value of the Madelung energy. This decrease of the lattice constant from group 1A to group 2A is reflected in an increased bulk modulus B. As in the alkali compounds, we predict that the bulk modulus does not change from the heavy to the light intercalants.

In the  $A_3C_{60}$  phase, we find the compounds of Ca, Sr and Ba to be stable. The lattice constants decrease considerably as compared to the  $AC_{60}$  phase, which is accompanied by a strong increase in *B*. Superconductivity at 8.4 K has been observed in Ca intercalated fullerite with simple cubic structure and the stoichiometry  $Ca_5C_{60}$  [28]. Our predictions regarding stable phases of alkaline earth based compounds have been further confirmed by the recently observed stable phases of Sr and Ba compounds [64].

The alkaline earth elements, which form stable  $A_3C_{60}$  compounds, also form stable  $A_6C_{60}$  compounds. The large difference of 11.5 eV between the formation enthalpies of the Be and the Ba compounds is mainly caused by the difference of 12.3 eV between the first and second ionization energies of these elements. Based on our calculated formation enthalpies for the  $A_3C_{60}$  and  $A_6C_{60}$  we conclude that the  $A_3C_{60}$  phase can be formed by an exothermic reaction from a mixture of pristine  $C_{60}$  and  $A_6C_{60}$ , as indicated in Eq. (4.16). The strongly attractive Coulomb interactions reduce the lattice constant of the  $C_{60}$  matrix substantially, more in the group 2A than in the group 1A intercalation compounds. In the hypothetical  $Ca_6C_{60}$  compound, the lattice constant is 0.98 Å smaller than in the corresponding compound of the neighboring element K; the corresponding reduction of the  $C_{60}$ - $C_{60}$  nearest neighbor distance in the  $A_6C_{60}$  phase, typical values of *B* are more than twice as large as those in the more dilute  $A_3C_{60}$  phase, and comparable to metallic Fe.
As we pointed out above, the inability of Mg to form a stable intercalation compound is mainly due to its large first and second ionization potentials. At this point, it is instructive to speculate whether a stable compound could be formed based on Mg<sup>+</sup>. We have performed the calculations for the Born-Haber cycle of  $Mg_n^+C_{60}^{n-}$  and compared the results to those for  $Na_n^+C_{60}^{n-}$  and found that the equilibrium structures are very similar and most steps are energetically equivalent. The main difference between Na<sup>+</sup> and Mg<sup>+</sup> based compounds is the first ionization potential of the atoms, which is 7.65 eV for Mg and 5.14 eV for Na. This reduces the formation enthalpy of fullerite compounds based on monovalent Mg by 2.5 eV with respect to comparable Na compounds, and hence makes the  $Mg_n^+C_{60}$  compounds unstable. The only possibility for a Mg-based fullerite compound to be stable exists if the bonds between Mg intercalants and the C<sub>60</sub> matrix are covalent. This seems to be confirmed by the recent synthesis of a Mg-based C<sub>60</sub> compound which has nonmetallic character [64].

#### Group 7A

We find that none of the halide compounds are stable with respect to pure  $C_{60}$  and the halide gas. In order to understand this fact, we compared the individual energies occurring in the Born-Haber cycles of alkali and halide compounds in the same row of the periodic table. We found that the energy associated with the first step, involving the vaporization of solid  $C_{60}$  and dissociation of molecular halide, and the last step, namely the formation of the intercalation compound from the respective ions, are very similar for the different group 1A and 7A systems. The large difference occurs during the ionization step on the atomic level, as we can illustrate for the  $A_3C_{60}$ compound. We find that the energy necessary to ionize an alkali atom is very similar to the energy gain associated with electron attachment to a halide atom. Yet the energy to triply ionize a  $C_{60}$  cluster, I = 34.96 eV, is much larger than the energy gain when attaching three electrons to a  $C_{60}$  molecule, A = 1.09 eV (see Tables 4.1 and 4.2). The large ionization energy of  $C_{60}$  enters the Born-Haber cycle for halide intercalation compounds, and hence can be viewed as the cause of their instability.

The arguments used to explain the positive value of the formation enthalpy  $\Delta H_f^0$ in the A<sub>3</sub>C<sub>60</sub> halide phase apply also to the AC<sub>60</sub> and A<sub>6</sub>C<sub>60</sub> phases. The stability of alkali compounds and the instability of halide compounds can again be explained by comparing the vastly different total ionization potentials and electron affinities of the C<sub>60</sub> cluster for the given ionic final state, which are given in Tables 4.1 and 4.2.

The variation of the formation enthalpy between the light and the heavy halides has two origins. First, the light halides have a larger electron affinity which results in the stabilization of the compound. Second, the lattice constant a decreases from the heavy towards the light elements, resulting in a larger Madelung energy gain during the formation of the solid from the ions. The decrease of a with decreasing atomic number is accompanied by a strong increase of the bulk modulus. There are two counteracting trends which change the lattice constant from the  $AC_{60}$  to the  $A_3C_{60}$ phase. As our results in Figures 4.7, 4.8, and 4.9 indicate, the lattice expansion due to the large halide ions occupying the smaller tetrahedral sites in the  $A_3C_{60}$  lattice is partly compensated by the Madelung energy gain during lattice contraction. This still applies in the hypothetical  $A_6C_{60}$  phase, where the lattice constant is significantly smaller than in the  $A_3C_{60}$  compounds, mainly due to the Madelung energy gain associated with lattice contraction. This lattice contraction is again reflected in the large increase of the bulk modulus in the  $A_6C_{60}$  phase as compared to the  $A_3C_{60}$ phase. Still, the bulk moduli of halide intercalated compounds are well below those of comparable alkali compounds, mainly due to the larger compressibility of the halide ions.

