Calculation of the photoemission spectrum of fullerene

Gattari Paolo

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advisor: Nicola Manini

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Abstract

Photoemission from a degenerate shell of a high-symmetry molecule, as the outer shell of C$_{60}$, is necessarily accompanied by characteristic vibronic structures in the measured spectrum, associated to Jahn Teller (JT) splitting of the orbital degeneracy through electron-phonon interaction in the final state. The experimental C$_{60}$ spectrum [1, 2] shows a characteristic strong broad satellite at 230 meV from the main peak, significantly higher in energy than any characteristic vibrational frequency of C$_{60}$.

The purpose of the present work is to understand and explain quantitatively the measured spectrum. We use a linear and harmonic Jahn-Teller model, based on the DFT-LDA frequencies and couplings of Ref. [3] (including all the 66 active modes), to compute numerically and virtually exactly the C$_{60}$ photoemission spectrum from the HOMO (highest occupied molecular orbital). The computed lineshape shows dominant features close to experiment, in particular the satellite at 230 meV (left panel),

Our analysis explains this satellite in terms of the JT-vibronic splitting of the highest frequency $H_g$ modes ($H_g7$, 180 meV and $H_g8$, 197 meV). The increase in
vibron energy is a characteristic signature of the dynamic JT effect and can be understood on the basis of symmetry: the symmetry $h_u$ of the bare hole produced by photoemission from the HOMO, remains $h_u$ even in the presence of interacting vibrations. On the other hand, the average of the multiplet of states derived from the 1-vibration manifold is, to second order in the electron-phonon coupling $g$, independent of $g$, because the JT coupling is a traceless perturbation within that manifold. Within this multiplet (made of $H_g \times h_u = a_u + t_{1u} + t_{2u} + 2g_u + 2h_u$), the $h_u$ vibronic states are the sole that have another $h_u$ state (the GS itself) lower in energy and "pushing" them upward. (right panel). Our calculations confirm that the DFT-LDA parameters of Ref. [3] account for this energy increase, from 190 to 230 meV.

Technically, to compute the spectrum we separate the degenerate modes from the nondegenerate ones. We compute the contribution of the quite medium JT-coupled degenerate $H_g$ and $G_g$ modes, by Lanczos diagonalization of the electron-vibration Hamiltonian by continued fraction expansion of the finite-temperature spectrum, assuming thermal equilibrium of the sample. The trivial nondegenerate $A_g$ modes distort the molecule without splitting the orbital degeneracy. Their contribution is evaluated analytically and their effect is a weak general broadening of the spectrum. However, the $T = 0$ spectrum appears much more resolved than the experimental one, which is measured at 800 K.

The technique used, very efficient at $T = 0$, gives converging spectra at low temperature ($< 100$ K), but it becomes useless at higher temperature, due to the large number of initial thermal excitations. However, thermal effects influence mostly the lowest-frequency $H_g$-mode (which is the most strongly coupled). The inclusion of the $H_g1$ mode only, for which our technique gives converging results up to 800 K, is sufficient to account for most of the experimental broadening (left panel).
Chapter 1

Photoemission spectroscopy

1.1 Introduction

When light of short enough wavelength interacts with free molecules, it can cause electrons to be ejected from the occupied molecular orbitals. Photoelectron spectroscopy is the study of the photoelectrons, whose energy, abundances and angular distribution are all characteristic of the individual molecular orbitals from which they originate. The quantity measured most directly in photoemission spectroscopy is the ionization potential for the removal of electrons from different molecular orbitals. It is a well known basic result (Koopmans' theorem) that each ionization potential $I_j$ is equal in magnitude to an orbital energy, $\epsilon_j$:

$$I_j = -\epsilon_j$$  \hspace{1cm} (1.1)

This approximate result is very useful in that it indicates that the photoelectron spectrum of a molecule is a direct representation of the molecular orbital energies. Moreover, for a molecule, the photoemission spectrum gives not only the orbital energies but also, less directly, the changes in molecular geometry caused by the removal of one electron from each orbital. These changes reveal the character of the orbitals, whether they are bonding, antibonding or non-bonding, and where their bonding power is localized in the molecule.

1.2 Basic features of photoelectron spectra

In a photoelectron spectrometer, an intense beam of monochromatic ultraviolet or X-ray light ionizes the molecules or atoms of a gas in a ionization chamber:

$$M + h\omega \rightarrow M^+ + e$$  \hspace{1cm} (1.2)
The light used must have an energy sufficient to ionize electrons at least from the highest valence shell of molecules or atoms, that is the highest occupied molecular orbital (HOMO). If $h\omega$ is larger, electrons may be ejected also from deeper levels. In each orbital $j$ of an atom or molecule, the electrons have a characteristic binding energy, the minimum energy needed to eject them to infinity. Part of the energy of the photon is used to overcome this binding energy, $|\epsilon_j|$, and, if the species is an atom, the remainder, $h\omega - |\epsilon_j|$, must appear as kinetic energy ($E^e_k$) of the ejected electron:

$$E^e_k = h\omega - |\epsilon_j|$$

The ejected photoelectron are separated according to their kinetic energy in an electron energy analyzer, detected and recorded. The photoelectron spectrum is a record of the number of electrons detected at each energy: a peak is found in the spectrum at each energy $h\omega - E^e_k$ corresponding to the binding energy $|\epsilon_j|$ of an electron in the atom, as illustrated schematically in Fig. 1.1.

If the species is a molecule, there are the additional possibilities of vibrational


Figure 1.1: Idealized photoionization process and photoelectron spectrum of an atom
and/or rotational excitation upon ionization, so the energy of the photoelectrons may be reduced:

$$|\epsilon_j| - E_{\text{vib,rot}}^{\text{ion}} = \hbar \omega - E_k^e$$

The spectrum may now be decorated by several vibrational structure for each orbital: the system of lines that correspond to ionization from a single molecular orbital constitutes a band.

Apart from Koopmans' theorem, there are two simple rules that usually make the relationship between photoelectron spectra and molecular electronic structure especially simple: 1) Each band in the spectrum corresponds to ionization from a single molecular orbital.

2) Each occupied molecular orbital of binding energy less than $\hbar \omega$ gives rise to a single band in the spectrum.

Because of these rules, the photoelectron spectrum is a simple reflection of the molecular orbital diagram (Fig 1.1)). These rules are a simplification, however, and there are five reasons why there may, in fact, be more or fewer bands in a spectrum than there are valence orbitals in a molecule. Firstly, additional bands are sometimes found that correspond to the ionization of one electron with simultaneous excitation of a second electron to an unoccupied excited orbital. This is a two-electron process, and the bands produced in the spectrum are normally much weaker than simple ionization bands. Secondly, ionization from a degenerate occupied molecular orbital can give rise to as many bands in the spectrum as there are orbital components, because although the orbitals are degenerate in the molecule, they may not be so in the positive ion. The mechanisms that remove the degeneracy are spin-orbit coupling and Jahn-Teller effect. Thirdly, ionization from molecules like $\text{O}_2$ or NO, which have unpaired electrons, can give many more bands than there are occupied orbitals in the molecules, and in such instances neither Koopmans' theorem nor the simple rules apply. Fourthly, molecular orbitals lying close in energy may give rise to overlapping bands. Finally, finite temperature and the finite life time of excited electronic states usually lead to broadening and thus to the obliteration of some spectral features. In order to introduce these main features of photoelectron spectra, it is convenient to take practical examples, starting with the spectra of single atoms and proceeding to those of more complicated molecules.

### 1.2.1 Atoms

A typical atomic photoelectron spectrum is shown in Fig. 1.2. This is the photoemission spectrum of atomic mercury excited by helium resonance radiation. The vertical scale is the strength of the electron signal, usually given in electron per second. The absolute intensities have no physical significance because they depend on physical and experimental factors which, although constant throughout
the measurement of the spectrum, are not precisely known. The relative intensities of different peaks in the spectrum are meaningful, however, as they are equal to the relative probability of photoionization to different states of the positive ion, which are called the relative partial ionization cross-sections. Three horizontal scale are given on Fig. 1.2 to illustrate the relationship between measured electron energy, ionization potential and the internal excitation energy of the ions, including electronic excitation energy.

The spectrum in Fig. 1.2 show that Hg\(^{+}\) ions are formed by photoionization in three electronic states, with ionization energies of 10.44, 14.84, and 16.71 eV. The states involved are well known from the atomic spectrum of mercury and have the designation \(^2\text{S}_{\frac{1}{2}},\) \(^2\text{D}_{\frac{5}{2}}\) and \(^2\text{D}_{\frac{3}{2}},\) respectively. In particular, the \(^2\text{S}_{\frac{1}{2}}\) state of Hg\(^{+}\) is produced by the ejection of one of the 6s electrons (the neutral electron configuration is 5d\(^{10}\)6s\(^2\)), but both the \(^2\text{D}\) states are produced by the ejection of 5d electrons. Notice the energy difference between the \(^2\text{D}_{\frac{5}{2}}\) and \(^2\text{D}_{\frac{3}{2}}\) states arising from 5d ionization: it represents a breakdown of the rule of one band per orbital, in this instance due to spin-orbit coupling. Then the Koopmans’ theorem (1.1) cannot be used directly to derive the orbital energy for 5d electron in mercury, and a weighted mean of all the energies for ionization for a single orbitals must be taken, where the weights are the statistcal weight of the ionic states produced.

In spite of these small intricacies the photoemission spectrum of an atom is quite
1.2. BASIC FEATURES OF PHOTOELECTRON SPECTRA

1.2.2 Molecules

The photoemission spectrum of the diatomic molecule $N_2$ is shown in Fig. 1.3 as the next step in the hierarchy of complication. Three electronic states of $N_2^+$ are reached by photoionization, and they appear in the spectrum as the sharp peak at 15.6 eV, the group of peaks between 16.7 and 18 eV and the weak peak at 18.8 eV. Each electronic state actually gives a group of peaks in the spectrum because of the possibility of vibrational as well as electronic excitation. Every resolved peak in the spectrum of a molecule is a single vibrational line and represents a definite number of quanta of vibrational energy in the molecular ion.

As was the case for mercury, the ionic states of $N_2^+$ seen in the photoemission spectrum are well characterized by other forms of spectroscopy. They have the designation X $^2\Sigma_g^+$, A $^2\Pi_u$, and B $^2\Sigma_u^+$ in order of increasing ionization potential, and correspond to the process $\sigma_{g}^{-1}$, $\pi_{u}^{-1}$ and $\sigma_{u}^{-1}$ respectively.

It is clear that the bands in the spectrum of this three ionization are very different both in the spacing of the lines within each bands, i.e. the sizes of the vibrational quanta in the ions, and also in the intensity of the vibrational lines. The spacings...
between the lines depends on the vibrational frequencies in the different electronic states of the ion, since for the vibrational excitation energies $E_{\text{vib}}^{\text{ion}}$:

\[
E_{\text{vib}}^{\text{ion}} = (v + \frac{1}{2})\hbar \omega
\]

Here $v$ is the vibrational quantum number and $\omega$ the vibrational frequency, which depends on the strength of the N-N bond in the different electronic states. Therefore if a bonding electron is removed, the bond becomes weaker, and the vibrational frequency $\omega$ becomes lower than in the neutral molecule. This is exactly what happens in $\pi_u^{-1}$ ionization of $N_2$, where the frequency drops from 2360 cm$^{-1}$ in the molecule to 1800 cm$^{-1}$ in the $A^2\Pi_u$ state of $N_2^+$, indicating the strongly bonding character of $\pi_u$ electrons. Vice versa any antibonding character of the electrons removed on ionization is revealed by an increase in frequency, and an example of this is the $\pi_g^{-1}$ ionization of molecular oxygen (giving a single state in the molecular ion, $X^2\Pi_g$ and a single band in the spectrum), shown in Fig. 1.4.

The relative intensities of the vibrational lines in a ionization band are also related to the bonding power of the removed electron. Strong vibrational excitation is associated to a change in equilibrium bond length up on ionization and the relation between them is given by the Franck-Condon principle. According to this principle when strongly bonding electrons are removed many peaks appear corresponding to different final vibrational states of the ion. For antibonding electrons instead one, or
few peaks appear, given by the transition to the ground or lower excited vibrational states.

The spectra of molecules with more than two atoms are naturally more complex, because there are generally more molecular orbitals from which ionization can take place and many different modes of vibration that may be excited by ionization. As example, in Fig. 1.5 we show the photoemission spectrum of the water. H$_2$O is a simple triatomic molecule, with 3 modes of vibration, and its spectrum is still quite clean.

One important principle is that the vibration that corresponds most closely to the change in equilibrium molecular geometry caused by a particular ionization will be one that is most strongly excited. In a band that shows excitation of several modes, it can easily happen that the vibrational structure is so complex that the individual lines cannot be resolved and a continuous contour is observed. Such unresolved bands are, in fact, much more common that resolved bands in the spectra of molecules with five or more atoms.

In addition to the complexity of overlapping vibrational structures, one more reason of the presence of continuous bands in the spectra is short lifetime of the ion in the molecular ionic states in which they are initially formed. If a molecular ion in a given state has a lifetime $\tau$ for dissociation, radiative decay or internal conversion to another electronic state, the original state will have an energy width $\Delta E$, given
CHAPTER 1. PHOTOEMISSION SPECTROSCOPY

Figure 1.6: The gas phase photoemission spectrum is a probe of the valence orbitals of C$_{60}$, while matrix-isolated C 1s XAS data probe its empty molecular orbitals. The data are placed on a common binding energy scale (from Ref. [5]).

by the uncertainty principle:

$$\Delta E \sim \frac{\hbar}{\tau}. \quad (1.6)$$

This energy uncertainty causes a broadening of all spectral lines and may make the band continuous. This cause of broadening occurs even in the photoelectron spectra of diatomic molecules.

1.3 Fullerene C$_{60}$

Figure 1.6 shows a wide-range gas-phase photoemission spectrum of fullerene C$_{60}$, the main object of our investigation. One can immediately get a sense of the high degree of orbital degeneracy which is the hallmark of C$_{60}$: although the system has 60 $\pi$-electrons, the photoemission spectrum shows only an handful of distinct bands at low binding energy. It is in fact relatively straightforward to correlate the features in the spectrum with the different molecular orbitals of icosahedral C$_{60}$. The peaks nearest the chemical potential originates from the $h_u$ HOMO. The peak which comes next in energy is due to the $h_g$ and $g_g$ states and is generally referred as the HOMO-1. Both the HOMO and HOMO-1 are pure $\pi$ molecular orbitals. The features at higher
1.3. FULLERENE $C_{60}$

energy results from the overlaps of both $\pi$ and $\sigma$ molecular orbitals. Figure 1.6 shows also the corresponding C 1s excitation spectrum of matrix isolated $C_{60}$ measured using XAS, and placed on a common binding energy scale, revealing the $t_{1u}$ LUMO (Lowest Unoccupied Molecular Orbitals), as well as structures at higher energy.

In this work we are interested to investigate the vibronic structures that necessarily accompany the photoemission from the HOMO. In fact photoemission from a closed-shell high-symmetry molecule, as $C_{60}$, involves the Jahn-Teller effect in the final states, splitting the orbitals degeneracy, and this reflects in a higher complexity of the corresponding band. We therefore concentrate in understanding the detailed features of the broad peak labeled HOMO in Fig. 1.6.
Chapter 2

Molecular physics

The purpose of this chapter is to summarize the basic theoretical concepts of molecular physics and single out the approximations which lead to the choice of the model, described in detail in the following chapter, for photoemission of a molecule such as $C_{60}$.

If the wave equation for a molecule composed of electrons and nuclei is set up, a procedure (the so-called Born-Oppenheimer approximation) exists whereby this equation may be separated into two equations, one of which governs the electronic motions and yields the forces holding the atoms together, whereas the other is the equation for motions of rotation and vibration of the positive ions. On the basis of this approximation, the forces between the atoms are routinely calculated numerically from the electronic wave equation, by means of standard techniques generically indicated by \textit{ab-initio} methods. The separation of the electronic and ionic motions is an approximation which often works very well, but can break down in the presence of electronic degeneracies or large excitation energy of the ionic motion [6].

2.1 The Born-Oppenheimer approximation

The total non relativistic Hamiltonian for a molecule can be written

$$
H = -\frac{\hbar^2}{2} \sum_k \frac{\nabla^2_{\bar{R}_k}}{M_k} - \frac{\hbar^2}{2m_e} \sum_i \nabla^2_{\bar{r}_i} - \sum_{k,i} \frac{Z_k e^2}{|\bar{R}_k - \bar{r}_i|} + \sum_{k>t} \frac{Z_k Z_t e^2}{|\bar{R}_k - \bar{R}_t|} + \sum_{i>j} \frac{e^2}{|\bar{r}_i - \bar{r}_j|} \tag{2.1}
$$

where $i, j$ refer to electrons and $k, t$ refer to nuclei, $M_k$ is the mass of the $k$-th nucleus, $m_e$ is the mass of the electron, $e^2 = \frac{q^2}{4\pi\epsilon_0}$ is the electromagnetic coupling constant, with $q_e$ representing the elementary charge. Indicating collectively with $R$ all the nuclear coordinates $\bar{R}_k$, and $r$ all the electron coordinates $\bar{r}_i$, the Hamiltonian (2.1)
can be written more compactly as
\[ H = T_n + T_e + V_{en}(r, R) + V_{nn}(R) + V_{ee}(r) \] (2.2)
where \( T_n \) and \( T_e \) are the nuclear and electronic kinetic energies, \( V_{en} \) is the electron-ion attraction, \( V_{nn} \) and \( V_{ee} \) are the ion-ion and the electron-electron repulsion respectively. The \( V_{en} \) term prevents us from separating \( H \) into nuclear and electronic parts, thus separating the molecular wavefunction into a product of nuclear and electronic terms
\[ \Psi(r, R) = \psi(r)\phi(R). \] (2.3)
Moreover, the attractive term \( V_{en} \) is large and can neither be neglected nor treated as a perturbation. It is responsible, in particular, of the cusp-like behavior of the electronic wavefunction at \( r_i \to R_k \), and, more importantly, of chemical bonding.