The arguments for the stability of halide intercalation compounds apply, of course, only to the structures we studied here. Other possible structures we can think of could contain endohedrals or halide molecules. The latter possibility has been confirmed recently, when varying amounts of I<sub>2</sub> have been found in C<sub>60</sub> following exposure to iodine [65, 66]. Fluorine atoms, on the other hand, tend to form covalent bonds with C<sub>60</sub>, giving rise to a new compound based on fluorinated fullerenes such as C<sub>60</sub>F<sub>36</sub> [67].

#### Group 6A

Our results in Figures 4.7, 4.8, and 4.9 indicate that group 6A elements, same as group 7A elements, do not form stable intercalation compounds. Free doubly charged group 6A  $A^{2-}$  ions are known to be unstable [68]. Since no reasonable estimate is available for the second electron affinity of these ions [69], we simply assume the second electron affinity to be the same as the first electron affinity. When used in the Born-Haber cycle, this value gives the lower limit of the formation enthalpy of the compound. The positive values for  $\Delta H_f^0$  which we find for all group 6A elements are again to be blamed mainly on the large ionization potential of the  $C_{60}$  molecule, which dominates over the increased Madelung energy due to the larger charge of the acceptor ions. Again, our results only apply to the three hypothetical geometries we studied here. We cannot exclude the existence of other different group 6A based intercalation compounds, such as compounds containing intercalant molecules. As for group 7A elements, the variations in  $\Delta H_f^0$  within the 6A group are linked with variations of the lattice constant of the compound and changes of the electron affinity of the elements. We find the trends in the structural properties (a, B) of group 6A based compounds to closely follow those found in group 7A intercalation compounds.

#### Phonon Spectra and Superconductivity

One of the most important properties of intercalated fullerite is superconductivity, which has been observed in many alkali intercalation compounds with the  $A_3C_{60}$  stoichiometry [23, 24, 25, 26, 27, 29]. The observed nonzero isotope effect [70, 71, 72] in these compounds makes the electron-phonon coupling mechanism a likely candidate for the pairing of electrons. Reliable phonon spectra are an essential prerequisite for the resolution of the remaining uncertainties regarding the important phonon modes which are responsible for superconductivity in these compounds [53, 54, 55, 56, 57, 58]. Our results for the phonon spectra of  $KC_{60}$ ,  $K_3C_{60}$ , and  $Rb_3C_{60}$  are shown in Figs. 4.10 and 4.11.

The phonon spectra consist of low lying  $C_{60}$  derived acoustic modes which are well separated from high-frequency optical modes due to the alkali intercalants. The latter modes have low dispersion and can be interpreted as Einstein modes. The frequency of the optical modes increases with increasing stiffness of the interaction potential between the alkali atom, acting as Einstein oscillator, and the matrix. For a given intercalant A, this frequency is expected to be lower in the AC<sub>60</sub> structure, where only the octahedral sites are filled, than in the A<sub>3</sub>C<sub>60</sub> structure, which contains occupied tetrahedral sites. In the latter case, we expect two optical bands, one due to octahedral sites at a frequency comparable to AC<sub>60</sub>, and the other at a much higher frequency due to alkali atoms in tetrahedral sites. This is clearly the case for the optical modes at  $\nu = 1.8$  THz (due to octahedral K) and at  $\nu = 2.7$  THz (due to tetrahedral K) in KC<sub>60</sub> and K<sub>3</sub>C<sub>60</sub>, as shown in Figs. 4.10(a) and (b). Figure 4.10(c) reflects the fact that the bonding in Rb<sub>3</sub>C<sub>60</sub> and K<sub>3</sub>C<sub>60</sub> are similar. The comparison of the corresponding spectra indicates that the optical modes of alkali atoms are reduced in frequency according to the large 2:1 mass ratio between Rb and K. The acoustic  $C_{60}$ -derived part of the spectrum is much less affected by the change form K to Rb.

The absence of hybridization between the alkali and the  $C_{60}$  derived modes has also been predicted previously by Zhang et al. [33], albeit due to different physics. Our results indicate that in the equilibrium geometry of  $K_3C_{60}$ , the K-C<sub>60</sub> bonds are compressed in the tetrahedral sites, while the  $C_{60}$ -C<sub>60</sub> bonds are stretched. The stiff K-C<sub>60</sub> interaction potentials — especially in the tetrahedral sites — push the corresponding Einstein modes above the highest C<sub>60</sub> derived acoustic modes, hence suppressing hybridization. The calculation in Ref. [33] is based on the simplifying assumption that *all* individual bonds in the lattice are relaxed. The consequence of this model is a suppressed hybridization between the K-derived optical and C<sub>60</sub>derived acoustic modes in spite of the fact that the Einstein modes due to tetrahedral K atoms are predicted [33] to lie in the frequency range of C<sub>60</sub> fullerite.

### 4.3 Conclusions

Among the structural properties of  $C_{60}$  in the solid, I have investigated the elastic response of the pristine and intercalated crystals to hydrostatic pressure, and the stability of the intercalation compounds.

In pristine fullerite, our results indicate that at zero pressure, carbon atoms in neighboring "buckminsterfullerene" clusters are no closer than 2.65 Å apart and interact by pairwise Van der Waals forces. At increasing pressures, we observe a gradual transition to a hard-core repulsion between neighboring clusters. Only at high pressures beyond  $\approx$ 70 GPa, the bulk modulus of fullerite exceeds that of diamond and a fullerite to diamond transformation should occur.

In C<sub>60</sub> fullerite intercalation compounds with the AC<sub>60</sub>, A<sub>3</sub>C<sub>60</sub>, and A<sub>6</sub>C<sub>60</sub> stoichiometries, T = 0 K formation enthalpies have been predicted using a thermodynamic Born-Haber cycle. Energies associated with the individual steps in the cycle have been carefully estimated using available experimental and theoretical data for both donor and acceptor compounds. The corresponding calculations provide details of the structure, lattice constant, and the bulk modulus of the intercalation compounds as well as the phonon spectrum.

We have evaluated and listed the corresponding structural and elastic data together with the predicted formation enthalpies for groups 1A, 2A, 6A and 7A of the periodic table. Phonon spectra, available from our total energy calculations, are presented for selected alkali intercalation compounds which show superconducting behavior.

Our results indicate that alkali elements form stable fullerite intercalation compounds. We found alkaline earth elements Ca, Sr, and Ba to be the most prominent candidates for intercalation. The corresponding calculations for acceptor intercalants indicate that none of the group 6A and 7A based ionic intercalation compounds is stable with respect to solid  $C_{60}$  and the intercalant in the standard form. Our results, however, do not address the possibility of intercalating molecules, or modifying the  $C_{60}$  matrix in a chemical reaction.

The usefulness of our approach to estimate formation enthalpies can ultimately only be judged by corresponding experiments. We also hope that future experiments can reduce the uncertainty regarding some of the quantities used in the Born-Haber cycle, such as the higher electron affinities and ionization potentials of  $C_{60}$  molecules, and equilibrium structures, lattice constants and bulk moduli of the compounds. We have also successfully applied the Born-Haber cycle method to calculate the formation enthalpy of rare earth intercalation compounds [73]. The stability of these compounds depends crucially on the charge transfer between the components, which is also responsible for their superconducting properties. Similar calculations for the stability of endohedral A@C<sub>60</sub> compounds [74] indicate the importance of the polarization energy of the C<sub>60</sub> shell for their stability, in agreement with available *ab initio* results.

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### Chapter 5

# Electronic Properties of the C<sub>60</sub> Clusters

In Section 1.2, I briefly discussed the equilibrium structure and the electronic structure of the  $C_{60}$  fullerene. In this Chapter, I will present results of my calculations, based on the tight-binding Hamiltonian described in Chapter 2, for the electronic properties of this cluster. In Section 5.1 I will discuss the static polarizability and hyperpolarizability of  $C_{60}$  and in Section 5.2, I will present results for the dynamical response of the  $C_{60}$  cluster to an external electromagnetic field.

The following results for the static polarizability have been published in Ref. [1] and those for the dynamical response in Ref. [2].

# 5.1 Linear and nonlinear static polarizability of $C_{60}$

 $C_{60}$  is a unique molecule with a hollow spherical cage structure. One of the most important properties of such a system is the static polarizability. This quantity describes the induced dipole moment in an external electrical field, and hence provides a direct measure of the degree of mobility for the electrons. Once the polarizability of

the  $C_{60}$  cluster is known, the susceptibility of the  $C_{60}$  solid, a macroscopic property, can be determined using the Clausius-Mossotti relation. Of great importance, specifically for applications in sensor technology, is the nonlinear component of the static polarizability. In analogy to long conjugated polymers, a large nonlinear polarizability in  $C_{60}$  would appear highly plausible. My investigation has been motivated by a report of Blau and coworkers [3] of a very large absolute value<sup>1</sup> of the third-order polarizability  $|\gamma| = 1.5 \times 10^{-42} \text{ m}^5/\text{V}^2 = 1.07 \times 10^{-28}$  esu for C<sub>60</sub> molecules in benzene solution. This value is enormous compared to that of the benzene solvent [4],  $\gamma = 3.85 \times 10^{-36}$  esu, and would make these systems prime candidates for a direct application in nonlinear optical devices. An independent study of the same property, performed on  $C_{60}$  in solution using second harmonic generation measurements [5], indicated a substantially smaller value of the hyperpolarizability  $|\gamma| = 7.5 \times 10^{-34}$  esu. Similar results to the latter study have been obtained using degenerate four-wave mixing for  $C_{60}$  films [6, 7], yielding the third order optical susceptibility for the solid  $\chi^{(3)} = 7 \times 10^{-12}$  esu, which corresponds to<sup>2</sup>  $|\gamma| \approx 3.13 \times 10^{-34}$  esu. On top of the discrepancy between the different experimental data, the expression for the nonlinear susceptibility [8] which has been applied to calculate  $\gamma$  in C<sub>60</sub> is of doubtful applicability, and fails by several orders of magnitude to reproduce the data in Ref. [3], as also shown in Ref. [9].

In an attempt to clarify the situation for these interesting systems [10, 11], we have calculated the optical response of an isolated  $C_{60}$  cluster. Since this is not easy even for simple molecules, we first verified the validity of our approach by applying the same computational techniques to the benzene molecule which is well understood.

<sup>&</sup>lt;sup>1</sup>Present experimental methods are unable to determine the sign of  $\gamma$  in C<sub>60</sub>.

<sup>&</sup>lt;sup>2</sup>As we discuss later on,  $\chi^{(3)}$  is related to  $\gamma$  through the density of C<sub>60</sub> clusters and the Lorentz field factors associated with the shielding of the external field.

Let us consider an isolated  $C_{60}$  molecule in the electric field  $\mathcal{E}$ . The induced dipole moment p is given (to the lowest three orders) by

$$p = \alpha \mathcal{E} + \gamma \mathcal{E}^3 , \qquad (5.1)$$

where  $\alpha$  is the (linear) polarizability and  $\gamma$  is the (third order) hyperpolarizability. Here we also note that the second order hyperpolarizability is zero in centrosymmetric systems such as the C<sub>60</sub> cluster. These polarizabilities can be determined from the energy change<sup>3</sup> of a molecule due to an external field  $\mathcal{E}$ 

$$\Delta E = -\frac{1}{2}\alpha \mathcal{E}^2 - \frac{1}{4}\gamma \mathcal{E}^4 .$$
(5.2)

For the corresponding solid, the polarization density P is related to p and  $\mathcal{E}$  by the density of constituents N. In cgs units, it is given by<sup>4,5</sup>

$$P = Np = \chi^{(1)}\mathcal{E} + \chi^{(3)}\mathcal{E}^3 .$$
 (5.3)

Calculations of higher-order static polarizabilities are very nontrivial due to the high accuracy requirements even in relatively simple systems such as benzene [12]. To evaluate the energy change  $\Delta E$  in Eq. (5.2) due to an applied electric field, we use the tight-binding Hamiltonian discussed in Chapter 2. In the presence of the static electric field  $\mathcal{E}$  along the z direction, we consider a shift of the on-site energies by  $\Delta \epsilon = -e\mathcal{E}z$ .