The best progress toward a reasonable separation of the nuclear and electronic motion can be achieved by introducing a parametric \( R \) dependence in the electronic wavefunction, so that the total wavefunction reads
\[ \Psi(r, R) = \psi(r; R)\phi(R). \] (2.4)
This ansatz is justified by the following observations: a) The electron mass \( m \) is much smaller than the ionic mass \( M_k \), thus the time scale for the electronic motion is much faster than that for the ionic movement; b) Different energy levels corresponding to different electronic eigenstates are separated by energy gaps which are large with respect to the corresponding separation between ionic eigenstates (i.e. with respect to the characteristic energies associated to the motion of the ions).

According to this adiabatic (or Born-Oppenheimer) approximation, once an electronic state has been selected, the ions move without inducing transitions between different electronic states. The electronic wavefunction \( \psi(r; R) \) hence describes the electronic state corresponding to a given frozen geometrical configuration of the nuclei. By definition \( \psi(r; R) \) satisfies the parametric Schrödinger equation:
\[ H_e \psi_{\alpha}(r; R) = U_\alpha(R)\psi_{\alpha}(r; R), \] (2.5)
where
\[ H_e = T_e + V_{en}(r, R) + V_{nn}(R) + V_{ee}(r) \] (2.6)
With \( \alpha \) we represent the set of quantum numbers characterizing a given eigenstate with electronic energy \( U_\alpha(R) \), to be recognized as the (adiabatic) potential energy surface that governs the motion of the nuclei. Notice that \( \psi_{\alpha}(r; R) \) is a many-body eigenstate, since no mean field approximation has been introduced yet.

Consider again the original complete Hamiltonian (2.2). It can be rewritten using (2.6)
\[ H = T_n + H_e \] (2.7)
2.1. THE BORN-OPPENHEIMER APPROXIMATION

The most general solution of the complete molecular Schrödinger equation

$$(H - E)\Psi(r, R) = 0$$  \hspace{1cm} (2.8)

can be obtained, in terms of the individual electronic wavefunctions $\psi_\alpha(r; R)$, by using an (in principle infinite) expansion of the form

$$\Psi(r, R) = \sum_\alpha \psi_\alpha(r; R)\phi_\alpha(R).$$  \hspace{1cm} (2.9)

Here $\phi(R)$ are nuclear-coordinate dependent coefficients, we interpret as the nuclear wave functions. To the extent that the Born-Oppenheimer approximation is valid, accurate solution can be obtained using only one (Eq. (2.4)) or a few terms. Substituting Eq. (2.9) into Eq. (2.8), multiplying it from the left by $\psi_\beta^*(r; R)$ and integrating over the electronic coordinates while recalling Eqs. (2.7) and (2.5), yields the following set of coupled equations

$$\int \psi_\beta^*(r; R)T_n\phi_\alpha(R)\psi_\alpha(r; R)dr + \left(U_\beta(R) - E\right)\phi_\beta(R) = 0$$  \hspace{1cm} (2.10)

where, from now to the end of this section, we omit the sum over the repeated index $\alpha$. Using the explicit expression for $T_n$ the molecular kinetic term gives three contributions: one \textit{adiabatic} term involving only the nuclear wavefunction

$$T_n\phi_\beta(R) = \sum_k -\frac{\hbar^2}{2M_k}\nabla^2_{R_k}\phi_\beta(R)$$  \hspace{1cm} (2.11)

and two \textit{non-adiabatic} contributions coupling the electronic and nuclear motion

$$N^1_{\beta\alpha}\phi_\alpha(R) = \sum_k -\frac{\hbar}{M_k}\int [\psi_\beta(r; R)\nabla_{R_k}\psi_\alpha(r; R)]dr \nabla_{R_k}\phi_\alpha(R)$$  \hspace{1cm} (2.12)

and

$$N^2_{\beta\alpha}\phi_\alpha(R) = \sum_k -\frac{\hbar}{2M_k}\int \left[\psi_\beta(r; R)\nabla^2_{R_k}\psi_\alpha(r; R)\right]dr \phi_\alpha(R)$$  \hspace{1cm} (2.13)

The Schrödinger equation is finally rewritten compactly as

$$\left(T_n + U_\beta(R) - E\right)\phi_\beta(R) + \left(N^1_{\beta\alpha} + N^2_{\beta\alpha}\right)\phi_\alpha(R) = 0$$  \hspace{1cm} (2.14)

The non-adiabatic terms $N^1$ and $N^2$, coupling together the motions associated to different electronic eigenvalues, become negligible if the variation of $\psi_\alpha(r; R)$ with the nuclear coordinates is sufficiently slow. Born and Oppenheimer have shown, using the mathematical expression of the arguments at points a and b above, that
this conditions is usually fulfilled to a satisfactory approximation. In this case the nuclear equation is totally decoupled from the electronic ones and it can be written

\[
(T_n + U_\beta(R) - E_\beta,w) \phi_{\beta,w}(R) = 0
\] (2.15)

With \( w \), we represent the set of quantum number characterizing a given ionic eigenstate \( \phi_{\beta,w}(R) \) with eigenvalues \( E_\beta,w \) where the subscript \( \beta \) labels the choice of the electronic state. \( U_\beta(R) \) are the adiabatic molecular potential energy surfaces that govern the motion of the nuclei. They contain the direct Coulomb repulsive nuclear interaction \( V_{nn} \) and the electronic contributions that can be considered as the "glue" which keeps the atoms together. \( U_\beta(R) \) are in general complicated functions of all the nuclear coordinates \( R \). In particular, they cannot be generally expressed as a simple sum of two body contributions.

Every electronic state of a polyatomic molecule is characterized by a different potential surface. If a given electronic potential surface \( U_\beta(R) \) shows no minimum as a function of \( R \), that electronic state is unstable and the molecule in that state is likely to dissociate. If \( U_\beta(R) \) has at least one deep enough global minimum \( R_0 \), then the molecule is stable in the electronic state \( \beta \). The minimum \( U_\beta(R_0) \) of the potential surface of a given stable electronic state is considered as the electronic energy of this state and designated \( E_\beta^e \).

The total energy may then be written, in this approximation

\[
E_{\beta,w} = E_\beta^e + E_{\beta,w}^{vib}
\] (2.16)

where \( E_{\beta,w}^{vib} \) is the vibrational energy obtained from the solution of the Schrödinger equation for the ions Eq. (2.15). The corresponding adiabatic eigenstate is then simply as in (2.4)

\[
\Psi_{\beta,w}(r, R) = \psi_\beta(r; R) \phi_{\beta,w}(R)
\] (2.17)

The potential minima \( R_0^{(\beta)} \) of different electronic states occur, in general, at different values of internuclear distances and angles often characterized by different geometrical symmetries. Moreover, potential surfaces with several minima occur not infrequently (sometimes corresponding to different isomers)\( \text{[7]} \), for example for the electronic ground state of NH\(_3\) and cis/trans difluoro etylene (CHF)\(_2\). In \( E_{\beta,w}^{vib} \) the roto-translational contributions are tacitly included, which can be seen as zero-frequency normal vibrations essentially decoupled from the other ones. They can be ignored if we choose a reference system rigidly tied to the molecule.

There is a whole class of interesting situations where the Born-Oppenheimer approximation fails. The non-adiabatic terms in (2.14) become sizable and in the expression for the total energy (2.16) non-adiabatic contributions need to be accounted for. These terms couple electronic and nuclear motion, inducing transitions between electronic states. Typical examples are molecules with degenerate or almost degenerate ground state, where transitions between the degenerate states are
easily induced by this coupling. The true eigenstates then will be expanded as linear combinations of the Born-Oppenheimer solutions (2.17)

\[ \Psi^g(r, R) = \sum_{\beta, w} c_{\beta, w}^g \psi_\beta(r; R) \phi_{\beta, w}(R). \] (2.18)

Here \( c_{\beta, w}^g \) are expansion coefficients, and the subscript \( g \) has been added as a reminder that there are multiple solutions to the Schrödinger equation. (2.18) is an infinite expansion, but normally few terms are needed to get accurate solutions.

### 2.2 Electronic states

The equation for the electronic system (2.5) is a many-body equation depending on the coordinates \( r = \tilde{r}_1, \tilde{r}_2, \ldots \) of all the electrons of the system and parametrically on the nuclear configuration \( R \). It must necessarily be treated by standard approximate methods of quantum many-body theory, such as the Hartree-Fock method [8], or the Density Functional Theory [9], or Quantum Monte Carlo techniques [10].

As mentioned in section above, in a first approximation (which is normally a good approximation) the electronic motion is studied at the equilibrium positions of the ions. Therefore, for the rest of this section, we do not indicate explicitly the dependencies of the electronic eigenfunctions from the nuclear equilibrium configurations \( R_0 \).

Mean-field approximations typically reduce Eq. (2.5) to a single one-body equation for the one-electron wavefunctions of the system, typically to be solved self-consistently. If \( \epsilon_a \) and \( \tilde{\psi}_a(\tilde{r}_i) \) are respectively the eigenvalues and the corresponding eigenstates of this one-body equation, the total electronic energy can be written

\[ E_e^\alpha = E_{MB} + \epsilon_{a_1} + \epsilon_{a_2} + \ldots + \epsilon_{a_{n_e}} \] (2.19)

where \( E_{MB} \) is some many-body energy and the corresponding eigenstates are in the form of Slater determinants of single-particle wavefunctions:

\[ \psi_\alpha(r) = \frac{1}{\sqrt{n_e}} \sum_P (-)^P \tilde{\psi}^{P}_{a_1}(\tilde{r}_1) \tilde{\psi}^{P}_{a_2}(\tilde{r}_2) \ldots \tilde{\psi}^{P}_{a_{n_e}}(\tilde{r}_{n_e}) \] (2.20)

where \( n_e \) is the total number of electrons of the molecule, \( a_i \) are the sets of quantum numbers for the single particle problem and \( \alpha = (a_1, \ldots, a_n) \) is given in terms of those. The summation involves all the permutations \( P \) of the \( n_e \) quantum numbers.

In the second-quantized language, the electronic Hamiltonian can be represented on the basis of the fixed single-particle orbitals as

\[ H^e = \sum_a \epsilon_a c_a^\dagger c_a + E_{MB} \] (2.21)
where the operator $c^\dagger_a$ creates an electron in the single particle level $a$ and $c_a$ is the corresponding annihilator. The operator $N_a = c^\dagger_a c_a$ gives the number of electrons in spin-orbital $a$ and it can be either 0 or 1 for fermions. The many-body term in Eq. (2.21)

$$E^{MB} = F_{ee}(\{c^\dagger\}, \{c\}) \quad (2.22)$$

is a function of all the creators and annihilators, globally indicated with $\{c^\dagger\}$ and $\{c\}$. The subscript $ee$ underlines the electron-electron character of this interaction. To treat electron correlations explicitly, nontrivial linear combinations of Slater determinants (2.20) may be considered (configuration interaction - CI - method).

### 2.3 Molecular vibrations

Useful information for the solution of the adiabatic equation (2.15), describing the motion of the ions, are obtained within a classical scheme. Specifically, the classical small oscillations around the equilibrium positions, form the basis for the solution of the quantum problem (2.15).

Consider the adiabatic potential energy surface $U_\alpha(R)$ governing the motion of the nuclei, given by equation (2.23). The dependence on the electronic state $\alpha$ will be left implicit in this Section. By taking $\bar{u}_i = \bar{R}_i - \bar{R}_{0i}$ to represent the displacement of the $i$-th atom away from its equilibrium position $\bar{R}_{0i}$, we can write an expansion of $U(R)$ around its minimum value

$$U = U(R_0) + \sum_{i,z} \frac{\partial U}{\partial u_{i,z}} \bigg|_{u_{i,z}=0} u_{i,z} + \frac{1}{2} \sum_{i,j,z,r} \frac{\partial^2 U}{\partial u_{i,z} \partial u_{j,r}} \bigg|_{u_{i,z}=0} u_{i,z} u_{j,r} + \ldots \quad (2.23)$$

where $i, j$ label the $N$ atoms of the molecule, whereas $z, r$ for their Cartesian coordinates and $U(R_0) = E_\alpha^e$ is the electronic contribution at the minimum. The first-order derivatives are zero since $R_0$ is a minimum. We indicate the force constant matrix $\Phi_{ij\alpha}$ (or Hessian matrix) as follows:

$$\Phi_{ij\alpha} = \frac{\partial^2 U}{\partial u_{i,z} \partial u_{j,r}} \bigg|_{u_{i,z}=0} \quad (2.24)$$

It represents the $r$ component of the force generated on the atom $j$, when the atom $i$ is displaced by a small amount in the direction $z$. For isolated systems, the translation and rotational invariance conditions reduce the number of independent elements in this matrix.

For vibration of small amplitude, it is safe to truncate the expansion (2.23) of the total potential to second order. This is called harmonic approximation. The
2.3. MOLECULAR VIBRATIONS

classical Lagrangian corresponding to the quadratic potential

$$\mathcal{L} = \frac{1}{2} \sum_{i,z} M_i \ddot{u}_{i,z}^2 - \frac{1}{2} \sum_{i,j,z,r} \Phi_{ijzr} u_{i,z} u_{j,r}$$  \hspace{1cm} (2.25)$$
yields the following Lagrange equations

$$M_i \ddot{u}_{i,z} + \sum_{j,r} \Phi_{ijzr} u_{j,r} = 0.$$  \hspace{1cm} (2.26)$$
This is a system of $3N$ coupled linear differential equations. Since we want to include on the same footing also the case of a system containing different masses, its convenient to scale the displacement coordinates $\bar{u}$ introducing a mass-weighted displacement coordinates, defined as

$$\bar{q}_i = \sqrt{M_i} \bar{u}_i$$  \hspace{1cm} (2.27)$$
The linear system (2.26) becomes, in terms of $\bar{q}_i$

$$\ddot{q}_{i,z} + \sum_{j,r} D_{ijzr} q_{j,r} = 0$$  \hspace{1cm} (2.28)$$
where $D$ is the dynamical matrix of the system

$$D_{ijzr} = \frac{1}{M_i M_j} \Phi_{ijzr}$$  \hspace{1cm} (2.29)$$
Substituting a general oscillatory solution $q_{i,z} = A_{i,z} \cos(\omega t + \phi)$ in (2.26) we get

$$\sum_{j,r} (\delta_{ij} \delta_{zr} \omega^2 - D_{ijzr}) A_{j,r} = 0$$  \hspace{1cm} (2.30)$$
The problem reduces to a canonical algebraic diagonalization for the dynamical matrix $D$. The non vanishing eigensolutions are those which satisfy the secular equation

$$\det(\omega^2 \mathbf{I} - D) = 0$$  \hspace{1cm} (2.31)$$
The dynamical matrix is a real and symmetric $3N \times 3N$ matrix and can be diagonalized by an orthogonal transformation (i.e. a basis change). The new set of coordinates $Q_v$ which diagonalize the dynamical matrix are called normal coordinates of vibration, and defined by a linear transformation of displacements. The $3N$ eigenvalues of $D$, $\omega_v^2$, are the squared frequency of the normal modes of vibration for the system considered. Due to the translational and rotational invariance, it is possible to show that for a system with $N$ non-collinear atoms, only $N_{osc} = 3N - 6$
eigenvalues are nonzero ($N_{\text{osc}} = 3N - 5$ for linear molecules). The six (five) zero-frequency modes correspond to the rigid translations and rotations of the system.

In terms of the $Q_k$ the quadratic part of the potential energy expansion (2.23) has the form

$$U = \sum_{k=1}^{N_{\text{osc}}} \omega_k^2 Q_k^2$$  \hspace{1cm} (2.32)

It can be easily shown that the kinetic energy retains its original quadratic form when expressed in normal coordinates. The Hamiltonian, describing the nuclear motion can then be written, in terms of the normal modes, as

$$H_{\text{vib}} = \sum_{k=1}^{N_{\text{osc}}} \left( \frac{1}{2} P_k^2 + \frac{1}{2} \omega_k^2 Q_k^2 \right)$$  \hspace{1cm} (2.33)

where $P_k = \hat{P}_k$ are the conjugated moments to the normal coordinates $Q_k$. In Eq. (2.33) we have left out the translational and rotational contributions, which decouple if we choose a reference system rigidly tied to the molecule.