<sup>&</sup>lt;sup>3</sup>We will use electrostatic cgs units (esu) from now on. For isolated molecules, the conversion factors from SI to esu are as follows.  $\alpha$  is given in Cm<sup>2</sup>/V [SI] or cm<sup>3</sup> [esu], and  $\alpha$  [SI] =  $(4\pi\epsilon_0/10^6)\alpha$  [esu].  $\gamma$  is given in Cm<sup>4</sup>/V<sup>3</sup> [SI], and the corresponding conversion is  $\gamma$  [SI] =  $4\pi\epsilon_0/(9 \times 10^{14})\gamma$  [esu]. Note that our definition of  $\gamma$  in Eq. (5.1) does not contain  $\epsilon_0$ . Consequently, the conversion of  $\gamma$  values in  $m^5V^{-2}$  units to our SI units involves a multiplication by  $\epsilon_0 = 0.885 \times 10^{-11}CV^{-1}m^{-1}$ .

<sup>&</sup>lt;sup>4</sup>For the solids, the conversion factors from SI to esu are  $\chi^{(1)}$  [SI] =  $4\pi \chi^{(1)}$  [esu] and  $\chi^{(3)}$  [SI] =  $4\pi/(9 \times 10^8)\chi^{(3)}$  [esu].

<sup>&</sup>lt;sup>5</sup>In SI units, P is defined by  $P = \epsilon_0(\chi^{(1)}\mathcal{E} + \chi^{(3)}\mathcal{E}^3)$ , hence it contains an extra factor  $\epsilon_0$  as compared to the definition in Eq. (5.3).

To obtain the static polarizabilities, we use two approaches. We determine the energy change of the system due to  $\mathcal{E}$  using perturbation theory and check the numerical results by directly diagonalizing the Hamiltonian in the presence of the electric field.

The perturbative vacuum amplitude diagrams for the second and fourth order perturbation terms are shown in Figure 5.1. As discussed above, the linear polarizability is related to the energy change of the system. In second-order perturbation theory, this energy change is given by

$$\Delta E^{(2)} = 2 \sum_{h} \sum_{p} \frac{V_{hp} V_{ph}}{E_h - E_p} \,. \tag{5.4}$$

Here, p and h label single particle and hole states, respectively, and  $E_p(E_h)$  denote the corresponding energies. For the electric field along the z direction, the transition matrix elements are given by  $V_{ij} = \langle i | -e\mathcal{E}z | j \rangle$ . The prefactor 2 takes care of the spin degeneracy. The third-order nonlinear polarizability is related to the energy change in fourth-order perturbation theory which is given by [13]

$$\Delta E^{(4)} = 2 \left[ \sum_{h} \sum_{p} \sum_{p'} \sum_{p''} \frac{V_{hp} V_{pp'} V_{p'p''} V_{p''h}}{(E_h - E_p)(E_h - E_{p'})(E_h - E_{p''})} - 2 \sum_{h} \sum_{p} \sum_{p'} \sum_{h''} \frac{V_{hp} V_{pp'} V_{p'h'} V_{h'h}}{(E_h - E_p)(E_h - E_{p'})(E_{h'} - E_{p'})} + \sum_{h} \sum_{p} \sum_{h'} \sum_{h''} \frac{V_{hp} V_{ph''} V_{h''h'} V_{h'h}}{(E_h - E_p)(E_{h'} - E_p)(E_{h''} - E_p)} - \sum_{h} \sum_{p} \sum_{p'} \sum_{h'} \frac{V_{hp} V_{ph'} V_{h'p'} V_{p'h}}{(E_h - E_p)(E_h - E_{p'})(E_{h'} - E_p)} \right].$$
(5.5)

Diagrams 2 and 3 in the fourth order diagrams are equal, giving the prefactor of 2 in the second term. The fourth term of the Eq. (5.5) is the sum of diagrams 5 and 6.  $\Delta E^{(4)}$  can also be calculated in perturbation theory using a basis of many-particle



Figure 5.1: The Graphs for (a) the second order, and (b) the fourth order perturbation theory expressions in Eqs. (5.4) and (5.5).  $\rightarrow$ - represents a particle state and  $-\leftarrow$  denotes a hole state.

states [14, 15]. However, that formula is more difficult to use numerically since its energy denominators can be small, unlike the particle-hole energies in Eq. (5.5). The expressions in Eqs. (5.4) and (5.5), together with Eq. (5.2), yield directly the optical polarizabilities  $\alpha$  and  $\gamma$ . We find that the values for  $\alpha$  and  $\gamma$  obtained using perturbation theory agree with values which we calculate directly by diagonalizing the tight-binding Hamiltonian.

In order to determine the reliability of our approach, we first calculate the linear and third-order polarizabilities of the benzene molecule, a system which has been studied extensively both experimentally [4, 16] and theoretically [12]. For this purpose, we have to augment our tight-binding Hamiltonian for carbon by parameters suitable for hydrogen. We adjust the difference between the H1s and C2p energies to the difference of the atomic ionization potentials, which gives  $\epsilon(H1s) = -2.3$  eV. For the hydrogen-carbon hopping integrals, we use  $V_{ss\sigma} = -3.15$  eV and  $V_{sp\sigma} = 1.7$  eV at the H-C distance of 1.07 Å found in C<sub>6</sub>H<sub>6</sub>, obtained by fitting the level spectrum of a CH radical which we calculated using the Local Density Approximation [17].

Our results for C<sub>6</sub>H<sub>6</sub> are presented in Table 5.1. The calculated polarizability in the plane of the benzene molecule is  $\alpha_{||} = 31.1$  Å<sup>3</sup>. Assuming the same value of the polarizability along the two principal axes in the molecular plane and zero perpendicular to it, we would predict  $\langle \alpha \rangle = (2/3)\alpha_{||} = 20.7$  Å<sup>3</sup>. This value is consistent with the experimental result  $\langle \alpha \rangle = 10.0$  Å<sup>3</sup> obtained for the solution [4] in view of the fact that we have neglected internal screening in the benzene molecule. The third order polarizability turns out to be  $\gamma_{||} = 13.5 \times 10^{-36}$  esu, giving  $\langle \gamma \rangle =$  $9.0 \times 10^{-36}$  esu. This is again comparable to the *ab initio* results [12] in the range of  $\langle \gamma \rangle = 1.3 - 1.7 \times 10^{-36}$  esu and experimental data of Ref. [4] giving  $\langle \gamma \rangle =$  $3.85 \times 10^{-36}$  esu. Our hyperpolarizability is somewhat larger than the *ab initio* results

	$< lpha_{bare} > ({ m \AA}^3)$	$< lpha_{screened} > ({ m \AA}^3)$	$\chi^{(1)}$ (esu)	$<\gamma_{bare}>$ $(10^{-36}  ext{ esu})$	$<\gamma_{screened}>$ $(10^{-36} \text{ esu})$	$\chi^{(3)}$ (10 <sup>-12</sup> esu)
C <sub>6</sub> H <sub>6</sub> <sup>a</sup>	20.7			9.0		
C <sub>6</sub> H <sub>6</sub> <sup>b</sup>		10.02			3.85	0.101
C <sub>60</sub> <sup><i>a</i></sup>	215.0	35.7	0.063	346.2	2.3 <sup>c</sup>	$0.05^{d}$
C <sub>60</sub> e	195	56	0.116			
$C_{60}^{f}$					$1.07 \times 10^{8}$	
$C_{60}^{\tilde{g}}$					750	
C <sub>60</sub> <sup>h</sup>			$0.239^{d}$		313	7

Table 5.1: Calculated and observed optical susceptibilities of  $C_{60}$  and  $C_6H_6$  molecules.

- Present calculation.
- <sup>b</sup> Experimental values of Ref. [4].
- <sup>c</sup> This value is obtained using  $< \alpha_{bare} >$  and  $< \alpha_{screened} >$  of Ref. [18].
- <sup>d</sup> This value is obtained using the experimental value n = 2 of Ref. [6] in the expression  $n^2 = 1 + 4\pi \chi^{(1)}$ .
- <sup>e</sup> Theoretical values of Ref. [18].
- <sup>f</sup> Experimental values of Ref. [3].
- <sup>8</sup> Experimental values of Ref. [5].
- <sup>h</sup> Experimental values of Ref. [6].

which again is to be expected due to our neglect of intramolecular screening.

Screening is even more important in the large  $C_{60}$  cluster than in benzene, and we shall include it in our calculations of this system. For a spherical molecule such as the  $C_{60}$  fullerene, the screened linear and third order nonlinear polarizabilities are given by

$$\alpha_{screened} = \alpha_{bare} / (1 + \frac{\alpha_{bare}}{R^3}) , \qquad (5.6)$$

and

$$\gamma_{screened} = \gamma_{bare} / (1 + \frac{\alpha_{bare}}{R^3})^4 , \qquad (5.7)$$

where R is the radius of the fullerene. The matrix surrounding the cluster in a bulk sample also modifies the external field and hence the screening. We determine the bulk linear susceptibility using

$$\chi^{(1)} = N\alpha_{screened} / \left(1 - \frac{4\pi}{3} N\alpha_{screened}\right), \qquad (5.8)$$

which is equivalent to the Clausius-Mossotti relation. In the same way, we calculate the third-order nonlinear susceptibility using

$$\chi^{(3)} = N\gamma_{screened} / \left(1 - \frac{4\pi}{3} N\alpha_{screened}\right)^4.$$
(5.9)

In these equations,  $N \approx 1/720$  Å<sup>3</sup> is the density of clusters and  $\alpha_{screened}$  and  $\gamma_{screened}$  are the screened linear and nonlinear polarizabilities of an isolated cluster, respectively.

Our results for the C<sub>60</sub> clusters and the solid are given in Table 5.1. As mentioned above, our perturbation theory calculations are consistent with results obtained by a direct diagonalization of the Hamiltonian in a weak external field. We fit the energy to Eq. (5.2) using  $\mathcal{E} = 0 - 0.01$  V/Å which is much weaker than the field  $\mathcal{E} \approx 0.7$  V/Å when the first level crossing occurs. We find a large bare polarizability  $\alpha_{bare} = 215$  Å<sup>3</sup>, which is reduced considerably due to the internal depolarization field to  $\alpha_{screened} =$ 35.7 Å<sup>3</sup>, close to  $R^3 = 42.8$  Å<sup>3</sup> the linear polarizability of a metallic sphere. It is also in agreement with the quantum-chemical result [19]  $\alpha \approx 300 - 400$  a.u., depending on the basis set. The latter value is very close to that for a classical metallic sphere with a radius R = 3.5 Å,  $\alpha_{screened} = R^3 = 42.9$  Å<sup>3</sup>. Of course, such large screening cannot be expected in the planar benzene molecule.

The polarizability of an isolated cluster can be inferred from the linear susceptibility or index of refraction of the bulk material using the Clausius-Mossotti equation. Our predicted susceptibility is  $\chi^{(1)} = 0.06$ , in relatively poor agreement with the experimental value  $\chi^{(1)} = 0.24$  [6]. Part of the reason for this discrepancy is that Coulomb interaction is overestimated by the approximation of Ref. [2]; a better treatment of the Coulomb interaction with the tight-binding Hamiltonian yields a susceptibility of  $\chi^{(1)} = 0.116$  [18]. Also, the crystal field in the bulk breaks the symmetry of the C<sub>60</sub> molecule, so that direct HOMO—>LUMO transitions can occur. The susceptibility of the solid would also be increased by the possibility of a virtual electron transfer between C<sub>60</sub> molecules.