The system is hence equivalent to a collection of $N_{\text{osc}}$ independent harmonic oscillators. As anticipated, the quantum solution is immediately obtained from the classical one by quantizing each harmonic oscillator in the standard way, promoting $Q_k$ and $P_k$ to operators with the canonical commutation rules, $[\hat{Q}_k, \hat{P}_{k'}] = i\hbar \delta_{kk'}$. It is convenient to rescale the normal coordinates by a non-canonical transformation to dimensionless ones: $\sqrt{\frac{m}{\hbar}} \hat{Q}_k \rightarrow \hat{Q}_k$ and $\sqrt{\frac{1}{\hbar \omega_k}} \hat{P}_k \rightarrow \hat{P}_k$ with $[\hat{Q}_k, \hat{P}_{k'}] = i\hbar \delta_{kk'}$. Then Hamiltonian (2.33) reads

$$H_{\text{vib}} = \frac{1}{2} \sum_{k=1}^{N_{\text{osc}}} \hbar \omega_k (\hat{P}_k^2 + \hat{Q}_k^2)$$  \hspace{1cm} (2.34)

The usefulness of this form is that it yields naturally the phonon description of the molecular vibration in terms of creation and annihilator operators, respectively defined, for each normal mode, by

$$a_k \equiv \frac{1}{\sqrt{2}} (\hat{Q}_k + i\hat{P}_k), \hspace{1cm} a_k^\dagger \equiv \frac{1}{\sqrt{2}} (\hat{Q}_k - i\hat{P}_k)$$ \hspace{1cm} (2.35)

In this language, Eq. (2.34) can be rewritten

$$H_{\text{vib}} = \sum_{k=1}^{N_{\text{osc}}} \hbar \omega_k \left( a_k^\dagger a_k + \frac{1}{2} \right)$$ \hspace{1cm} (2.36)
with nonnegative integer eigenvalues of the number operator $a_k^\dagger a_k$, that following
the standard notation of molecular spectroscopy, we shall indicate as $v_k$. Hence, the
quantum many-body problem for the nuclei, if adiabaticity and harmonicity condi-
tions are satisfied, can be solved exactly. The solutions of the Schrödinger equation
(2.15) for the vibrational motion are expressed in terms of the eigenvalues $E_{v_k}$ and
the corresponding eigenstates $\varphi_{v_k}$ of the single normal modes $Q_k$ of frequency $\omega_k$, given by:

$$E_{v_k} = \hbar \omega_k (v_k + \frac{1}{2})$$

(2.37)

$$\varphi_{v_k}(Q_k) = N_{v_k} e^{-\frac{Q_k^2}{2}} H_{v_k}(Q_k), \quad N_{v_k} = \left( \frac{1}{\pi^{1/2} v_k!} \right)^{1/2}$$

(2.38)

where $H_{v_k}(Q_k)$ are Hermite polynomials [11]. $\varphi_{v_k}(Q_k)$ are eigenstates of the number operators $a_k^\dagger a_k$ with eigenvalues $v_k$ and can be interpreted as states containing exactly $v_k$ “phonons” of frequency $\omega_k$. The complete eigenvalues are

$$E_{v}^{\text{vib}} = E_{v_1} + E_{v_2} + \ldots + E_{v_{\text{Nosc}}} = \sum_{k=1}^{\text{Nosc}} \hbar \omega_k (v_k + \frac{1}{2}),$$

(2.39)

and the corresponding eigenstates

$$\phi_{v}(Q) = \varphi_{v_1}(Q_1) \varphi_{v_2}(Q_2) \ldots \varphi_{v_{\text{Nosc}}}(Q_{\text{Nosc}}).$$

(2.40)

$v$ indicates collectively the set of phonons’ quantum numbers $v_1, v_2, \ldots, v_{\text{Nosc}}$. The state $\phi_{v}(Q)$ is then a state with $v_1$ phonons of frequency $\omega_1$, $v_2$ phonons of frequency $\omega_2$ and so on. It is useful to observe that the ground-state, for which all quantum numbers are zero, has energy equal to $\frac{1}{2} \sum_{k=1}^{\text{Nosc}} \hbar \omega_k$ above the bottom of the adiabatic potential well $U(R_0)$, which may be of considerable magnitude in polyatomic molecules. This is just a quantum effect. Sometimes in this work we use the more compact Dirac form for the total vibrational eigenstate $\phi_{v}(Q)$

$$|v\rangle = |v_1 v_2 \ldots v_{\text{Nosc}}\rangle$$

(2.41)

In the general cases, when we have large distortions and the harmonic approx-
imation fails, higher-order terms of the potential expansion (2.23) are to be con-
sidered. They may be interpreted as interactions between the phonons. Collective
terms $\Delta E_{v}$ have to be added to the simple expression (2.38) for the total energy. Moreover, the eigenstates will be linear combinations of the harmonic ones (2.40). The general Hamiltonian, in terms of the normal modes $Q$, takes the form

$$H = \frac{1}{2} \sum_{k=1}^{\text{Nosc}} \hbar \omega_k \left( \hat{P}_k^2 + \hat{Q}_k^2 \right) + G_{pp}(\hat{Q})$$

(2.42)
where $G_{pp}$ is a function of all the normal coordinates $\hat{Q}$ globally accounting for the anharmonic terms of the potential energy (2.23). Inverting relations (2.33)
\[
\hat{Q}_k = \frac{1}{\sqrt{2}}(a_k^\dagger + a_k), \quad \hat{P}_k = \frac{i}{\sqrt{2}}(a_k^\dagger - a_k)
\]
we can rewrite Eq. (2.42) in terms of creators and annihilators
\[
H = \frac{1}{2} \sum_{k=1}^{N_{osc}} \hbar \omega_k \left( a_k^\dagger a_k + \frac{1}{2} \right) + G_{pp}(\{a^\dagger\}, \{a\})
\]
where with $\{a^\dagger\}$ and $\{a\}$ we compactly indicate all creators and annihilators. This picture underlines the phononic character of the vibronic motion and the subscript $pp$ indicates the phonon-phonon character of the anharmonic interactions.

### 2.4 The full molecular Hamiltonian

Combining the results of the previous sections, we can rewrite the vibronic Hamiltonian (2.4) in a form which explicitly shows the approximations used to approach the problem. Recalling Eqs. (2.21), (2.22) and (2.42), the adiabatic part of Hamiltonian (2.1) reads
\[
H^{adi} = \sum_a \epsilon_a \ c_a^\dagger c_a + \frac{1}{2} \sum_{k=1}^{N_{osc}} \hbar \omega_k \left( \hat{P}_k^2 + \hat{Q}_k^2 \right) + F_{ee}(\{c^\dagger\}, \{c\}) + G_{pp}(\hat{Q})
\]
Here, the first term represents the single-electron contributions, the second term is the harmonic phonon Hamiltonian, as a function of the normal modes of frequency $\omega_k$, where it is implicitly understood that $\omega_k$, the equilibrium positions $R_0$ and the normal-mode coordinates $Q_k$ depend on the electron occupancies. The next two terms, $F_{ee}$ and $G_{pp}$ (Eqs. (2.22) and (2.42)), can be seen as corrections to independent-electrons and independent-vibrations approximations: they describe respectively electron-electron correlations terms and anharmonic phonon-phonon interactions. The electron-phonon picture of the system can equivalently well be expressed in terms of phonon creators and annihilators as in Eq. (2.44) or in terms of the normal distortions $\hat{Q}$, related to the creation operators by Eq. (2.43). In this electron-phonon picture, the non-adiabatic terms, ignored until now, appear as electron-phonon interactions which can globally be described by a function $I_{ev}$ of the electronic creators and annihilators $\{c^\dagger\}$, $\{c\}$ and of the normal distortions $\hat{Q}$. The Hamiltonian (2.4) can then be rewritten as
\[
H = H^{adi} + I_{ev}(\{c^\dagger\}, \{c\}, \hat{Q})
\]
2.5. SYMMETRY AND VIBRONIC STATES CLASSIFICATION

For example, a linear e-v interaction, like $c^\dagger_a c_b Q_v$, describes a process in which a phonon absorption or creation induces an electron to jumps from state $b$ to state $a$. In general the form of these interactions terms (this is true also for $F_{ee}$ and $G_{pp}$) is restricted by some symmetry property they have to satisfy, e.g. translational and rotational invariance, point group symmetry. Electron-phonon terms are especially relevant when the electronic and vibrational excitation energies are of comparable size: typically, significant effects are observed only involving electrons states close to the Fermi energy. In particular e-v couplings are important for orbitally degenerate or almost degenerate electronic ground states, where inducing transitions between different electronic levels is especially easy.

2.5 Symmetry and vibronic states classification

We conclude this chapter with some note about the importance of symmetry considerations to classify molecular states. Each molecule in its equilibrium configuration may be characterized by a certain set of symmetry operations under which it is invariant. This set forms the point symmetry group of the molecule and may be composed mainly by three kinds of operations: rotations by an integer fraction of $2\pi$ about an axis, reflections with respect to a plane and reflections around a point (space inversion)

In the Schrödinger equation for the electron motion (2.3), $V_e = H_e - T_e$ is the potential energy that the fixed nuclei in their equilibrium position induce on the electrons (2.6). Therefore $V_e$ has the symmetry of the molecule in that particular equilibrium configuration. Thus, if a symmetry operation is carried out, the Schrödinger equation for the electronic motion remains unchanged. As a consequence, the electronic eigenfunction for nondegenerate states can only be symmetric or antisymmetric for each of the symmetry operations permitted by the symmetry of the molecule in the equilibrium position. For degenerate states, the eigenfunction can only change into a linear combination of the other degenerate eigenfunctions such that the square of the eigenfunction in an equally populated statistical ensemble of the degenerate states, which represents the electron density, remains unchanged.

Different eigenfunctions may behave differently with respect to the various symmetry operations of a given point group; but in general not all symmetry elements of a point group are independent of one another: only certain combinations of behavior of the eigenfunctions with regard to the symmetry operations are possible. Such combinations of symmetry properties are the irreducible representations of the point group, also called symmetry species or types. Each electronic eigenfunction and therefore each electronic state, belongs to one of the possible symmetry types of the point group of the molecule in its equilibrium position.
If the ions were fixed in positions other than their equilibrium positions and if the symmetry of the displaced positions is different from that of the equilibrium positions, the species of the electronic wavefunctions would be different. However, since there must clearly be a one-to-one correspondence between the electronic eigenfunctions in the two conformations, we can still at least for small displacements (vibrations), classify the electronic eigenfunctions according with their species at the equilibrium conformation.

We must note, however, that in degenerate electronic states, for certain displacements from the equilibrium configuration, there may arise a splitting of the potential surface, since in the displaced conformation the symmetry may be lower and degenerate species may not exist.

As seen in Sect. 2.2 the manifold of electronic states is a tensor product of the single-particle ones. In a first approximation, also the single-particle wavefunctions are irreducible representations of the point group and we can classify the total eigenstates in terms of the symmetry of the occupied single-particle levels. It is the same that happens in the standard treatment of many-electrons atoms. The average potential acting on each electron is approximatively symmetric under rotations. In the Hartree-Fock approximation, single-electron levels are typically labeled by quantum number $j$ and $m_j$ corresponding to the total angular momentum of single-particle levels and to its component along the z-axis: these quantum numbers characterize an irreducible representations of the group of all the 3-dimensional rotations. The symmetry of the total eigenstates is the result of the composition of these single particle levels. In particular, concretely, all totally symmetric closed shells give vanishing contributions and the symmetry properties of the total eigenstates just depend on the partly filled outer shell.

Similar considerations hold for the phonons wavefunctions. The energy potential $U_\alpha(R)$ governing the nuclear motion Eq. (2.15), is invariant under the point-group transformations when the molecule occupies the equilibrium configuration $R_0$. Again, distorted configurations generally break the equilibrium symmetry. However, for small displacements, it can be easily shown that a symmetry transformation of the coordinates induces a linear transformation of the displacements (a one-by-one correspondence). Then, the single-mode wavefunctions given by Eq. (2.38), are labeled by irreducible representations of the point group of the molecule. The symmetry of the total phonon eigenfunction is given, as for the electronic states, by the composition of single-mode symmetry. Note that the $N^{osc}$ normal frequency $\omega_k$ satisfying the secular equation (2.31), are not necessarily all distinct. These degeneracies reflect the degenerate representations of the point group and the components of one degenerate normal mode mix among each other upon a symmetry transformation.

Hence, the adiabatic harmonic vibronic states (2.17) are naturally classified through the irreducible representation of the point group they belong to, deter-
minded by the composition of the phononic and electronic characters.

In the general case, anharmonic interactions between phonons, electron-electron interactions or non-adiabatic electron-phonon couplings do not lower the symmetry of the molecule: the general solution (2.18), a linear combination of the symmetric adiabatic harmonic eigenstates shell, involves only vibronic states belonging to the same representation of the point group of the equilibrium configurations. As a familiar example, the spin-orbit interaction in a one-electron atoms breaks the rotational symmetry in separate spin and orbital space, but it is invariant under global rotations of both spin and orbital degrees of freedom: as a consequence, the eigenstates of the interacting system are labeled by the total angular momentum and projection quantum number $j$ and $j_z$.

For the subject of the present work, systems with degenerate or almost degenerate electronic ground state, where e-v couplings induce a spontaneous symmetry breaking, are the most interesting. These systems are the so-called Jahn-Teller molecules to which we devote the final of this Chapter.

2.6 Dynamic Jahn-Teller effect in molecules

The Jahn-Teller effect (JT), first suspected by Landau in 1934 [13], takes place in any case of (partly filled) degenerate electronic level in nonlinear molecules and in complexes. It is due in last analysis to the very general tendency of any system toward a closed shell. There is always some energy to gain by splitting an electronic degeneracy (typically breaking the associated symmetry), and filling the lowest split-off levels. Some energy has to be paid, of course: the splitting is obtained by changing the geometric configuration of the ions, which move away from their original equilibrium positions. The restoring energy, however, is typically quadratic in the displacement from the potential minimum, while the leading term in the splitting of a degenerate level, and thus the gain in electronic energy, is usually linear in the perturbing distortion (at least until the split levels remain far apart from the neighboring electronic levels): the balancing of these two terms brings the molecule to a new minimum of the potential energy, in a distorted configuration.

It is customary to consider an expansion, with linear, quadratic, cubic...terms in the distortion coordinates $Q$ of the e-v interaction of Eq. (2.46). We refer to neglect of all terms beyond the lowest one, as linear coupling approximation. In the following we will indicate with $g$ the Hamiltonian parameter tuning the strength of the linear e-v coupling term. Usual second-order perturbation theory, applied to degenerate state, yields a net ground state energy lowering proportional to $g^2 \Delta E$ with a distortion proportional to $g$. Here $\Delta E$ is the energy difference between the ground state and the closest interacting excitation, typically a vibrational quantum $\hbar \omega$. 

\[ \text{2.6 Dynamic Jahn-Teller effect in molecules} \]
If, as in most cases, the degeneracy was originally due to an exact symmetry of the system, then the symmetry-breaking distortion has to choose to take place in one of the possible symmetry-equivalent directions. If the vibrations can be regarded as classical, then any energy barrier among the system-equivalent minima freezes the molecule in one specific symmetry-broken configuration, around which it performs low-energy oscillations. This picture is known as static JT effect: thermal effects may allow jumps to the other equivalent minima of the potential surface. Static JT systems occur whenever JT distortions are very large.

Far more attractive phenomena arise when a quantum mechanical description of the motion of the ions is necessary. The minima of the adiabatic potential can now communicate with one another through quantum tunneling. Thus, instead of having a symmetry broken distorted ionic configuration, the ground state resonates among the equivalent minimum-energy distortions, thus restoring the original symmetry. Tunneling is present in any system, but when its reciprocal frequency is large compared to the time scale of any experiment, a static picture is satisfactory. On the contrary, when the energy barriers separating different minima are low or even absent, a full quantum description of the state of the system is essential to its correct understanding. The denomination dynamical JT (DJT) applies in such cases.

The name DJT only applies when the vibration modes interacting with the degenerate electronic state are themselves degenerate. The only trivial effect of JT coupling to non-degenerate vibrational coordinates is to shift the equilibrium
position of the oscillator, without splitting the electronic degeneracy. Degenerate vibrations instead often split the degeneracy of the electronic orbitals. This fact introduce a generalized concept of adiabatic (BO) potential surface. For zero distortion, the electrons can equivalently well occupy any one of the degenerate orbitals. When the levels are split, we get a multi-valued adiabatic potential surface, with a conic intersection of several sheets at zero distortion (see Fig. 2.2). For weak JT coupling \((g \to 0)\), the terms mixing the different almost degenerate BO sheets are crucial, all the eigenstates involve coherent mixtures of different electronic states and distortions: a traditional BO description, in term of the lowest sheet only, is completely inaccurate. Instead, for strong JT distortion \((g \to \infty)\), the so-called adiabatic limit, the separation of different electronic levels is large, thus most spectral features can be extracted from the study of the lowest BO sheet (see Sect. 2.1), treating electronic excitations from the lowest to higher adiabatic sheets as unlikely virtual process.

The structure of the set of absolute minima of the BO potential of a JT-coupled system is crucial in the determination of its low-energy spectral properties for intermediate to strong JT coupling. The minima are usually a discrete set of isolated point, as depicted in Fig. 2.1 (for a beautiful example see Ref. 14), related by the
symmetry operations of the molecular point group, and joined by “energetically cheapest” paths (i.e. path such that at every point on them the potential energy increases in all the direction perpendicular to the path) passing through saddle points of the potential surface. In many cases, such as the linear $e \otimes E$ and $t \otimes H$ models, the set of potential minima becomes a continuous manifold, called JT valley or trough as in Fig. 2.2. It is exactly flat only in the ideal case of perfectly linear JT coupling. Higher-order coupling in practice reintroduce always the isolated minima - saddle point structure, but they are often small corrections, and a description in terms of a flat valley yields quantitative results.

The vibron spectra in the case of many perfectly isolated minima (adiabatic limit) is characterized by vibrational spectra having the additional degeneracy given by the many possible equilibrium configurations. As the barriers become finite, these vibronic state give rise to tunnel-split states carrying a label of the molecular point group, increasingly separated for increasing tunneling amplitude. When the saddle-points vanish and we get a flat JT valley, the ions undergo a free-rotation-like motion along this locally sphere-like manifold plus harmonic vibration orthogonal to it. Vibronic states correlate continuously as the interminima barriers are reduced.

The next chapter is devoted to apply these concepts to $C_{60}$ ions which, for their high symmetry, are well known DJT systems. In particular, the positive ions, which are the main subject of this work, realize the so called $h \otimes (G + H)$ DJT system, which is characterized by isolated minima. The following Chapter discusses the relevant model for degenerate electron-phonon interaction (DJT) in $C_{60}^+$. 
Chapter 3

The model for dynamic Jahn-Teller in C$_{60}$

The C$_{60}$ molecule has a completely filled highly degenerate outer orbital and photoemission generates C$_{60}^+$ cations with electronically degenerate ground state, for which e-v coupling induces DJT distortion. In this chapter we review only a few basic aspect of C$_{60}$, namely those useful for studying e-v couplings in C$_{60}$ ions. In particular, with an emphasis on the icosahedral molecular symmetry, we give a brief introduction to the electronic (Sect. 3.2) and vibrational (Sect. 3.3) structure of C$_{60}$, and describe the JT coupling in C$_{60}^+$ with the model of Sect. 3.5. The aim is to provide the framework for the DJT model we use for our calculation, setting up the notations used throughout this work. For more complete reviews of C$_{60}$ properties we suggest Refs. [15, 16, 17, 18].

3.1 The fullerene molecule

The 60 carbon atoms of fullerene are all threefold coordinated and arranged as a truncated icosahedron (Fig. 3.1), a regular, roughly spherical cage, of about 7 Å in diameter, [19]. The cluster may be thought of as a small piece of graphite sheet wrapped to spherical shape. The regular hexagonal structure of graphite is distorted, and 12 five-membered rings intercalate 20 six-membered ones, in such an ordinate way that all atoms are equivalent, each shared among one five-membered ring and two six membered rings, as shown in Fig. 3.2. The 90 chemical bonds divide into two classes: 30 of them belong to six membered rings only, the others are in common between the two kinds of rings. They have a different length, with a mean value of about 1.44 Å. The σ-bonding $sp^2$ graphite orbitals still constitute the backbone of molecular binding. Spherical curvature alters their character to $sp^{2.28}$ [20]. The σ-bonding orbitals range from several eV’s to a few tens of eV below the
vacuum, the antibonding states lying +10 eV and higher above the vacuum \cite{21}. The chemically-active electronic states, mainly of \( \pi \)-type, are those derived from the \( p_z \) carbon orbital (actually of hybrid \( s^{0.09}p \) nature \cite{20}) aligned in the radial direction. These orbitals concur to form a set of delocalized molecular orbitals, providing an energy gain which accounts for extra molecular stability. In fact, despite the formally large number of unsaturated bonds, \( C_{60} \) is a pretty stable allotropic form of carbon, both as an isolated molecule and as a fcc solid. The next section contains a few more details about the \( \pi \)-bonding/antibonding molecular orbitals, characterizing the electronic structure.

The overall molecular symmetry group is the icosahedral group \( I_h \), the largest point group in 3D (except for axial groups), composed by 120 elements. \( I_h \) is the product group of \( \mathcal{I} \times \iota \), where \( \iota \) is composed by the identity and the space inversion, and \( \mathcal{I} \) contains 60 rotations organized in the following classes \cite{6}: the identity, 12 \( C_5 \), 12 \( C_5^2 \) (through the center of opposite pentagonal rings), 20 \( C_3 \) (through the center of opposite hexagonal rings), and 15 \( C_2 \) (through the middle of the bonds shared between two hexagonal rings). The great richness of this group is directly related to the large degree of symmetry carried by this unique molecule, appearing in particular in the complete equivalence of all its 60 atoms. The large symmetry is also reflected in the large degeneracy of the group's irreducible representation \cite{6}: \( A \) (1-dimensional), \( T_1, T_2 \) (3-dimensional), \( G \) (4-dimensional), \( H \) (5-dimensional). In \( I_h \), the character of inversion adds a \( g/u \) subscript for even/odd representation, but leaves the degeneracies unchanged. As discussed in Sect. 2.3, all of (electronic, vibrational, vibronic) molecular states and excitations are basis of irreducible representations: degeneracies up to fivefold are therefore very common. This makes \( C_{60} \) a promising system for novel Dynamic Jahn-Teller structures \cite{16, 22, 23, 24, 25, 26}. 

Figure 3.1: A truncated icosahedron
This large symmetry, however, is also delicate. For example, isotope substitution of one carbon atom is enough to reduce $I_h$ to simple bilateral reflection $C_v$. Due to 1.10\% isotope abundance of $^{13}$C in natural carbon, only 51.5\% of fullerene is pure $^{12}$C$_{60}$. However, isotope substitution induces very small splittings of vibron modes and electronic orbitals, and can be safely neglected for many purposes. $^{13}$C$^{12}$C$_{59}$ ions have almost-degenerate ground states still affected by Jahn-Teller effect (Sect. 2.6) in essentially the same way as $^{12}$C$_{60}$.

C60 forms a Van der Vaals fcc insulating solid (lattice parameter 14.17 Å) of loosely bound individual molecules. It sublimes at approximately 800 K, without passing through a liquid phase. Doping C60 can form ionic materials (fullerides), showing novel and exciting properties such as superconductivity, organic magnetism, correlated Mott-insulating states.

## 3.2 The electronic structure

As anticipated, in this section we concentrate on the $\pi$ orbitals and electrons, which are those in the chemically relevant region of the spectrum. We use a one-electron orbital picture, neglecting e-e effects at this stage. Although in principle unjustified (the bare Coulomb repulsion of two electrons separated by a fullerene radius is about 3 eV), the one electron picture is, as always, pretty useful (Sect. 2.2).

Many approaches have been taken to the electronic structure of C$_{60}$, such as tight-binding [27, 20, 21], local density approximation [21], or renormalization group methods, yielding increasing degrees of quantitative accuracy.
Figure 3.3: A particle-on-a-sphere schematic representation of the electronic levels of C\textsubscript{60}. The HOMO and LUMO, originating from the $L = 5$ orbitals, are evidenced. (adapted from Ref. [28])

For the purpose of this chapter, we review a more intuitive method, of a particle-on-a-sphere, giving a simple qualitative description of the electronic structure. It treats the $\pi$ electrons as independent particles sliding on a spherical shell of radius $R$, mimicking the attractive potential generated by the carbon ions as if they were smeared on this shell [28]. As long as icosahedral perturbations can be neglected, the single-electron $\pi$-states are atomic-like spherical harmonics $Y_{Lm}$, with energy

$$E(L) = \frac{L(L+1)\hbar^2}{2m_e R^2}, \quad (3.1)$$

proportional to the angular momentum of rotation around the center of the sphere. Hence, $2 + 6 + 10 + 14 + 18 = 50$ out of 60 $\pi$ electrons (1 per atom) of neutral C\textsubscript{60} fill completely the molecular orbitals up to $L = 4$, whereas the remaining 10 are
left in the \( L = 5 \) shell, which is therefore only partly filled.

An icosahedral perturbation is subsequently added accounting for the actual positions of the ions. The lowest \( L = 0, 1, 2 \) orbitals fit exact icosahedral labels \( a_g, t_{1u}, h_g \). The icosahedral field generated by the cage splits the \( L > 2 \) spherical states into icosahedral representation, as shown in Fig. 3.3. In particular the splitting of the partly filled outer shell, \( L = 5 \rightarrow h_u + t_{1u} + t_{2u} \), generates a closed shell configuration. In accord with previously mentioned theoretical approaches and with experiment, the completely-filled Highest Occupied Molecular Orbital (HOMO) has \( h_u \) symmetry, and the Lowest Unoccupied Molecular Orbital (LUMO) is \( t_{1u} \). The HOMO-LUMO gap opened in the \( L = 5 \) shell is about 2 eV. A direct experimental measure of this gap is not easy, therefore that is just an indicative value. More accurately known are the values of the ionization potential, 7.58 eV, and the electron affinity, 2.65 eV.

This description is certainly an approximation, but it provides a simple mnemonic, fairly accurate picture of molecular orbitals of fullerene. We are mainly interested in the HOMO, to which photoemission subtracts electrons (or equivalently adds holes), producing positive ions. Given the large size of \( \text{C}_{60} \), it is reasonable to assume that the inner orbitals feel negligible change upon ionization of the molecule, so that \( \text{C}_{60}^+ \) has generally the same shape and bonding as neutral \( \text{C}_{60} \), the effects of charging being mainly restricted to the one-particle effects induced by the hole in the HOMO.

### 3.3 The vibrational modes

In a complex molecule as \( \text{C}_{60} \), vibrations play an important role, and a complete understanding of the spectral features cannot leave them out (Sect. 2.3).

\( \text{C}_{60} \) has 174 vibrational degrees of freedom, but thanks to symmetry-induced degeneracy and selection rules, the vibrational spectra show relatively few peaks, and nowadays there is general agreement on their identification. The cleanliness of the observed vibrational spectra pays the price of leaving most vibrational modes inaccessible to direct infrared and Raman spectroscopy. In particular only the four \( T_{1u} \) dipolar modes are seen in infrared, while the two \( A_g \) and eight \( H_g \) modes have the correct symmetry for Raman scattering. Neutron scattering experiments are sensitive to all the modes, but with rather poor resolution. Computations are therefore useful, for getting a global view of the vibrational spectrum.

Many routes to the calculation of vibron eigenfrequencies and normal modes have been pursued, either based on force fields fitted on the experimentally accessible data \cite{29, 31, 32}, or based on \textit{ab initio} computations of the molecular structure \cite{3, 33, 34, 35}. The agreement among different computations is surprisingly poor. Phenomenological models have typical deviations of the order of the 10 meV, while
Figure 3.4: Spherical resolution of the vibrational spectrum of $C_{60}$. The modes are organized according to the three series $\omega_{1/2/3}$. The spherical parent $L$ is indicated before the icosahedral label [From Ref. [30]]. The highlighted modes are the active modes which couple to the HOMO.
3.4. E-V COUPLING: SYMMETRY CONSIDERATIONS

typical discrepancies of good \textit{ab-initio} calculations are on the order of 1 meV, well
above nowadays’ experimental resolution. All the calculations in this work are based
on the \textit{ab-initio} frequencies and normal modes of Ref. [3]. We report them for conve-
nience in Table 3.1, together with the experimental frequencies. We do not use the
measured values because accurate measurements for the \textit{G}_g modes, are unavailable.

Like for the electronic structure, here we content ourselves with a qualitative
understanding of the vibrational structure. The schematic logical framework that
we briefly summarize here exploits the analogy of the C\textsubscript{60} cage with a hollow elastic
sphere [30]. There are three classes of eigenmode solutions of a homogeneous shell
with a stretching and a bending constant. The first class contains levels of parity
\((-1)^L\), with \(L = 0, 1, 2, 3, \ldots\); the levels in the second class have the same parity, but
start off at \(L = 1\); in the third series the parity is reversed \((-1)^{L+1}\), and they also
start at \(L = 1\). The vibrations of the third class have purely tangential character,
while those of series 1 and 2 have mixed radial-tangential nature (series 1, at higher
energy involve mostly stretching, series 2 mostly bending). The zero-energy \(L = 1\)
states of series 2 and 3 are the modes of rigid translation and rotation of the sphere.

Of course, when the homogeneous balloon is replaced by discrete 60 atoms bound
together by the molecular adiabatic potential, the infinite set of spherically sym-
metric eigenmodes is cut off to a finite number of modes, now labeled by \(\mathcal{I}_h\)
representation. \(L = 0, 1, 2\) states have the icosahedral counterparts in \(A_g/u, T_{1u}/g, H_g/u\)
respectively: the first label corresponds to series 1 and 2. The second labels the
third series, which has inverted parity. As for the electronic orbitals, the states with
\(L > 2\) are split, according to rules given in TABLE III of Ref. [30]; for example
both \(L = 3\) odd-parity spherical modes generate a \(T_{2u}\) and a \(G_u\) icosahedral mode.

The explicit eigenmodes, computed for example by force field methods, can be
easily analyzed in term of the spherical basis, to obtain their parentage in terms of
hollow-sphere modes [30]. The three series are readily identified in the three columns
of Fig. 3.4, labeled \(\omega_1, \omega_2, \omega_3\). Inter-mode mixing is present, but most vibrons have
a well defined parentage, with few exceptions. At any rate, this spherical picture
remains generally a valid and useful conceptual scheme.

3.4 Electron-vibration coupling: symmetry consid-
erations.

Photoemission from C\textsubscript{60} produces a molecular ion, C\textsubscript{60}\textsuperscript{+}, with a hole in the five-
fold degenerate \(h_u\) HOMO. The adiabatic approximation (Sect. 2.1) fails, and non-
adiabatic electron-phonon interactions have to be included (Sect. 2.4). JT effect
takes place and, according to the discussion of Sect. 2.6, the molecule immediately
starts to distort into one of the six symmetry-equivalent static minima, calculated
### Table 3.1: Computed vibrational eigenfrequencies of C$_{60}$, and e-v linear coupling parameters for the $h_u$ HOMO [3]: comparisons with experimental values of the Raman-active vibrational modes $A_g$ and $H_g$ [23, 31, 36].

<table>
<thead>
<tr>
<th>mode symmetry</th>
<th>Raman</th>
<th>DFT-LDA calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_u$ HOMO</td>
<td>$\omega_{\Lambda j}$ [cm$^{-1}$]</td>
<td>$\omega_{\Lambda j}$ [cm$^{-1}$]</td>
</tr>
<tr>
<td>$A_g1$</td>
<td>496</td>
<td>500</td>
</tr>
<tr>
<td>$A_g2$</td>
<td>1470</td>
<td>1511</td>
</tr>
<tr>
<td>$G_g1$</td>
<td>-</td>
<td>483</td>
</tr>
<tr>
<td>$G_g2$</td>
<td>-</td>
<td>567</td>
</tr>
<tr>
<td>$G_g3$</td>
<td>-</td>
<td>772</td>
</tr>
<tr>
<td>$G_g4$</td>
<td>-</td>
<td>1111</td>
</tr>
<tr>
<td>$G_g5$</td>
<td>-</td>
<td>1322</td>
</tr>
<tr>
<td>$G_g6$</td>
<td>-</td>
<td>1519</td>
</tr>
<tr>
<td>$H_g1$</td>
<td>271</td>
<td>261</td>
</tr>
<tr>
<td>$H_g2$</td>
<td>437</td>
<td>429</td>
</tr>
<tr>
<td>$H_g3$</td>
<td>710</td>
<td>718</td>
</tr>
<tr>
<td>$H_g4$</td>
<td>774</td>
<td>785</td>
</tr>
<tr>
<td>$H_g5$</td>
<td>1099</td>
<td>1119</td>
</tr>
<tr>
<td>$H_g6$</td>
<td>1250</td>
<td>1275</td>
</tr>
<tr>
<td>$H_g7$</td>
<td>1428</td>
<td>1456</td>
</tr>
<tr>
<td>$H_g8$</td>
<td>1575</td>
<td>1588</td>
</tr>
</tbody>
</table>

For a Hamiltonian description of e-v coupling, it is customary to consider an expansion of the electron-phonon interaction of Eq. (2.46), with linear, quadratic, cubic...terms in the distortion coordinate. For our calculation we use a linear harmonic JT model including only the leading term. We also neglect anharmonic terms in the distortions (see Eq. (2.44)). Several theoretical papers [37, 24, 26, 38] formulate the so-called $h_u \otimes (H_g + G_g + A_g)$ JT problem, describing a hole in molecular C$_{60}$. In this section we highlight the features of this model, and set up explicitly the notations we use in the present work.

Basic symmetry considerations are crucial to determine the form of the coupling Hamiltonian, for fullerene ions, and in general.

The e-v coupling operator must, on general grounds, be a scalar, i.e. a totally symmetric representation of the group. In the C$_{60}$ case it must be $A_g$ (or $L = 0$, if we enlarge to the full spherical group). The general structure of the linear coupling
operator in tensor notation is

\[ H^{e-v} \propto \sum_{\gamma} \left[ \mathcal{D}^{(\gamma_{el})} \otimes \mathcal{D}^{(\gamma_{el})} \right]^{(s)}_{s} \times \mathcal{D}^{(\gamma_{ vib})}^{(A_g)}, \]  

(3.2)

where \([ \cdot \otimes \cdot ]^{(s)}\) represent the symmetric coupling of two tensors to a representation \(\mathcal{D}^{(s)}\) in standard group-theoretical notation.

In particular, the symmetric product of a \(h_u\) icosahedral representation with itself results

\[ \{h_u \otimes h_u\}_s = a_g \oplus h_g \oplus (g_g \oplus h_g), \]  

(3.3)

like in spherical symmetry \([\mathcal{D}^{(2)} \otimes \mathcal{D}^{(2)}]^{(0,2,4)}, \) with the correspondence \(\mathcal{D}^{(0)} \rightarrow a_g, \mathcal{D}^{(2)} \rightarrow h_g \) and \(\mathcal{D}^{(4)} \rightarrow (g_g \oplus h_g)\). The modes interacting with the HOMO are therefore the Raman-actives ones, 2 \(A_g\) and 8 \(H_g\), plus the 6 \(G_g\) modes, highlighted in Fig. 3.4: the fact that the Hamiltonian is entirely determined by symmetry (up to a constant) explains the name \(h_u (H_g + G_g + A_g)\) model. Although this \(O(3)\) picture is suggestive [30], clearly a quantitative description of \(C_{60}\) ions had better involve icosahedral symmetry from the beginning.

In the icosahedral group, indeed, in the \(h_u \otimes h_u\) tensor product of Eq. (3.3), the \(h_g\) representation appear twice. This reflects the non simple reducibility of the icosahedral symmetry group. Accordingly, Butler [39] provides two orthogonal sets of Clebsch-Gordan (CG) coefficients

\[ H^{C_m}[r] = \langle h, \mu; h, \nu|H, m\rangle^{[r]}, \quad r = 1, 2 \]  

(3.4)

which couple an \(h\) electronic state (quadratically) with an \(H\) vibrational mode (linearly) to give a scalar. Each set of coefficients is identified by a multiplicity index \(r = 1, 2\). Since the two \(H\) states labeled \(r = 1, 2\) are indistinguishable symmetry-wise, the choice of these two sets of coefficients is perfectly arbitrary, as long as they are kept orthogonal to each other. This arbitrariness is the source of the different notations taken in the literature of this field. Here, we stick to Butler [39], which is basically equivalent to Ceulemans’ convention [40]. Also, we label the states within a degenerate multiplet by the labels of the subgroup chain \(I_h \supset D_5 \supset C_5\). For brevity, we indicate only the \(C_5\) index \(m\) \((m = 0\) for \(a, m = \pm 1, \pm 2\) for \(g\) and \(m = -2, \ldots, 2\) for \(h\) states) in the labeling of states since, for the representations relevant to our problem, the \(D_5\) label is just the absolute value of \(m\). In particular, we use \(\mu, \nu\) to label the orbital multiplet \(h_u\), and \(m\) to label the multiplets corresponding to normal modes.

Given the tabulated CG coefficients, to describe the coupling of an actual vibrational mode of an actual icosahedral molecule, it is necessary for generality to consider the linear combination

\[ H^{C_m}[\mu, \nu] (\alpha) \equiv \cos \alpha H^{C_m}[1] + \sin \alpha H^{C_m}[2] \]  

(3.5)
of the two sets. The coefficient \( hC^m_{\mu,\nu}(\alpha) \) coincides with Butler’s \( r = 1 \) and \( r = 2 \) values for \( \alpha = 0 \) and \( \alpha = \frac{\pi}{2} \) respectively. Different values of \( \alpha \) can be compared with the conventions of previous authors \[25, 26, 37\]. The \( \alpha \)-dependence of these CG coefficients indicates that belonging to the \( h_g \) group representation in icosahedral symmetry does not determine completely the form of the JT coupling. The mixing angle \( \alpha \) is needed for that. In the present case of fullerene, each \( H_g \) vibrational mode is thus characterized not only by its frequency and scalar coupling (as the \( A_g \) and \( G_g \) modes), but also by its specific mixing angle \(-\pi/2 \leq \alpha \leq \pi/2\), reported in Table 3.1.