We find a very large positive value of  $\langle \gamma_{bare} \rangle = 3.5 \times 10^{-34}$  esu for the bare third order hyperpolarizability, more than one order of magnitude larger than in benzene. Our value is in fact within the range of two of the experiments, Refs. [5] and [6]. However, this value gets screened by the induced dipole field in the C<sub>60</sub> which will be much stronger than in the planar C<sub>6</sub>H<sub>6</sub> structure [20]. Using the screening factor  $\alpha_{screened}/\alpha_{bare} = 3.5$  from Ref. [18], we find  $\langle \gamma_{screened} \rangle = 2.3 \times 10^{-36}$  esu, about the same as in benzene. For the solid, we obtain  $\chi^{(3)} = 5 \times 10^{-14}$  esu using the empirical susceptibility, which is almost two orders of magnitude smaller than the experimental value of Ref. [6].

We do not understand the origin of this large discrepancy. One possible reason is the high laser frequency  $\hbar \omega \approx 1.2$  eV used in the experiments. We have considered the effect of the frequency dependence in the perturbation calculation, Eq. (5.5). We find that a substantial change in the hyperpolarizability only occurs due to virtual two-photon transitions within a very narrow energy range of the HOMO-LUMO transition. Since the transition is spread out by crystal field effects, we ignore this enhancement in the present paper. Another possibility is that one must go beyond the tight-binding approximation to calculate this quantity, as seems to be the case for the linear susceptibility. In any case, our result is more than seven orders of magnitude below the data quoted in Ref. [3], and we conclude that these data are probably in error.

### **5.2** Collective electronic excitations of $C_{60}$

In this Section I will discuss the dynamical response of a C<sub>60</sub> cluster to an external electromagnetic field. Motivated by a measurement of the photoabsorption strength in C<sub>60</sub> clusters in the low frequency region [21], we have calculated the electromagnetic response of this remarkable system at nonzero frequencies. As I discuss in the following, we obtain quantitative agreement with the experiment for  $\hbar \omega \leq 10$  eV. Moreover, our calculations predict a giant Mie-type resonance at  $\hbar \omega \approx 20$  eV, which was later observed experimentally [22].

We use linear response theory, which is most appropriate for large systems with mobile electrons where screening can be significant. Within the one-electron theory, for which we shall use mostly a tight-binding model, the dipole operator has two contributions, from a dipole moment due to intersite charge transfer, and from the dipole moment on a site. We write the dipole operator as

$$D_{z} = D_{z}^{(1)} + D_{z}^{(2)}$$
  
=  $\sum_{\alpha,i} a_{\alpha,i}^{\dagger} a_{\alpha,i} z(i) + d \sum_{i} (a_{s,i}^{\dagger} a_{p_{z},i} + a_{p_{z},i}^{\dagger} a_{s,i}),$  (5.10)

where z(i) is the z-coordinate of the *i*-th carbon atom and *d* is the  $s \to p_z$  dipole matrix element on a carbon atom.

Starting from an independent particle picture, we define the polarization propagator for the free dipole response by [23]

$$\Pi_{D_{z}}^{(0)}(\omega) = \sum_{p,h} |< p|D_{z}|h > |^{2} \frac{2(\epsilon_{p} - \epsilon_{h})}{(\epsilon_{p} - \epsilon_{h})^{2} - (\omega + i\eta)^{2}} .$$
(5.11)

Here, p and h label particle and hole eigenstates of the single-particle Hamiltonian and  $\epsilon_p$  and  $\epsilon_h$  are the corresponding particle and hole energies.

The full response requires the interaction between electrons, which we shall approximate as a pure Coulomb interaction. For the dipole response we only need to consider the fields generated by  $D_z^{(1)}$  and  $D_z^{(2)}$ . We shall first consider a simple approximation, keeping only the charge operator  $D_z^{(1)}$ . Then the electron-electron interaction is  $e^2 D_z^{(1)} D_z^{(1)}/R^3$ , where  $R \approx 3.5$  Å is the radius of the C<sub>60</sub> cluster. The screened response function due to  $D_z^{(1)}$  in Eq. (5.1) is given in this approximation by [23]

$$\Pi_1^{RPA}(\omega) = (1 + \Pi_1^{(0)}(\omega) \frac{e^2}{R^3})^{-1} \Pi_1^{(0)}(\omega) .$$
(5.12)

Note that in the present approach the  $\Pi$ 's are ordinary functions and the equation is algebraic and easily computed. We shall later consider a more refined approximation by including the dipole moments on the sites, described by  $D_z^{(2)}$ . The effect will be to replace Eq. (5.3) by a 2 × 2 matrix equation

$$\tilde{\Pi} = (\tilde{1} + \tilde{\Pi}^{(0)} \tilde{V})^{-1} \tilde{\Pi}^{(0)} , \qquad (5.13)$$

Here, we have separated the charge and the internal dipole operators and write the free response as a  $2 \times 2$  matrix with elements

$$\Pi_{nm}^{(0)}(\omega) = \sum_{p,h} < h | D_z^{(m)} | p > \frac{2(\epsilon_p - \epsilon_h)}{(\epsilon_p - \epsilon_h)^2 - (\omega + i\eta)^2} .$$
(5.14)

 $\tilde{V}$  in Eq. (5.4) is the 2 × 2 matrix of the interaction, given by

$$\tilde{V} = \frac{e^2}{R^3} \begin{pmatrix} 1 & 1/2 \\ 1/2 & R/2d \end{pmatrix}.$$
(5.15)

The HOMO to LUMO transition is forbidden by parity, and the lowest optically allowed transitions are  $h_u \rightarrow t_{1g}$ ,  $h_g \rightarrow t_{1u}$ , and  $h_u \rightarrow h_g$ , with tight-binding excitations energies of 2.8 eV, 3.1 eV, and 4.3 eV. These values compare well with the LDA values 2.9 eV, 3.1 eV and 4.1 eV [24] and are reflected in the free response shown in Figure 5.2(a). As we discuss in the following, the electron interaction changes the excitation energies significantly and is essential for even a qualitative understanding of the transitions strengths.

Our results for the screened response, based on the RPA treatment of the tightbinding Hamiltonian and the charge dipole operator  $D_z^{(1)}$ , are shown in Figure 5.2(b). A comparison to the free response shows that the lowest allowed particle-hole transition is slightly shifted in energy to 2.9 eV and agrees well with the observed [21, 25] value of 3.1 eV. The oscillator strength<sup>6</sup> of this transition is drastically reduced by a factor of 400 from the value 3.8 in the free response to 0.010 in the RPA. This brings the transition strength close to the measured [25] oscillator strength of 0.004. An independent calculation of the interacting response has been performed using the quantum-chemical CNDO/S method [26], but this method yielded an oscillator strength of 0.08, which is considerably less screening than in RPA.

Turning to the next few excitations, we find the transitions to be shifted substantially upward in energy as compared to the free response shown in Figure 5.2(a). This brings them into fair agreement with the observed [21, 25] dipole excitations at 3.76 eV, 4.82 eV and 5.85 eV. These transitions are also screened, but the screening factor is only in the range 10-30. They thus appear relatively strong compared to the low transition, in agreement with the experimental data of Ref. [25] [see Figure 5.2(c)].

The results for the low-lying excitations are essentially unaffected when the on-

<sup>&</sup>lt;sup>6</sup>The oscillator strength is defined by  $f = 2m_e |\langle f|D_z|i \rangle |i\rangle |i\rangle |E_f - E_i)/\hbar^2$ .



Figure 5.2: Free response (a) and RPA response (b) of  $C_{60}$  clusters to an external electromagnetic field (solid line). The sharp levels have been broadened by adding an imaginary part  $\hbar \eta = 0.2$  eV to the energy. The dashed line indicates the integrated oscillator strength. (c) Observed photoabsorption spectrum of  $C_{60}$  in solution [From H. Ajie et al, J. Phys. Chem. 94, 8630 (1990) and G. F. Bertsch, A. Bulgac, D. Tománek, and Y. Wang, Phys. Rev. Lett. 67, 2690 (1991)].

site dipole operator  $D_z^{(2)}$  is added to the response<sup>7</sup>. For example, the positions of the low states are shifted by less then 0.1 eV, and the strength of the lowest transition is changed by only 5%. As we will discuss below, the effect of  $D_z^{(2)}$  on the higher excitations is much more pronounced.

Turning to the plasmon-like transitions at high energy, we first note that the tight-binding Hamiltonian with the operator  $D_z^{(1)}$  has a total oscillator strength of  $N = 2m/\hbar^2 \sum_{p,h} | |^2 (\epsilon_p - \epsilon_h) \approx 180$ , which is, of course, the same in both the free response and in RPA. This value is close to the theoretical upper bound of 240, ignoring the core electrons, giving some credibility to the model for the entire energy range. Figure 5.3 displays the excitation spectrum of  $C_{60}$  extending up to plasmon energies, obtained using several approximations. The  $D_z^{(1)}$  free response function, shown in Figure 5.3(a), has a broad band of transitions in the "intermediate" energy range  $\hbar\omega \approx 10 - 20$  eV. With the electron-electron interaction present, the main effect of the Coulomb field is to collect the strength of these transitions into a single collective excitation, a Mie-type plasmon. The spectrum shown in Figure 5.3(b) has this giant resonance at an unusually high frequency  $\hbar\omega \approx 30$  eV, well beyond the typical plasmon range ( $\hbar \omega < 10 \text{ eV}$ ), which has not been observed so far. In contrast to the low energy region, the inclusion of the on-site dipole term  $D_z^{(2)}$  has a substantial effect on the high-frequency response. The total integrated oscillator strength is reduced to 71, leaving most of the total strength outside the model space. We find that these extra terms shift the plasmon energy to  $\hbar\omega \approx 20$  eV and decrease the oscillator strength by a factor of  $\approx 2$  when compared to the results in Figure 5.3(b). A similar plasmon mode at  $\hbar\omega \approx 22$  eV has been observed previously [27] in amorphous carbon films.

<sup>&</sup>lt;sup>7</sup>The oscillator strength is defined by  $f = 2m_e | < f |D_z| i > |^2 (E_f - E_i)/\hbar^2$ .



Figure 5.3: Dipole response of  $C_{60}$  clusters to an external electromagnetic field, shown in an expanded energy region. (a) Free response, (b) RPA response based on the charge term  $D_z^{(1)}$ , and (c) RPA response based on both the charge and the dipole terms  $D_z^{(1)}$  and  $D_z^{(2)}$  in Eq. (5.6). (d) Interacting response of a thin jellium shell, describing the electron-electron interactions in LDA. The response function is given by the solid line, and the integrated oscillator strength is shown by the dashed line [From G. F. Bertsch, A. Bulgac, D. Tománek, and Y. Wang, Phys. Rev. Lett. **67**, 2690 (1991)].

This high frequency Mie-like plasmon has its origin in the high valence electron density  $\rho$  in the C<sub>60</sub> cluster, and can be understood qualitatively by considering a conducting spherical shell with a radius  $R \approx 3.5$  Å and 240 conduction electrons. The Mie frequency for a solid conducting sphere is given by  $\hbar \omega = [4\pi \rho e^2/(3m)]^{1/2} \approx 25 \text{ eV}$ . We have also made a jellium calculation for a charged spherical shell using the program JELLYRPA [28], and find the strength function shown in Figure 5.3(d). The energy agrees with Figure 5.3(c), but in the jellium model the total oscillator strength is concentrated in the plasmon. An additional plausibility argument for the jellium picture of C<sub>60</sub> follows from the static polarizability  $\alpha$ . We find the classical conducting sphere value  $\alpha = R^3 = 290$  a.u. to be in good agreement with the tight-binding value of 250 a.u. and the quantum-chemical result [19]  $\alpha \approx 300 - 400$  a.u., depending on the basis set.