### 3.5 The \( h_u \otimes (H_g + G_g + A_g) \) model

The linear JT Hamiltonian for the \( h_u \otimes (H_g + G_g + A_g) \) model, besides the electron-vibration interaction term \( H_{e-v} \) itself, contains also a single-electron Hamiltonian \( H_0 \), and a vibrational Hamiltonian \( H_{vib} \) as follows:

\[
H = H_0 + H_{vib} + H_{e-v} .
\]  

(3.6)

The individual terms can be written as

\[
H_0 = \epsilon \sum_{\mu} c^\dagger_{\mu} c_{\mu} ,
\]

(3.7)

\[
H_{vib} = \sum_{j\Lambda m} \frac{\hbar \omega_{\Lambda j}}{2} \left( P^2_{\Lambda jm} + Q^2_{\Lambda jm} \right) ,
\]

(3.8)

\[
H_{e-v} = \sum_{j\Lambda} \frac{k^j g_{\Lambda j} \hbar \omega_{\Lambda j}}{2} \sum_{m \mu} \Lambda C^m_{\mu,\nu}(\alpha_{\Lambda \mu}) Q_{\Lambda jm} c^\dagger_{\mu} c_{\nu} .
\]

(3.9)

Here \( \epsilon \) represents the energy position of the HOMO level where electrons are photoemitted from. \( \mu, \nu, m \) label the components within the degenerate multiplets. \( j \) counts the phonon modes of symmetry \( \Lambda \) (\( j = 1, 2 \) for \( \Lambda = A_g \), \( j = 1 \ldots 6 \) for \( \Lambda = G_g \), \( j = 1 \ldots 8 \) for \( \Lambda = H_g \) ). \( \omega_{\Lambda j} \) are the frequencies of the active modes of \( C_{60} \), listed in Table 3.1. \( g_{\Lambda j} \) are the parameters tuning the strength of the linear e-v coupling, also listed in Table 3.1. \( \Lambda C^m_{\mu,\nu}(\alpha_{\Lambda \mu}) \) are Clebsch-Gordan coefficients for coupling the two \( h_u \) fermion operators \( c^\dagger_{\mu} \) to phonons of symmetry \( \Lambda \) \[39\]. Clearly \( \alpha_{\Lambda j} \) is relevant for \( H_g \) vibration only, according to Eq. (3.5). \( Q_{\Lambda jm} \) are the dimensionless molecular normal-mode vibration coordinates (measured from the adiabatic equilibrium configuration of neutral \( C_{60} \), in units of the length scale \( x_0(\omega_{\Lambda j}) = \sqrt{\hbar/(\omega_{\Lambda j} m_C)} \) associated to each harmonic oscillator, where \( m_C \) is the mass of the C atom), and \( P_{\Lambda jm} \) the corresponding conjugate momenta (Sect. 2.3). Finally, to keep the notation as simple as possible, we omit all spin indexes and sums, because linear JT
3.5. **THE $H_U \otimes (H_G + G_G + A_G)$ MODEL**

coupling is a purely orbital phenomenon, completely diagonal in spin, and spin-orbit, exceedingly small in $C_{60}$ [11], is neglected throughout.

In our calculations we adopt the numerical values of the e-v coupling parameters $g_{\Lambda_j}$ and $\alpha_{\Lambda_j}$ listed in Table 3.1, obtained from first-principles Density Functional Theory (DFT) electronic structure calculation of Ref. 3. A second DFT calculation [42], based on a different functional, reports couplings that are similar on the whole to those of Table 3.1.

Finally, this model can equally well describe the JT effect of the LUMO, relevant for negative $C_{60}$ ions, and indicated by $t \otimes (A + H)$. The only modifications involve eliminating the $G_g$ modes, replacing the CG coefficients with suitable ones, extending the $\mu/\nu$ sums from -1 to 1 and interpreting the $c^\dagger$ operators as creators of electrons instead of holes. For the $t \otimes (A + H)$ JT, the product decomposition is unique, thus no $r$ index is necessary.

The e-v couplings $g_{\Lambda_j}$ in Eq. (3.9) are dimensionless, measured in the units of the corresponding harmonic vibrational energy quantum $\hbar \omega_{\Lambda_j}$. Modes (e.g. the second $G_g$ mode) with $g_{\Lambda_j} \ll 1$ are thus only weakly coupled; conversely, modes (in particular the lowest $H_g$ mode) with a large $g_{\Lambda_j} > 1$ are strongly e-v coupled. The numerical factors $k^{A_g} = 5\frac{1}{2}$, $k^{G_g} = (\frac{5}{2})\frac{3}{2}$, $k^{H_g} = 1$ for the HOMO, and $k^{A_g} = 3\frac{1}{2}$, $k^{H_g} = 6\frac{1}{2}$ for the LUMO are introduced for compatibility with the normalization of the e-v parameters in Ref. 3. The coupling of Table (3.1) are in the medium-coupling regime, for which neither a perturbative approach nor the classic adiabatic limit give good results: it is a regime characteristic of DJT-effects (Sect. 2.6).

The symmetric form of the Hamiltonian $H$ (3.6) grants that its vibronic eigenstates belong to some $I_h$ symmetry species. As discussed in Sect. 2.6, in the distorted configuration, symmetry is recovered by resonating tunneling among the equivalent $D_5$ minima.

In the single-particle $H_0$ (3.7), the hole counterpart of Eq. (2.21), the relaxation of the inner shells induced by the presence of the hole is implicitly accounted for by the coupling constant $g$ [3]. Moreover, for a single-hole $C_{60}^+$, also intrashell hole-hole [43] interaction terms (2.22) are irrelevant. The only real approximation in this terms is to neglect the dependence of the normal frequency $\omega_{\Lambda_j}$, of the symmetric configuration, on the numbers of holes. In addition, we neglect anharmonic contributions (Eq. (2.42)) in the vibrational Hamiltonian $H_{\text{vib}}$ (3.8) (partly justified by the rigidity of $C_{60}$), and the higher-order non-linear terms in the coupling Hamiltonian $H_{\text{e-v}}$ (3.9). The approximations made should however capture the important physics of the problem we address here, within the simplest possible model.

We complete the theoretical framework of this work in the next Chapter, where, starting from the Fermi’s Golden Rule, we derive a useful mathematical expression for the photoemission spectrum of $C_{60}$, suitable for the numerical approach presented in final chapters.
Chapter 4

The photoemission spectrum

4.1 Fermi’s Golden Rule

If a molecular system, in some initial quantum state $\Psi^i$, is acted upon by an electromagnetic perturbation of frequency $\hbar \omega$, represented by some energy perturbation operator $V_i$, the spectral response function, representing the rate of transition to the final states is given by Fermi’s Golden Rule \[44\]

$$I_i(\hbar \omega) = \frac{2\pi}{\hbar} \sum_f |\langle \Psi^f | V_i | \Psi^i \rangle|^2 \delta(\hbar \omega - (E_f - E_i))$$ \hspace{1cm} (4.1)

where the summation is carried out on all possible final states $\Psi^f$. $\Psi^i$ and $\Psi^f$, in general, are many-body eigenfunctions of the system Hamiltonian, of energy $E_i$ and $E_f$ respectively, describing both electronic and ionic motion. Eq. (4.1) is a semi-classical approach, treating the electromagnetic field classically. For simplicity, we use discrete indexes only, but, in general, the sum of Eq. (4.1) involves also unbound final states for which the sum is replaced by a suitable integration. The spectrum is then composed by a sequence of “sticks” placed at energy $E_f - E_i$ with relative strength $|\langle \Psi^f | V_i | \Psi^i \rangle|^2$, plus the continuum of unbound final states (Chap. 1). In practice, experimental resolution will always broaden the $\delta$-function sticks to continuous structures.

Obviously, different experiments highlight different spectral features. Many techniques have been developed, to investigate different details of the spectrum. The precise interpretation of Eq. (4.1) depends on the character of the experiment. For example, in optical absorption experiments, spectral features appear at energy, coinciding with the energy separation $E_f - E_i$ between the final and initial molecular states. Promotions occur when the photon energy $\hbar \omega$ matches any energy separation, provided that the matrix elements of the perturbation is non-vanishing. Instead, in photoemission, the final state is an unbound state of the
ionized molecule and of the emitted electron and $E_f = E_f^{\text{ion}} + E_e$. To investigate the molecular features of the spectra $E_f^{\text{ion}}$, it is sufficient to measure the energy of the emitted electron, as discussed in Sect. 1.2 and 4.3 below. If before excitation we have not a single $\Psi^i$ but a statistical ensemble of initial states $\{\Psi^i\}$ with probability $\rho_i$, in terms of the density matrix $\rho = \sum_i \rho_i |\Psi^i\rangle \langle \Psi^i|$, the total spectrum is the weighted average

$$I(h\omega) = \sum_i \rho_i I_i(h\omega). \quad (4.2)$$

Eq. (4.2) has Eq. (4.1) as a special case at zero temperature for a non-degenerate ground state $\Psi^i=0$, which we can regard as the well-determined initial state of the molecule. At finite temperature, the molecules occupy the thermally accessible vibrational levels according to the Boltzmann distribution $\rho_i = Z^{-1} e^{-\beta E_i}$, and the spectrum becomes:

$$I(h\omega) = Z^{-1} \sum_i e^{-\beta E_i} I_i(h\omega), \quad Z = \sum_i e^{-\beta E_i} \quad (4.3)$$

Thermal effects, in general affect the shape of spectrum, typically introducing some amount of broadening. For a degenerate ground state, even at $T = 0$ one has to average over the contributions of all the $d$ degenerate components, as in Eq. (4.2), with $\rho_i = 1/d$.

### 4.2 Green’s function approach

The resolvent of the Hamiltonian $H$ is defined as

$$G(z) = \frac{1}{z - H} \quad (4.4)$$

where the real energy $z = E + i\epsilon$ is accompanied by an infinitesimal positive imaginary part $\epsilon$.

A diagonal matrix elements of $G(z)$, $G_{ii}$ is known as Green’s function. A most useful property of the Green’s function is its connection with the spectral function $I_i$ of Eq. (4.1): consider in fact the diagonal matrix element of the resolvent, on the state $V_i |\Psi^i\rangle$ of Eq. (4.1) produced by the electromagnetic perturbation on the initial state:

$$G_{ii}(h\omega + i\epsilon) = \langle \Psi^i | V_i^\dagger \frac{1}{h\omega + i\epsilon - H + E_i} V_i |\Psi^i\rangle, \quad (4.5)$$

where we have shifted $z = h\omega \to h\omega + E_i$ for direct comparison with Eq. (4.1) It is possible to put in evidence some properties of the resolvent inserting the unit operator $\mathcal{I} = \sum_f |\Psi^f\rangle \langle \Psi^f|$ into Eq. (4.5), where $\Psi^f$ form a complete set of eigenfunctions
4.2. GREEN’S FUNCTION APPROACH

of the Hamiltonian $H$ with eigenvalues $E_f$. We have

$$G_{ii}(\hbar \omega + i\epsilon) = \langle \Psi^i | V_1^\dagger \sum_m |\Psi^f\rangle \langle \Psi^f | \frac{1}{\hbar \omega + i\epsilon - H + E_i} V_1 |\Psi^i \rangle =$$

$$= \sum_f |\langle \Psi^i | V_1 |\Psi^f\rangle|^2 \frac{1}{\hbar \omega + i\epsilon - (E_f - E_i)} =$$

$$= \sum_f |\langle \Psi^i | V_1 |\Psi^f\rangle|^2 \frac{\hbar \omega - (E_f + E_i) - i\epsilon}{(\hbar \omega - (E_f - E_i))^2 + \epsilon^2} \quad (4.6)$$

From Eq. (4.6), we see that for any $\epsilon > 0$, $G_{ii}(\hbar \omega + i\epsilon)$ is analytic and its imaginary part is negative (Herglotz property). Close to the real energy axis, $G_{ii}(\hbar \omega)$ exhibits poles at $E_f - E_i - i\epsilon$, the difference between the eigenvalues of $H$ and the energy of the initial state $\Psi^i$. As a consequence, for small enough $\epsilon$, the real part of $G_{ii}(\hbar \omega)$ exhibits characteristic positive-negative oscillations around $E_f - E_i$, while the imaginary part exhibits negative peaks of Lorenzian shape centered around $E_f - E_i$; in the limit $\epsilon \to 0^+$ each Lorenzian narrows into a $\delta$ distribution:

$$\lim_{\epsilon \to 0^+} \frac{1}{\pi} \frac{\epsilon}{(\hbar \omega - (E_f - E_i))^2 + \epsilon^2} = \delta(\hbar \omega - (E_f - E_i)) \quad (4.7)$$

Comparing Eq. (4.4) and Eqs. (4.6),(4.7), we relate the spectrum to the Green’s function:

$$I_i(\hbar \omega) = -\frac{2}{\hbar} \text{Im} \, G_{ii}(\hbar \omega + i\epsilon) \quad (4.8)$$

The total spectrum at finite temperature can then be expressed, combining Eq. (4.8) and Eq. (4.3), as

$$I(\hbar \omega) = -\frac{2}{\hbar} \sum_i \frac{e^{-\beta E_i}}{Z} \text{Im} \, G_{ii}(\hbar \omega + i0^+), \quad Z = \sum_i e^{-\beta E_i} \quad (4.9)$$

Relations (4.8) and (4.9) hold regardless the fact that the energy spectrum of $H$ is discrete or continuous. In practice the finite experimental energy resolution may be simulated by a small but finite $\epsilon$, which replaces the $\delta$ functions at the poles with Lorenzians.

We conclude that calculating the spectrum means basically to find the poles $E_f - E_i$ and residues $|\langle \Psi^i | V_1 |\Psi^f\rangle|^2$ of the Green’s function (4.6). The usefulness of expressions (4.8) and (4.9) is that these can be treated numerically through standard algorithms such as the Lanczos method and the continued fraction, summarized in Chapter 4.
CHAPTER 4. THE PHOTOEMISSION SPECTRUM

4.3 Photoemission: the sudden approximation

In photoemission, a radiation of known frequency \( \omega \) ionizes the molecule, generating the final unbound state of a free electron plus a molecular ion (Chap. 1). The final eigenfunctions \( \Psi^f \) are product of the wavefunctions \( \Psi^f_{\text{ion}} \), describing the ionized molecule, times the free-particle wavefunctions of the emitted electron, \( \psi_\mathbf{k}^e \), characterized by its wave vector \( \mathbf{k} \). In angular-integrated photoemission, the electron detector selects a well defined energy \( E^e_{\mathbf{k}} = \frac{\hbar^2 |\mathbf{k}|^2}{2m_e} \) of the outcoming photoelectron. Indicating with \( E^i_{\text{ion}} \) the final energy of the molecular ion, Eq. (4.1) specializes to photoemission as follows:

\[
I_i(E) = \frac{2\pi}{\hbar} \sum_{f, \mathbf{k} : E^e_{\mathbf{k}}=E^e} |\langle \Psi^f_{\text{ion}} \psi_\mathbf{k}^e | V | \Psi^i \rangle|^2 \delta(\hbar \omega - E^e_{\mathbf{k}} - (E^i_{\text{ion}} - E_i))
\]

(4.10)

Eq. (4.10) explicitly shows what is actually measured in a photoemission experiment, i.e. the binding energy \( E = \hbar \omega - E^e_{\mathbf{k}} \) by fixing the kinetic energy \( E^e_{\mathbf{k}} = E^e \) of the emitted electron.

Having clarified these points, it is better to rewrite Eq. (4.10), more compactly, in the familiar form (4.1), as

\[
I_i(E) = \frac{2\pi}{\hbar} \sum_f |\langle \Psi^f | \tilde{V}_1 | \Psi^i \rangle|^2 \delta(E - (E_f - E_i))
\]

(4.11)

where from now on we refer to \( \Psi^i \) and \( \Psi^f \) respectively as the initial neutral molecular state and the final ionized molecular state, with energy \( E_i \) and \( E_f \), including implicitly the angular integration on the free electron final states in the perturbation Hamiltonian \( \tilde{V}_1 \).

Moreover, we suppose that radiation pulls up the electron instantaneously, in a time much shorter than the characteristic vibrational times, so that the ions have no time to relax during the electronic transition. Immediately after photoemission, \( C_{60}^+ \) starts evolving from its initially symmetrical configuration, characteristic of neutral \( C_{60} \), and relaxes toward equilibrium (sudden approximation).

In the sudden approximation the perturbation Hamiltonian \( \tilde{V}_1 \) is the purely electronic operator

\[
\tilde{V}_1 = \sum_{\alpha \mu} C(\hbar \omega, \alpha, |\mathbf{k}|) c^\dagger_{\alpha \mu}
\]

(4.12)

where \( \alpha \) labels the molecular orbital, and \( \mu \) its degenerate component. Each term in Eq. (4.12) creates a hole in a specific orbital without perturbing the other orbitals or the phonon state of the molecule. All the details of the interaction are contained in the quantities \( C(\hbar \omega, \alpha, |\mathbf{k}|) \), which have the dimensions of an energy. In general,
these coefficients depend on the radiation frequency \( \omega \), on the wavevector \( \vec{k} \) of the photoelectron, and on the particular orbital \( \alpha \), where electron is emitted. The angular integration on all the photoelectron at fixed \( |\vec{k}| \), eliminates the dependence of \( C \) on the degenerate component \( \mu \) within a multiplet.

If we are interested at an energy range corresponding to photoemission from some precise orbital \( \tilde{\alpha} \), only one term of Eq. (4.12) is relevant, and the spectrum (4.11) becomes

\[
I_i(E) = \frac{1}{d_{\tilde{\alpha}}} \sum_{\mu} \sum_f |\langle \Psi^f | c_{\tilde{\alpha}\mu}^\dagger | \Psi^i \rangle|^2 \delta(E - (E_f - E_i))
\] (4.13)

or in term of the Green’s function (4.8)

\[
I_i(E) = -\text{Im} \frac{1}{\pi d_{\tilde{\alpha}}} \sum_{\mu} \sum_f \frac{|\langle \Psi^f | c_{\tilde{\alpha}\mu}^\dagger | \Psi^i \rangle|^2}{E + i0^+ - (E_f - E_i)}
\] (4.14)

where \( d_{\tilde{\alpha}} \) is the degeneration of the orbital \( \tilde{\alpha} \). The choice made in Eq. (4.14) for the coefficient \( \frac{2\pi}{h} |C(h\omega, \tilde{\alpha}, |\vec{k}|)|^2 = \frac{1}{d_{\tilde{\alpha}}} \) fixes the normalization of the spectrum

\[
\int_{-\infty}^{+\infty} I_i(E) dE = 1.
\] (4.15)

This arbitrary choice is handy for comparison with experimental data, which are usually only available in “arbitrary units”, i.e. up to a multiplicative constant. After the sudden appearance of the hole in the molecular orbital \( \tilde{\alpha}, \mu \), the ion evolves according to the dynamics described by some electron-phonon Hamiltonian, containing the displaced equilibrium position of the ion with respect to the neutral species. This dynamical evolution is expressed in the energy domain by the spectral function \( I_i(E) \).