Our predictions for the Mie plasmon at  $\hbar \omega \approx 20$  eV have been confirmed by photoionization experiments on free C<sub>60</sub> clusters [22]. The C<sub>60</sub> photoion yield as a function of photon energy is reproduced in Figure 5.4 and shows a clear maximum in the predicted energy range. Note the low frequency cutoff in the experimental spectrum at the ionization potential of C<sub>60</sub> at 7.54 eV.

I would like to mention that there are several other effects that should be included in a more refined treatment of the response function. We have neglected higher multipolarities of the Coulomb screening field, as well as the exchange and correlations terms in the residual interaction. These additional terms could alter the very large screening factor for the lowest transitions. However, we feel that the dipolar Coulomb interaction is dominant in the Mie plasmon region, and a refinement of this interaction would not significantly affect the results. This has been confirmed by a subsequent calculation of Bulgac and Ju [18].



Figure 5.4: Observed  $C_{60}^+$  photoion yield as a function of photon energy displaying excitation of the giant plasmon resonance [From I. V. Hertel et al, Phys. Rev. Lett. **68**, 784 (1992)].

#### **5.3** Conclusions

I have presented results for the static and dynamic dielectric response of the  $C_{60}$  cluster, based on a tight-binding Hamiltonian for the single-particle states.

Our calculations of the polarizability and hyperpolarizability of the  $C_{60}$  cluster have shown that the valence electrons are quite delocalized. Its linear polarizability is close to that of a metal sphere and the hyperpolarizability is close to that of conjugated polymers which can be understood in the free electron model.

Our RPA calculations of the dynamical response indicate strong dynamical screening which results in a collective electronic plasmon mode in  $C_{60}$ . Due to the strong Coulomb interaction between the electrons, the lowest allowed excitation at  $\hbar\omega \approx$  $3 \ eV$  is strongly screened by a factor of 400 as compared to the free response, in good agreement with experiment. Other low lying dipole excitations are moderately suppressed. We predict a giant collective resonance at an unusually high energy  $\hbar\omega \approx 20 \ eV$ , which has been recently observed experimentally [22]. We interpret this mode as a Mie plasmon caused by the large delocalization of the carbon valence electrons and the large charge density.

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## Chapter 6 Summary and Conclusions

Cluster physics is a fascinating new field of growing importance. Thanks to my advisors, I have been able to actively participate in the research in this field, and to witness its rapid growth. In this Thesis I have investigated both metallic clusters and nonmetallic clusters. The main achievements of this Thesis are: (1) predictive calculations for the optical response of small Li<sub>n</sub> and Na<sub>n</sub> clusters, specifically the evolution and fragmentation of the plasmon mode; (2) predictions of the stiffness of C<sub>60</sub> fullerite as a function of external pressure; (3) prediction of the stability of the fullerite intercalation compounds; (4) investigations of the linear and nonlinear polarizability of the C<sub>60</sub> cluster; (5) predictions of the dynamical dielectric response of C<sub>60</sub>, specifically the high-frequency Mie plasmon mode.

In Chapter 1, I presented a brief overview of cluster properties. I have focused on the structural and electronic properties of alkali metal clusters and the  $C_{60}$  cluster and discussed the experimental techniques as well as theoretical concepts pertinent to my Thesis.

Chapter 2 has been devoted to the theoretical tools used in the study of clusters in this Thesis. I reviewed the techniques used in this Thesis, namely the Density Functional Formalism and the Local Density Approximation (LDA) as well as the tight-binding formalism for ground-state properties of clusters, and the Random Phase Approximation (RPA) for electronic excitations.

In Chapter 3, I have presented results for the equilibrium structure of small  $Na_n$ and  $Li_n$  clusters and collective electronic excitations and their damping in these systems. The results for the collective excitations in the first two closed-shell clusters with n = 2,8 atoms are given in detail. Our results indicate that the coupling of electronic levels to vibrational degrees of freedom accounts quantitatively for the observed width of the collective electronic excitations in alkali dimers. The origin of the analogous line broadening in  $Na_8$  is presently unresolved.

In Chapter 4, I have presented calculations of the equilibrium structure of  $C_{60}$  fullerite as a function of external pressure. I found that at zero pressure, carbon atoms in neighboring  $C_{60}$  clusters are no closer than 2.65 Å apart and interact by pairwise Van der Waals forces. Consequently, the bulk modulus of  $C_{60}$  should be very low, similar to a molecular solid. With increasing hydrostatic pressure, a gradual transition to a hard-core repulsion between neighboring clusters is predicted. Only at high pressures beyond  $\approx$ 70 GPa, the bulk modulus of fullerite is expected to exceed that of diamond, and a transition to diamond is predicted.

In order to sort out the likely candidates for  $C_{60}$  based superconductors, I have also calculated T = 0 K formation enthalpies of donor and acceptor based  $C_{60}$  fullerite intercalation compounds with the  $AC_{60}$ ,  $A_3C_{60}$ , and  $A_6C_{60}$  stoichiometries, as well as their structural and elastic properties. The results indicate that all alkali and some alkaline earth elements form stable fullerite intercalation compounds. The corresponding calculations for acceptor intercalants indicate that none of the group 6A and 7A based ionic intercalation compounds is stable with respect to solid  $C_{60}$ and the intercalant in the standard form. I have devoted Chapter 5 to the study of the electronic properties of the C<sub>60</sub> cluster. Our calculations, based on a parametrized tight-binding Hamiltonian, have proven the valence electrons to be quite delocalized, giving rise to a large polarizability and hyperpolarizability of the C<sub>60</sub> cluster. Our RPA calculations of the dynamical response indicate strong dynamical screening resulting in significant screening of low-lying excitations, and a giant collective resonance at an unusually high energy  $\hbar\omega \approx 20 \ eV$ . This mode, which has been recently observed experimentally, has been interpreted as a Mie plasmon mode, which results from the large delocalization of the valence electrons and their large charge density in C<sub>60</sub>.