When an electron is ejected from the fivefold degenerate \( h_u \) HOMO of \( C_{60} \) (the \( \tilde{\alpha} \) orbital), the dynamics is described by the \( h_u \otimes (H_g + G_g + A_g) \) JT Hamiltonian (3.6). The photoemission spectrum \( I(E) \) at finite temperature becomes, using Eq. (4.3), (4.14)

\[
I(E) = \frac{1}{5} \sum_{\mu} \frac{e^{-\beta E_i}}{Z} I_{i\mu}(E)
\] (4.16)

\[
I_{i\mu}(E) = -\frac{1}{\pi} \sum_f \text{Im} \frac{|\langle \Psi^f | c_{\mu}^\dagger | \Psi^i \rangle|^2}{E + i0^+ - (E_f - E_i)}
\] (4.17)

where \( I_{i\mu} \) is the contribution of the different initial vibrational states \( i \) and different electronic components \( \mu = 0, \pm 1, \pm 2 \) of the HOMO, and \( Z = \sum_i e^{-\beta E_i} \) accounts for
the thermal distribution of the initial vibrational states of neutral C\textsubscript{60}. In Eq. (4.17) and in the following we omit the label $\tilde{\alpha} = \text{HOMO}$, to which we concentrate our attention.

In this context, $\Psi_i$ represent the starting vibrational eigenstates of the neutral C\textsubscript{60}. These are unaffected by vibronic interaction and are therefore simple harmonic eigenstates of the 66 harmonic oscillators in $H_{vib}$ of Eq. (3.8), of energy $E_i = \sum \hbar \omega_{\lambda} (v_{\lambda} + \frac{1}{2})$, where $v_{\lambda}$ are the quantum vibrational numbers labeling the C\textsubscript{60} eigenstates. In Eq. (4.17), $c_{\mu}^i |\Psi_i\rangle$ is the initial excitation, right after the electron has been ejected from orbital labeled $\mu$ of the fivefold degenerate $h_u$ HOMO, but the phonon had no time to react yet. Its overlap with each DJT vibronic eigenstate of C\textsubscript{60}$^+$, $\Psi_f$, of energy $E_f$, gives the intensities of that spectral line.

The calculation of the photoemission spectrum of C\textsubscript{60} requires therefore complete knowledge of the neutral and singly-ionized states. In the next chapter, we describe the simple but instructive case of the coupling to nondegenerate vibrations, which can be solved analytically. For JT-coupling to degenerate vibrations relevant for C\textsubscript{60}$^+$, analytic tools fail, and recursive numerical method, such as Lanczos method, are called for: to these we devote Chapter 6.
Chapter 5

Nondegenerate vibrational modes

In this chapter, we investigate the e-v coupling of a generic (possibly degenerate) $x$ state to nondegenerate vibrations, such as the two active $A_g$ modes of $C_{60}$. The results in this chapter are valid independently of the symmetry point group of the system, and of the symmetry (and degeneracy) of orbital $x$. For simplicity, we label the nondegenerate representation of the vibration as $A$ (as, for example, in the icosahedral group). The $A$ modes couple to the total charge, and can therefore be treated separately. The trivial effect of electron-phonon coupling to nondegenerate vibrations is to shift the equilibrium positions of the oscillator. Any possible electronic degeneracy is not split.

The $x \otimes A$ Hamiltonian can be treated analytically, and the spectra calculated exactly. This simple theory is interesting *per se*, since it applies to all molecules (e.g. H$_2$O) whose point group affords only nondegenerate irreducible representations. We show some photoemission spectra, highlighting their dependence on coupling and temperature, to understand several general properties which will be useful to interpret the more complicated JT spectra of degenerate modes.

We will show that each $A$ mode acts independently of all other modes, thus, in particular, the nondegenerate modes can then be left out of the numerical calculation needed by the degenerate ones, and included analytically in a systematic way. As a preliminary exercise to apply the derived results, we compute a fictitious spectrum of $C_{60}$, treating all the modes as if they were nondegenerate.

5.1 $x \otimes A$ - shifted oscillator

Using the notation of Eq. (3.6), the Hamiltonian describing $n$ holes (or electrons) in a generic orbital $x$ coupled linearly to a nondegenerate molecular vibration can
be written has
\[ H = \epsilon \sum_{\mu} c^{\dagger}_{\mu} c_{\mu} + \frac{\hbar \omega}{2} (P^{2} + Q^{2}) + \frac{K g \hbar \omega}{2} \sum_{\mu\nu} Q \: c^{\dagger}_{\mu} c_{\nu} A C_{\mu \nu} - \nu \] (5.1)

Here \( Q \) and \( P \) are, respectively, the normal coordinate and the canonical conjugate momentum operators of the totally symmetric nondegenerate vibration \( A \) of frequency \( \omega \). \( g \) is the electron-vibration dimensionless coupling. \( \epsilon \) is the energy of the electronic orbital and \( c^{\dagger}_{\mu} \) are the fermion operators creating an hole in orbital \( \mu \) with the degenerate manifold. \( A C_{\mu \nu} \) are the Clebsch-Gordan coefficients of the symmetry group: for a \( d \)-degenerate electronic state we have \( A C_{\mu \nu} = \frac{1}{\sqrt{d}} \delta_{\mu \nu} \). The constant \( K = \sqrt{d} \) is chosen in such a way that \( \sum_{\mu\nu} K c^{\dagger}_{\mu} c_{\nu} A C_{\mu \nu} = \sum_{\mu} n_{\mu} = n \), the number of holes. We see that the nondegenerate vibration \( A \) couples only to the total charge, without breaking the orbital degeneracy. For fixed charge, the Hamiltonian (5.1) separates in an electronic:
\[ H_{0} = n \epsilon \] (5.2)

and in vibrational Hamiltonian
\[ H^{A} = \frac{\hbar \omega}{2} (P^{2} + Q^{2}) + \frac{ng \hbar \omega}{2} Q \] (5.3)

where the subscript \( A \) underlines this is the specific expression for the coupling to a nondegenerate mode. Eq. (5.3) can be easily simplified
\[
H^{A} = \frac{\hbar \omega}{2} (P^{2} + Q^{2}) + \frac{ng \hbar \omega}{2} Q = \\
\frac{\hbar \omega}{2} \left[ (P^{2} + Q^{2} + ng Q + \frac{1}{4} (ng)^{2}) - \frac{1}{4} (ng)^{2} \right] = \\
\frac{\hbar \omega}{2} \left[ P^{2} + \left( Q + \frac{1}{2} ng \right)^{2} - \frac{1}{4} (ng)^{2} \right].
\]

Making the canonical shift \( Q' = Q + \frac{1}{2} ng \), \( P' = P \) the vibrational Hamiltonian rewrites as:
\[ H^{A} = \frac{\hbar \omega}{2} (P'^{2} + Q'^{2}) - \frac{\hbar \omega}{8} (ng)^{2} \] (5.4)

The relevant part of the Hamiltonian (5.4), is the familiar harmonic oscillator Hamiltonian. The effect of the addition of \( n \) holes \((0 \rightarrow n)\) in the \( x \) orbital is to displace the equilibrium position to \( Q = -\frac{1}{2} ng \), and shift rigidly the energy levels by a constant \( n \epsilon - \frac{\hbar \omega}{8} (ng)^{2} \), as shown schematically in Fig 5.1.

The eigenvalues of (5.4), accounting for the non-trivial shift \(-\frac{\hbar \omega}{8} (ng)^{2}\) are simply:
\[ E_{w} = \hbar \omega \left[ (w + \frac{1}{2}) - \frac{1}{8} (ng)^{2} \right] \] (5.5)
and the corresponding eigenstates:

$$\varphi_w(Q') = \varphi_w(Q + \frac{1}{2}ng)$$  \hspace{1cm} (5.6)

where $\varphi_v$ are the harmonic-oscillator eigenfunctions, of Eq (2.38). The total eigenstates then simply factorize

$$\Psi^f_{\mu_1...\mu_nw} = \psi_{\mu_1...\mu_n}(r_1...r_n) \varphi_w(Q + \frac{1}{2}ng)$$  \hspace{1cm} (5.7)

and their eigenvalues write

$$E_{\mu_1...\mu_nw} = n\epsilon + \hbar\omega \left[ (w + \frac{1}{2}) - \frac{1}{8}(ng)^2 \right].$$  \hspace{1cm} (5.8)

$\psi_{\mu_1...\mu_n}$ are the wavefunctions describing $n$ holes in the orbital $x$ and $r_i$ are the holes coordinates. The eigenvalues $E_{\mu_1...\mu_nw}$ depend only on the total charge, reflecting the fact that the coupling to a nondegenerate mode does not split the orbital degeneracy. From now on, we set $\epsilon = 0$ to eliminate the trivial electronic contribution $n\epsilon$ and focus on the vibrational shift (5.3).
For \( n = 1 \), the eigenstates of Eq. (5.9) are just the final eigenstates to which photoemission leads. Then the photoemission spectrum can be calculated analytically in terms of the overlap of the final and initial states where sudden photoemission has created a hole. The initial state \( \Psi_v^i \) are characterized only by the vibrational quantum number \( v \) and expressed in term of the eigenstates \( \varphi_v \), with eigenvalues \( E_v \), of the normal harmonic oscillator in the undistorted configuration, given in Eqs. (2.38),(2.37). Throughout this chapter, we label with \( v \) the vibrational quantum number of the initial state (2.38),(2.37), and with \( w \) the final ones (5.6),(5.5).

The overlap between the initial and final state, factorized in the electronic and vibrational contribution:

\[
\langle \Psi_{v,w} | c_\mu^\dagger | \Psi_v^i \rangle = \langle \psi_w | \psi'_\mu \rangle \langle \varphi_w | T^\alpha | \varphi_v \rangle = \delta_{v\mu} \langle \varphi_w | T^\alpha | \varphi_v \rangle
\]  

(5.9)

where \( T^\alpha \) is the \( \alpha \)-translation of the normal coordinate \( Q \) with \( \alpha = \frac{1}{2} ng \). \( (T^\alpha)^\dagger | \varphi_w \rangle \) is the final vibrational eigenstates of Eq. (5.6), and \( \psi'_\mu \) is the hole wavefunction. From now on, we make abstraction of the electronic part of the matrix element, as \( 1/dP = 1 \). Then, for an initial state \( v \), the poles and residues of \( G_{vv}(E) \) (Eq. 4.5) are

\[
E_w^v = E_w - E_v = \hbar \omega (w - v - \frac{1}{8}(ng)^2)
\]

(5.10)

\[
R_w^v = |\langle \varphi_w | T^\alpha | \varphi_v \rangle|^2 = \left| \int_{-\infty}^{\infty} \varphi_w(Q + \alpha) \varphi_v(Q) dQ \right|^2
\]

(5.11)

The residues can be calculated analytically, using the explicit expression for \( \varphi_{v,w} \) in term of the Hermite polynomials given in Eq. (2.38):

\[
\langle \varphi_w | T^\alpha | \varphi_v \rangle = \int_{-\infty}^{\infty} \varphi_w(z + \alpha) \varphi_v(z) dz =
\]

\[
= N_v N_w \int_{-\infty}^{\infty} e^{-\frac{z^2}{2}} e^{-\frac{\alpha^2}{2}} H_w(z + \alpha) H_v(z) dz =
\]

\[
= N_v N_w e^{-\frac{\alpha^2}{2}} \int_{-\infty}^{\infty} e^{-(z+\alpha)^2} H_w(z + \alpha) H_v(z) dz =
\]

\[
= N_v N_w e^{-\frac{\alpha^2}{2}} \int_{-\infty}^{\infty} e^{-z^2} H_v(z - \frac{\alpha}{2}) H_w(z + \frac{\alpha}{2}) dz =
\]

\[
= N_v N_w e^{-\frac{\alpha^2}{2}} 2^w \sqrt{\pi} v! \left( \frac{\alpha}{2} \right)^{w-v} L_w^w\left( \frac{\alpha^2}{2} \right) \quad w \geq v
\]

where the last equality is a known result in the mathematics of special functions [11]. \( L_r^\lambda(z) \) are the Laguerre polynomials of degree \( r \)

\[
L_r^\lambda(z) = \frac{z^{-\lambda} e^z}{r!} \frac{d^r}{dz^r} \left( z^{r+\lambda} e^{-z} \right), \quad (5.12)
\]
and $N_{v/w}$ is the normalization constant of the harmonic oscillator wavefunction defined in Eq. (2.38). Substituting its explicit expression, and with some simplifications we get the final result

$$
\langle \varphi_w | T^\alpha | \varphi_v \rangle = \sqrt{\frac{2^v v!}{2^w w!}} e^{-\frac{\alpha^2}{4}} \alpha^{w-v} L_{w-v}^{w-v} \left( \frac{\alpha^2}{2} \right),
$$

which holds even for $w < v$.

Practically, only a finite number of state can be considered, as for large $w$ the overlap (5.11) with the initial states goes to 0, as shown by the asymptotic limit of Eq. (5.13), for $w \gg v$

$$
\langle \varphi_w | T^\alpha | \varphi_v \rangle \simeq \frac{w^w \left( \frac{\alpha}{\sqrt{2}} \right)^{w-v}}{\sqrt{w! v!}}, \quad [w \gg v].
$$

In particular, the number of nonnegligible overlaps (5.13) depends both on the distortion $\alpha = g/2$, and on the initial state $v$ considered. For strong coupling the diverging term $(\alpha/\sqrt{2})^{w-v}$ contrasts the factorial $w!$, slowing down the approach to 0. The same consideration applies to the $w^w$ factor, for large values of $v$. This means that for low initial excitation and weak coupling relatively few states have significant residues, while for large $\alpha$ and/or $v$ a lot of residues are comparable. In the special case $v = 0$ (accounting for the $T = 0$ spectrum), the Laguerre polynomial is unity and the matrix element simplifies to

$$
\langle \varphi_w | T^\alpha | \varphi_0 \rangle = \frac{1}{\sqrt{w!}} e^{-\frac{\alpha^2}{4}} \left( \frac{\alpha}{\sqrt{2}} \right)^{w}
$$

This has an asymmetric bell shape as a function of $w$, with the maximum close to $(\alpha^2 - 1)/2$.

Given the analytic expression for poles (5.10) and residues (5.11), the photoemission spectrum for initial state is expressed, in term of the Green’s function (4.14), as

$$
I_v(E) = -\frac{1}{\pi} \text{Im} G_{ii}(E + i0^+) = -\frac{1}{\pi} \sum_w \text{Im} \frac{R^w_v}{E + i0^+ - E^w_v}
$$

with $E^w_v$ and $R^w_v$ given by Eqs. (5.10),(5.11).

Before investigating thermal effects, it is instructive to study the shape of spectra produced by a given initial state. In Fig. 5.2 we compare the spectra from initial states $v = 0$ (ground state), 1, 3 and 10 phonons, for the following values of coupling: $g = 0.1, 1, 2, 3, 5, 10$. For small $g$ the e-v interaction induces only a weak change in the eigenfunction, and few weak satellite structures appear in the spectra, regularly separated by $\hbar \omega$. In particular, for $g = 0.1$ no visible structures appear, meaning
Figure 5.2: Comparison of the spectra for different values of coupling $g = 0.1, 1, 2, 3, 5, 10$. Each frame contains, from top to bottom, the photoemission spectra for initial excitation characterized by $v = 0, 1, 3, 10$ phonons. The vertical dashed line marks the final ground-state energy position $-g^2 \hbar \omega / 8$. The sticks are normalized so that the sum of the intensities equals unity. The vertical scale is the same for all panels within the same frame.
that the initial states are substantially unperturbed by the e-v coupling. This is reflected also by the imperceptible ground state energy lowering (vertical dashed line in Fig. 5.2). Increasing the coupling, the spectral weight displaces to final states corresponding to different phonon numbers. Starting from the ground state, only higher energy peaks appear, while for excited initial states also some lower-energy anti-Stokes structures appear, corresponding to less phonons in the final states. As is especially clear for strong coupling, we find an anti-Stokes peak for each of the accessible states, i.e. one peak for \( v = 1 \), corresponding to a transition to the ground state \( w = 0 \) of the distorted oscillator; three peaks for \( v = 2 \) corresponding to state with \( w = 0, 1 \) and 2 phonons and so on. For very strong coupling, in particular at \( g = 10 \), the final ground-state eigenfunction is substantially orthogonal to the initial one, due to the large distortion. Here the spectral weight is spread on a lot of final states. Note the approximate symmetry of these spectra around the zero-energy position, reflecting the fact that the final and initial mean energy, remains approximatively the same.

For a system in thermal equilibrium, a statistical approach is necessary, and the characteristic effects of temperature on the spectra are readily investigated through this simple model. The spectrum at finite \( T \) given by Eq. (4.9) can be written as

\[
I(E) = -2 \frac{\hbar}{\pi} \sum_v \frac{e^{-\beta E_v}}{Z} I_v(E) = -\frac{1}{\pi} \sum_{vw} \operatorname{Im} \frac{R_w^v(T)}{E + i0^+ - E_w^v}
\]

where \( Z = \sum_v e^{-\beta E_v} \), and

\[
R_w^v(T) = \frac{1}{Z} e^{-\beta E_v} R_w^v.
\]

with \( E_w^v \) and \( R_w^v \) are given by Eqs. (5.10),(5.11). The sum on all initial final states \( v, w \) amounts to a sum of all poles, with suitable weights.

In Fig. 5.3, we shown a few spectra, calculated at different temperature: \( T = 0.2 \, \hbar \omega, 4 \, \hbar \omega, 20 \, \hbar \omega \). Because of the Boltzmann factor \( e^{-\beta E_v} \), at low temperature substantially only the ground state is involved, and the spectra almost coincide with the 0-phonons spectra of Fig 5.2. At higher temperature, the main effect is to broaden the spectra, eventually reaching a Gaussian-like structure centered at \( E = 0 \). The broadening effect is stronger at larger coupling. At \( g = 0.1 \) only exceedingly weak satellites appear, even at a relatively high temperature \( (T = 20 \hbar \omega) \). For large coupling the contribution of many excited states becomes important and the large broadening makes the spectra very flat.

For an \( A \) mode, the overall effect of temperature is to make the spectra broaden and more regular, but not any denser: the constant separation \( \hbar \omega \) of neighboring structures is maintained in temperature, due to Eq. (5.10).

5.1. \( X \otimes A - \text{SHIFTED OSCILLATOR} \)
Figure 5.3: Temperature dependence of the photoemission spectrum, for several values of the coupling $g$. From top to bottom, each frame contains the spectrum corresponding to $k_B T = 0.2 \hbar \omega, 4 \hbar \omega, 20 \hbar \omega$. The vertical dashed line marks the final ground-state energy position $-g^2 \hbar \omega / 8$. 
5.2 The $A$ modes in a many-mode context

In this Section we extend the results of the previous Section to many-mode systems, in which, also degenerate modes may be active.

In the case of a degenerate orbital $x$ coupled to degenerate vibrations $X$, the coupling breaks the orbital degeneracy. The interaction of a given degenerate mode with the hole is correlated to the dynamics of all other modes interacting with the same hole state at the same time. They cannot be separated from each other, and no exact relation of the type (5.10),(5.11) are applicable for the degenerate JT modes. This more involved situation requires a numerical treatment introduced in Chapt. 6. However, it is still exactly true, regardless of any possible splitting of the electronic degeneracy, that the totally symmetric non degenerate $A$ vibrations only couple to the total charge in the orbital, and remain therefore completely decoupled from each other and from all modes of different symmetry $X$. The analytic treatment of $A$ modes of previous Section, remains therefore relevant to the many-mode context.

The Hamiltonian of a many-mode system is conveniently separated into two contributions:

$$H = \sum_i H_i^A + H^X. \tag{5.19}$$

The first term contains the $H_i^A$ harmonic and electron-phonon Hamiltonians of the nondegenerate $A$ modes, each given by Eq. (5.3) with its specific frequency $\omega_i$ and couplings $g_i$). The latter term $H^X$ describes collectively the coupling to all degenerate modes $X$ and include also the electronic Hamiltonian $H_0$ of Eq. (5.2).

We indicate with $\Psi^X_{\tilde{w}}(r, Q_X)$ the eigenstates of the Hamiltonian $H^X$ with eigenvalues $E^X_{\tilde{w}}$, describing the dynamics of one hole, whose coordinates are $r$, and of the nondegenerate normal vibration $Q_X$. They are, in general, vibronic states and do not factorize into electronic and vibrational wavefunctions, as in Eq. (5.7). $\tilde{w}$ globally indicates the quantum numbers characterizing these vibronic states. Then, the eigenstates of the total Hamiltonian (5.19) are factorized as:

$$\Psi^f_{\tilde{w} w_1 w_2 \ldots}(r, Q_{\tilde{w}}, Q_1, Q_2 \ldots) = \Psi^X_{\tilde{w}}(r, Q_X) \varphi_{w_1}(Q_1 + \frac{1}{2} n g_1) \varphi_{w_2}(Q_2 + \frac{1}{2} n g_2) \ldots \tag{5.20}$$

and the corresponding eigenvalues are

$$E_{\tilde{w} w_1 w_2 \ldots} = E^X_{\tilde{w}} + E_{w_1} + E_{w_2} + \ldots \tag{5.21}$$

$\varphi_{w_1}$ and $E_{w_1}$ are the eigenstates of the Hamiltonian $H_i^A$, for each of the nondegenerate modes, given by Eqs. (5.6),(5.5), with coordinates $Q_i$.

As in Eq. (5.3), the overlap between initial and final states factorizes

$$\langle \Psi^f_{\tilde{w} w} | c^\dagger_{\mu} | \Psi^i_{v} \rangle = \langle \Psi^X_{\tilde{w}} | c^\dagger_{\mu} | \Psi^X_{\tilde{w}} \rangle \langle \varphi_{w_1} | T^{\alpha_1} | \varphi_{v_1} \rangle \langle \varphi_{w_2} | T^{\alpha_1} | \varphi_{v_2} \rangle \ldots \tag{5.22}$$
The initial states are given in terms of the wavefunctions $\Psi_i^X$, of energy $E_i^X$, describing globally the degenerates modes $X$ and the electronic motion within the degenerate shell, and of the vibrational eigenstates $\varphi_i$ of each harmonic oscillator of symmetry $A$, whose eigenvalues are $E_{vi}$. $\langle \varphi_{wi} | T^a | \varphi_{vi} \rangle$ are again the residues $R_{vi}$ given by Eq. (5.11) for a single nondegenerate mode. Then the poles and residues of symmetry in Eqs. (5.18).

The initial states are given in terms of the wavefunctions of degenerates modes, completely independently from non-degenerate shell, and of the vibrational eigenstates through Eqs (5.23), (5.24), (5.27). This reduces the number of active degrees of freedom, making the numerical approach, required by the really JT-coupled degenerates modes, easier.

In the next Section we apply these analytical results to simple case of two $A$ modes, to show the effect of the coupling to many modes in the most transparent

\begin{align}
E_{\psi v_1 v_2 \ldots}^\psi &= X E_{\psi}^0 + E_{v_1}^v + E_{v_2}^v + \ldots \\
R_{\psi v_1 v_2 \ldots}^\psi &= X R_{\psi}^0 R_{v_1}^v R_{v_2}^v \ldots
\end{align}

in terms of the poles $E_{\psi}^0$ and residues $R_{\psi}^0$ of each $A$ mode, which can be calculated analytically through Eqs. (5.10), (5.11), and those of the degenerate modes $X$, given by $X E_{\psi}^0 = E_{\psi}^X - E_{\psi}^0$ and $X R_{\psi}^0 = \frac{1}{\mathbf{d}} \sum_{\mu} |\langle \Psi_{\psi}^X | c_{\mu}^\dagger | \Psi_{\psi}^X \rangle|^2$, which include the sum on the orbital components $\mu$. $X E_{\psi}^0$ and $X R_{\psi}^0$ do not have analytic expressions like (5.10), (5.11) and necessitate a numerical approach. In particular for nontrivial JT-systems the poles $X E_{\psi}^0$ are not simply multiples of the original frequency as in Eq. (5.10).

The total spectrum is then written, using (5.23) and (5.24), as

\begin{align}
I(E) &= \sum_{v_1 v_2 \ldots} \frac{1}{Z_X Z_1 Z_2 \ldots} e^{-\beta (E_{\psi}^X + E_{v_1}^v + E_{v_2}^v + \ldots)} I_{\psi v_1 v_2 \ldots}(E) \\
I_{\psi v_1 v_2 \ldots}(E) &= -\frac{1}{\pi} \sum_{v_1 v_2 \ldots} \text{Im} \frac{R_{\psi v_1 v_2 \ldots}}{E + i0^+ - E_{\psi v_1 v_2 \ldots}}
\end{align}

Using (5.23), (5.24), (5.27) we can write the spectrum at finite temperature, in a more useful form similar to Eq. (5.17), as

\begin{align}
I(E) &= -\frac{1}{\pi} \sum_{v_1 v_2 \ldots} \frac{X R_{\psi}^0(T) R_{v_1}^v(T) R_{v_2}^v(T) \ldots}{E + i0^+ - (X E_{\psi}^0 + E_{v_1}^v + E_{v_2}^v + \ldots)}
\end{align}

in terms of the thermally weighted residues of each separated subsystem, introduced in Eqs. (5.18).

The important result obtained here is that we can approach the complicated problem of the coupling to degenerate modes, completely independently from non-degenerate ones, whose contributions can be calculated analytically and included through Eqs (5.23), (5.24), (5.27). This reduces the number of active degrees of freedoms, making the numerical approach, required by the really JT-coupled degenerates modes, easier.

In the next Section we apply these analytical results to simple case of two $A$ modes, to show the effect of the coupling to many modes in the most transparent
situation. Some features of the spectra obtained, are characteristic of the many modes system, and their investigation are a preliminary step to the understanding of more complicated systems, such as C$_{60}$. We close the chapter, computing a fictitious spectrum of C$_{60}$, treating all the modes as they were nondegenerate.

5.3 Two A modes

The general results of Sect. 5.2 apply, in particular, to the the case of many non-degenerate A modes coupled to same orbital $x$. The spectra for such a system can be computed analytically through Eqs. (5.27), (5.18) and the expressions for the poles (5.10) and residues (5.11).

In this Section we study the system of two A modes, $A_1$ and $A_2$, of frequency respectively $\hbar \omega$ and $6.2 \hbar \omega$. In Fig. 5.4 we show the spectra for different values of the dimensionless coupling $g_1 = 1, 2, 3, 5$, at a fixed value of the coupling $g_2 = 1$, at a temperature $kT = 2 \hbar \omega$. We choose these values looking at the problem of C$_{60}$ which is the object of this work. In fact, the ratio between the modes $A_2$ and $A_1$ mimics the ratio between the highest and lowest frequency modes of C$_{60}$, $H_g 8$, of coupling $g \approx 1$, and $H_g 1$ of coupling $g \approx 3$ (Table 3.1). They are also the most strongly coupled and we will show them to be responsible of the important features of the C$_{60}$ photoemission spectrum. Also, for mode $H_g 1$ the temperature of $2 \hbar \omega$ corresponds at about the 800 K of the experimental measurement.

We plot the spectra $A_1 + A_2$ of this two modes system, together with those of the individual single modes, suitably shifted to align the ground-state energy. In fact, each mode gives independently an energy shift of $-\frac{1}{2} g_1^2$ as show schematically in Fig. 5.1. We broaden the spectra with Lorenzians of width $\epsilon = 0.5$, and show them together with their “stick” original structures. For relatively weak coupling of $A_1$, $g_1 = 1$ (left top of Fig. 5.4), the gross structures of the spectrum are determined by the higher frequency mode $A_2$: we find a satellite exactly $6.2 \hbar \omega$ above the main peak, given by the $A_2$ 1-phonon excitations. Also, a weak 2-phonons structure appears at $12.4 \hbar \omega$, but it is flattened by the adding of the low-frequency mode $A_1$. The effect of the low-frequency mode $A_1$ is just to broaden the peaks, through regular minor structures appearing at exactly $\hbar \omega$ separations. At larger coupling, $g_1 = 2$ (right top), the broadening of $A_1$ increases. The important features are still those of the $A_2$ mode, but the $A_1$ broadening displaces some spectral weight away from the main structures and the satellite at $6.2 \hbar \omega$ becomes broader. For $g = 3$ (left bottom) the contribution of the $A_2$ mode appears only as an asymmetric shoulder in an otherwise mainly $A_1$ spectrum. For a coupling as large as $g = 5$ (right bottom), we recover a Gaussian-like shape, while the $6.2 \hbar \omega$ satellite completely disappears. Looking at the stick structures of the spectra we can still see the weak poles corresponding to 1-$A_2$-excitations at $(6.2 \pm n) \hbar \omega$, aside of those of 0-$A_2$-
Figure 5.4: Solid lines: photoemission spectra for two nondegenerate modes $A_1$ and $A_2$, of frequency respectively $\hbar \omega$ and $6.2 \hbar \omega$, for different values of the dimensionless coupling $g_1 = 1, 2, 3, 5$, for $g_2 = 1$. The single-mode spectra (dashed) are shown for reference and shifted to the same ground-state energy of the two-mode calculation. The main satellite corresponds to the characteristic $1-A_2$-phonon excitation, at exactly $6.2 \hbar \omega$ from the main peak. The lower-frequency mode, with its dense structures at $\hbar \omega$, accounts for the broadening of both the main peak and the satellite and at strong coupling flattens them completely.
phonons at $\pm m \hbar \omega$, but the broadening covers easily these details.

In Fig. 5.5 we show the same calculation for larger values of the $A_2$ coupling, $g_2 = 3$. The difference from Fig. 5.4 is that several strong structures appear, corresponding to many-phonons excitations of the higher-frequency mode. But the interpretation of the spectral shape remains the same: the higher-frequency modes $A_2$ characterizes the main features of the spectrum, while the lower-frequency one, $A_1$, more sensible to thermal effects, accounts for the observed broadening. Note that the overall broadening of the lower right panel, where both $g_1$ and $g_2$ are large, follows the envelope of the $A_2$ spectrum.

These conclusions are bound to apply to the photoemission spectrum of any many-modes system characterized by some low frequency modes ($\hbar \omega < k_B T$) which are strongly thermally excited, plus some others high frequency mode ($\hbar \omega > k_B T$), whose contribution is to construct the gross structures of the spectrum. We are likely to find the same roles of different classes of modes even in the JT spectra. However, because the electronic and vibrational excitations are mutually entangled in the JT final state coupling, the vibronic excitation are bound to lose the regular phonon-like fine structure characteristic of $A$ modes and well illustrated in Fig. 5.4 and 5.5.

### 5.4 66 A modes: a fictitious spectrum of $C_{60}$

To conclude the chapter we apply the results of the previous Sections to calculate analytically the spectrum of a fictitious $C_{60}$, with all 66 active modes treated as nondegenerate $A$ modes. We are principally interested to highlight, through the comparison with experimental spectra [1, 2], the features which are not explainable by this approach, and which are instead typical JT-features associated to the degeneracy of the active modes.

For its calculation we use the frequencies of Table 3.1, and such coupling as to give the same adiabatic energy gain of the degenerate modes, also accounting for the zero-point quantum correction. For degenerate modes the adiabatic energy gain is given by a different expression from that of the nondegenerate modes. However it still holds true that the simultaneous coupling of several modes will generally lead to a cumulative classical distortion and to an adiabatic energy gain which is the sum of the individual energy gains [15, 16]. Given the energy gain for the $A$ mode $E_A = -(1/8)g_A^2$, for the $H$ modes $E_{H_g} = (1/18)(g_{H_g} \sin \alpha)^2 + (1/10)(g_{H_g} \cos \alpha)^2$ and for the $G$ modes $E_{G_g} = (1/18)g_{G_g}^2$ we use the relation

$$\frac{1}{8} \tilde{g}_\Lambda^2 = \frac{E_{\Lambda}^{adi}}{E_0} \frac{1}{d_\Lambda} E_\Lambda. \quad (5.28)$$

With $\tilde{g}$ we indicate effective couplings for each $A$ mode representing a mode of
Figure 5.5: Solid line: Photoemission spectra for a system of two nondegenerate modes $A_1$ and $A_2$, of frequency respectively $\hbar \omega$ and $6.2 \hbar \omega$, for different values of the dimensionless coupling $g_1 = 1, 2, 3, 5$, for $g_2 = 3$. The single-mode spectra (dashed) are shown for reference and shifted to the same ground-state energy of the two-mode calculation. The important features of the spectrum correspond to the characteristic higher-frequency phonons excitations, at $6.2 \hbar \omega$ separation. The lower-frequency mode, with its dense structures at $\hbar \omega$, accounts for the broadening of the $A_2$ peaks and at strong coupling completely washes them out.
5.4. 66 A MODES: A FICTITIOUS SPECTRUM OF $C_{60}$

Figure 5.6: Fictitious $C_{60}$ spectrum, calculated treating all the 66 vibrational normal modes as nondegenerate $A$ modes, rescaling the actual couplings of $C_{60}$ (Table 3.1) to give the correct JT energy shift. Comparison with the measured spectrum [1] (The broadening $\epsilon = 10$ meV mimicks the declared experimental resolution [1]).

symmetry $\Lambda$. The factor $1/d_\Lambda$ accounts for the fact we take $d_\Lambda$ $A$ modes for each $d_\Lambda$-degenerate mode $\Lambda$. The remaining factor is the ratio between the zero-point adiabatic energy $E_0^{\text{adi}}$ and the exact quantum value $E_0$ computed in Chap. 7. We rescale all modes to obtain the correct energy gain. We chose to ignore the fact that $G_g$ modes and the sin $\alpha$ part of the $H_g$ modes contribute to the $D_3$ minima, instead of the $D_5$, as these are small it would not make much difference even to leave them out.

In Fig. 5.6 we show the spectrum corresponding to the system of these 66 non-degenerate modes, together with the measured spectrum [1], shifting the spectra (i.e. the HOMO position with respect to the vacuum) to have them superimposed. We see that the general amount of broadening and the asymmetric shape of the spectra are accounted for by this simple model. But important features are missed by this calculation:

a) the main satellite at about 230 meV from the main structure disappears completely. This peak found at a frequency higher than each of the characteristic frequency: it must reflect some typical DJT effect as shell investigate in Chap. 7.

b) the secondary structures at multiples of $\hbar \omega_{H_g1}$ in the calculated spectra miss
the smooth structureless shape of the measured one. This reflects the fact that degenerate modes do not produce simple vibrational levels in the final state, but vibronic ones, strongly coupling dependent.
Chapter 6

The degenerate modes: Lanczos diagonalization

A degenerate molecular orbital coupled to degenerate vibrations, splits the orbital degeneracy. The motions of the degenerate modes are strongly correlated and cannot be separated from each other, as could be done for $A$ modes. No exact relation of the type (3.10, 3.11) are applicable here, and numerical approaches are needed, due to the large size of the Hilbert space.

In short, the problem we have to face is the diagonalization of the Hamiltonian matrix (3.6), or equivalently the resolvent (4.4), calculated on harmonic oscillator basis, in principle infinite dimensional. In practical only relatively few final states, in the distorted configuration, have nonnegligible overlaps with the initial excitation, as seen for $A$ modes in Sect. 5.1 and thus a finite number of orthonormal basis states can be considered. However, to obtain converged results, the basis to consider must often contain several millions states, due to the relative complexity of $C_{60}^+$ ion (it has 66 coupled vibrational degrees of freedom, plus the hole dynamics). Moreover finite temperature calculations imply numerous initial excitations, making the numerical approach computationally heavier.

The molecular symmetry and the form of the Hamiltonian is helpful in that, for a suitable choice of the basis, only a small fraction of the matrix elements of the linear JT-Hamiltonian (3.6) is nonzero. Then $H$ can be represented by a sparse matrix with $N^{st}$ rows and a few (about 7) nonzero elements in each row. This way, the memory required for storing the Hamiltonian matrix are not very severe, and matrices of $N^{st} \geq 10^6$ are treated routinely within computer memories of about 1 GB. Finding eigenvalues and eigenvector of such large matrices is not possible with standard algorithm performing the full diagonalization. The separation of the nondegenerate $A$ modes from the numerical calculation, illustrated in the previous Section, and symmetry considerations improve this situation only marginally. To approach the problem, one must instead resort to the power algorithms, among
which the Lanczos algorithm \[47\] is one of the most widely known and most efficient.

In this Chapter we introduce the Lanczos method, and its specific application to the calculation of photoemission spectrum from linear JT molecules, in particular from C\( _{60} \). We test the method through the calculation of single-mode, and few modes spectra at \( T = 0 \) and in Sect. 6.3 we show the results of the calculation of the collective contribution of the nondegenerate modes to the C\( _{60} \) spectrum at \( T = 0 \), concentrating on its convergence. We devote the next Chapter to the comparison with the measured spectrum, and its interpretation.

In spite of the impossibility of the calculation of C\( _{60} \) spectrum at high temperature (\( T > 100 \) K), we finally describe the specific technique used to approach finite temperature, based on the random sampling of the ensemble of the initial thermal excitations. We show the results of single-mode calculations, in particular for the lowest frequency modes \( H_{g1} \), which together with the \( T = 0 \) total spectrum of C\( _{60} \), will be the ingredient that, in the next Chapter, allows us to interpret the experimental spectra.

## 6.1 The Lanczos algorithm

The Lanczos method is a very convenient approach for the determination of eigen-solutions of matrices, especially those of very large size and sparse character (i.e. with many matrix elements equal zero). The essential principle of the Lanczos recursion method is very simple and very general at the same time. Consider a quantum system, a Hermitian operator \( H \), and a number \( N^{st} \) (arbitrary large) of orthonormal basis states \( \{ \Psi_k \} \) \( (k = 1, 2, \ldots, N^{st}) \). Starting from any given state \( |f_0\rangle \) belonging to the space spanned by \( \{ \Psi_k \} \), and operating with \( H \), the recursion method provides a one dimensional chain representation of the original quantum system.

To illustrate the procedure, consider an operator \( H \) (usually the Hamiltonian of the system) and an initial normalized state \( f_0 \), arbitrarily chosen; the starting state \( f_0 \) is often addressed as the seed state of the procedure. We apply the operator \( H \) to the initial state and subtract from \( H|f_0\rangle \) its projection on the initial state, so to obtain a new state \( F_1 \), orthogonal to \( f_0 \). The operation of orthogonalization can be conveniently performed by means of the projection operator \( P_0 = |f_0\rangle \langle f_0| \), and the state \( F_1 \) can be expressed as

\[
|F_1\rangle = (1 - P_0) \ H|f_0\rangle = H|f_0\rangle - a_0 |f_0\rangle
\]  

where clearly

\[
a_0 = \langle f_0| H |f_0\rangle.
\]

Let us indicate with \( b_1 \) the norm of \( F_1 \), and with \( f_1 \) the corresponding normalized
state, namely
\[ b_1^2 = \langle F_1 | F_1 \rangle, \quad |f_1\rangle = \frac{1}{b_1} |F_1\rangle. \] (6.3)

In a rather similar way we proceed now by applying the operator \( H \) to the state \(|f_1\rangle\); then \( H|f_1\rangle \) is orthogonalized to both \(|f_1\rangle\) and \(|f_0\rangle\), obtaining the state \(|F_2\rangle\).

We have
\[ |F_2\rangle = (1 - P_1)(1 - P_0) H|f_1\rangle = (1 - P_1 - P_0) H|f_1\rangle \] (6.4)
where \( P_1 = |f_1\rangle \langle f_1| \) denotes the projection operator on the state \( f_1 \). We thus obtain
\[ |F_2\rangle = H|f_1\rangle - a_1 |f_1\rangle - b_1 |f_0\rangle \] (6.5)
where
\[ a_1 = \langle f_1 | H|f_1\rangle, \quad b_1^2 = \langle F_2 | F_2 \rangle, \quad |f_2\rangle = \frac{1}{b_2} |F_2\rangle. \] (6.6)
and the last term \( b_1 |f_0\rangle \) in Eq. (6.5), is a direct consequence of (6.1) and (6.3).

Let us now proceed to the next logical step of the sequence, and here we arrive at the key point of the ingenious, and yet so simple, Lanczos procedure. Consider in fact the state \( F_3 \) obtained by orthogonalization of \( H|f_2\rangle \) to the previous states \( f_0, f_1, f_2 \); we have
\[ |F_3\rangle = (1 - P_2)(1 - P_1)(1 - P_0) H|f_2\rangle = (1 - P_2 - P_1 - P_0) H|f_2\rangle \] (6.7)
We notice that \( P_0 H|f_2\rangle \equiv 0 \) since \( \langle f_0 | H|f_2\rangle \equiv 0 \): thus the iterative procedure leads to a three-terms relation. This is the most remarkable feature of the Lanczos method: that it provides a recursive relation based on three terms only.

Iterating \( n \) times this procedure, orthogonalizing the new generated state \( H|f_n\rangle \) only with respect to its two predecessors \( |f_n\rangle \) and \( |f_{n-1}\rangle \), we obtain
\[ |F_{n+1}\rangle = H|f_n\rangle - a_n |f_n\rangle - b_n |f_{n-1}\rangle. \] (6.8)
The next pair of coefficients are given by
\[ b_{n+1}^2 = \langle F_{n+1} | F_{n+1} \rangle, \quad a_{n+1} = \langle f_{n+1} | H|f_{n+1}\rangle. \] (6.9)
The three term relation (6.8) is all we need to generate the orthonormal basis \(|f_0\rangle, |f_1\rangle, \ldots \) and the set of coefficients \( \{a_n\} \) and \( \{b_n\} \). Having to deal with only three large vector at the same time is a remarkable advantage, both conceptual and technical, in the specific calculations carried out by a computer code. On the basis set \( \{|f_n\}\) the operator \( H \) is represented by the tridiagonal matrix
\[ H = \begin{pmatrix} a_0 & b_1 & b_2 & b_3 & \cdots \\ b_1 & a_1 & b_2 & \cdots \\ b_2 & a_2 & \cdots \\ b_3 & \cdots \\ \vdots & \vdots & \vdots & \ddots & \ddots \end{pmatrix} \] (6.10)
The operator (6.10) can also be written in the form

\[ H = \sum_{n=0}^{\infty} a_n |f_n\rangle \langle f_n| + \sum_{n=0}^{\infty} b_{n+1} [ |f_n\rangle \langle f_{n+1}| + |f_{n+1}\rangle \langle f_n| ] \quad (6.11) \]

The recursion method allows (at least in principle) to bring in a tridiagonal form the Hamiltonian of any system, with an arbitrary number \( N^{st} \) of states. No explicit diagonalization of the original matrix \( H \) is required for performing such a transformation. The one-dimensional chain representation is interesting first of all since it describes economically the system through the \( 2N^{st} - 1 \) parameters \( a_n \) and \( b_n \), rather than the original \( N^{st}(N^{st} + 1)/2 \) matrix elements, for a generic basis (for \( N^{st} = 10^6 \) for instance, we have packed the spectral information in approximately two million numbers instead of \( 5 \times 10^{11} \) numbers).

An even more crucial feature of the tridiagonal representation (6.10), making the Lanczos procedure extremely convenient for spectral calculations, is the possibility to obtain very easily the Green’s function (4.4). In particular, by explicit expansion of the inverse matrix element \( G_{00} \) in terms of determinants, it is straightforward to show that the matrix element \( G_{00} \) on the seed state \( f_0 \) is given by the continued fraction expansion

\[ G_{00}(E) = \langle f_0 | \frac{1}{E - H} | f_0 \rangle = \frac{1}{E - a_0 - \frac{b_1^2}{E - a_1 - \frac{b_2^2}{E - a_2 - \ldots}}} \quad (6.12) \]

It has been verified that in most cases few terms \( M \sim 300 \) are normally sufficient to get converged spectra over the whole range of energies [18].

Besides computing the Green’s function, the Lanczos method is suitable for the calculation of approximate ground and excited energies. The first \( M \ll N^{st} \) steps of the Lanczos chain generate a relatively small tridiagonal matrix \( H_M \) (6.10), that is easily diagonalized using standard numerical routines to obtain approximate eigenvalues \( \epsilon_j \), with corresponding eigenvectors \( \Psi_j^L \), in the full space

\[ |\Psi_j^L \rangle = \sum_{i=0}^{M} v_{ji} |f_i\rangle, \quad j = 0 \ldots M \quad (6.13) \]

given in terms of the eigenvector \( v_{ji} \) of the tridiagonal matrix \( H_M \) in the space spanned by the Lanczos vectors \( |f_0\rangle, |f_1\rangle \ldots |f_M\rangle \). It is important to realize that \( |\Psi_j\rangle \) are in general not exact eigenfunction of \( H \), but show a remainder

\[ H|\Psi_j^L \rangle - \epsilon_j|\Psi_j^L \rangle = b_{M+1} v_{jM} |f_{M+1}\rangle \quad (6.14) \]

Generally, relatively few iterations \( M \) are needed to converge the most widely separated eigenvalues, especially those whose eigenfunctions have large overlap with
6.2. THE JT MODES OF C\textsubscript{60}: LANCZOS SPECTRA

the seed state. Few hundred iterations are typically suitable to our aim \[48\], and all the calculated spectra shown in the present work are completely converged with the $M = 300$ iterations we have used.

If in equation (6.8) $b_{M+1}$ happens to vanish, we have found a $(M+1)$-dimensional eigenspace where $H_M$ is already an exact representation of $H$. This unavoidably occurs when $M = N^{st} - 1$, but for $M < N^{st} - 1$ it can only occur if the starting vector $f_0$ is orthogonal to some invariant subspace of $H$. This is clearly true if the seed state $f_0$ belong to some particular symmetry species. Symmetry consideration are therefore very important to improve the numerical calculation.

The first column of matrix $v_{ji}$, containing the projections of the Lanczos eigenvectors $|\Psi^L_j\rangle$ on the basis $\{|f_0\rangle, |f_1\rangle \ldots |f_M\rangle\}$, contains the overlaps $v_{j0} = \langle f_0 | \Psi^L_j \rangle$ of the initial state to the eigenstates, which are useful for version (4.11) of the theoretical spectrum. This observation permits us to refrain from ever computing $v_{ji}$, with a large computational advantage.

6.2 The JT modes of C\textsubscript{60}: Lanczos spectra

In this Section we come to the specific application of the Lanczos method to the calculation of the photoemission spectrum of C\textsubscript{60}, described in term of linear JT Hamiltonian (3.6) for the final ion C\textsuperscript{+}\textsubscript{60}. Unlike the nondegenerate $A$ modes, whose dynamical response separates out, degenerate modes $H_g$ and $G_g$ are strongly correlated and cooperate to the final JT vibronic structure. In the medium-coupling regime of C\textsubscript{60} (Table 3.1), neither a static JT treatment, where tunneling between equivalent minima is neglected, nor the perturbation-theory approach do work.

Therefore we compute the photoemission spectrum by numeric Lanczos diagonalization of the Hamiltonian (3.6), on the product basis of the five HOMO hole states times the $N^{\text{osc}} = 64$ degenerate $H_g$ and $G_g$ modes of Table 3.1. As the JT-interaction term (3.9) connects only states with one phonon of difference, on this basis the Hamiltonian is a very sparse matrix, particularly suitable to Lanczos method. Moreover symmetry considerations allow us to restrict the calculation to invariant subspace, considerably relaxing the memory requirement. In fact, states belonging to different symmetry representations, constitute orthogonal invariant subspace of $H$, which are never connected by Lanczos iterations. Starting with a seed state of given symmetry, we can restrict to the corresponding invariant subspace, cutting off from the basis the eigenstates of different symmetry.

In particular for C\textsubscript{60}, each state (6.16) belongs to a $C_5$ representation, labeled by

$$M = \left( \mu + \sum_{\Lambda jm} m v_{\Lambda jm} \right), \quad (6.15)$$
reported into the $-2 \ldots 2$ range by suitable addition of an integer multiple of 5. This defines five invariant subspaces, that we treat separately, with an improvement of a factor 5 in the basis size\footnote{Even larger size gains would be obtained by labeling states with the full icosahedral symmetry, but that would mean much more intricate basis states: here we prefer to stick to the simple $C_5$ labeling only.}.

The states are then conveniently labeled by $M$ plus the vibrational quantum numbers $v_{\Lambda j}$

$$|M; v_{Hg1}, \ldots, v_{Hg8}, v_{Gg1}, \ldots, v_{Gg6}\rangle$$

where $v_{\Lambda j}$ indicates collectively the set of quantum numbers $v_{\Lambda jm}$ of the degenerate components, for each of the $j$ modes of symmetry $\Lambda$ ($j = 0 \ldots 8$ for $\Lambda = H_g$ and $j = 6$ for $\Lambda = G_g$), accordingly to notation of Sect. 3.5. Together with $M$, they identify uniquely the hole state $\mu$ through Eq. (6.15), and the sum over $\mu$ in Eq. (6.16) is equivalently replaced by a sum over $M$.

Moreover, the terms of that sum are not all independent. In fact, $M = 1$ and $M = 2$ pairs of $C_5$ representations are complex conjugate representations and produce therefore the same spectrum. In addition, the kaleidoscope symmetry \cite{49} of the $I_h$ group guarantees that $M = 1$ and $M = 2$ also give equivalent spectra. Therefore, in practice the only different spectra to be computed are $M = 0$ and, for example, $M = 1$, with a computational time gain of $2/5$.

At this point, each invariant subspace corresponding to a fixed $M$ still contains infinite states, because of the infinite possible bosonic vibrational excitations, thus some truncation is necessary. We cut off the basis by taking all the states below some maximum number of quanta $v_{\Lambda j}$ for each mode and dropping the infinitely many other modes. In fact, as seen in Sect. 5.1 for the trivial case of a single nondegenerate $A$ mode, the overlaps between an harmonic eigenstate and the eigenstates of a shifted oscillator rapidly vanish, when quantum number differences become very large. Each cut basis is then characterized by the set $\{\bar{v}_{\Lambda j}\}$ of the maximum number of phonons needed by each degenerate oscillator. To better illustrate the meaning of this mask, the simple example of Fig. 6.1 is illuminating. We build the basis states, distributing up to $1, 2, \ldots n$ phonons only among the modes for which $n \leq \bar{v}_{\Lambda j}$. For the example of Fig. 6.1 of a system of three modes and a mask $\{5, 2, 3\}$, this means to distribute up to 2 phonons among all modes, 3 phonons only between the modes 1 and 3, and up to 5 phonons only in mode 1, as represented graphically in the left side of Fig. 6.1. On the right side we show a more typical truncation, where a global cutoff is used, with $v_{\text{max}}$ representing the maximum number of quanta we distribute in all the modes.

It is evident the convenience of the our truncation (left side): setting the cutoff $\bar{v}_{\Lambda j}$ to a large value for the strongly coupled modes, we include much fewer states, only those giving the important structures of the spectra. The contribution of the
dropped states amounts to some broadening of the weaker structures corresponding to modes with small cutoff. These are negligible effects in particular at low temperature.

In Fig. 6.2 we investigate the single-mode convergence of the most strongly coupled modes of $C_{60}$: $H_g^1$, $H_g^2$, $H_g^3$, $H_g^7$ (the frequencies and coupling are listed in Table 3.1), at $T = 0$ (i.e. for the 0-phonons – ground state – initial excitation). All the spectra are calculated with the continued-fraction expansion (6.12) on a Lanczos chain of 300 iterations, and a Lorenzian broadening of 5 meV. For those single-mode systems the mask is simply the max number of phonons, and our truncation coincides with the standard one. However, it is interesting to observe that, in this medium-coupling regime, except the strongest mode $H_g^1$, which needs up to 10 phonons to converge completely, all the other modes already with two phonons give converging results. At this resolution, all these modes show only a one-phonon satellite at about $\hbar \omega_{\Lambda j}$ from the main zero-phonon peak. The position of the 1-phonon peak is blue-shifted with respect to the original frequency of the mode. It is also split into two vibronic final structures, only visible for mode $H_g^7$ in Fig. 6.2 due to the broadening: This is a typical JT-effect, crucial for the interpretation of the observed $C_{60}$ photoemission spectrum, as we will show in the next Chapter.

For a many modes system the cutoff must be slightly raised with respect to the
Figure 6.2: Convergence of the $T = 0$ K computed spectra of single degenerate mode, for the most strongly coupled modes of $C_{60}$, $H_g1$, $H_g2$, $H_g3$, $H_g7$ for increasing cutoff of the basis. All spectra are broadened with Lorentzians of width 5 meV. Except the strongly coupled $H_g1$, ($g_{H_g1} > 3$), which needs to include up to 10-phonon states, the other modes (whose coupling is $\approx 1$) are converged with the inclusion of only the 2-phonons states. They all show basically one satellite corresponding to the 1-phonon excitation. Note the splitted JT-vibronic structure of the $H_g7$ mode, appearing in spite of broadening.
values obtained for the single mode Fig. 6.2. Consider, for example, the 2-mode system consisting of the most strongly coupled mode $H_g1$ plus $H_g3$, also significantly coupled. The left panel of Fig. 6.3 shows the $T = 0$ spectrum calculated for different masks. The mask $\{15,2\}$, extracted by the single mode investigation (it would be $\{10,2\}$ but to add phonons into the strongest coupled mode is almost “free” in our cutoff scheme, so we stay on the safe side) is far from giving a converging spectrum, because states with one $H_g3$-phonon and more than two $H_g1$-phonons are dropped. Their inclusion, because of the strong coupling of the $H_g1$ mode, adds some broadening to the 1-phonon peak of the $H_g3$ mode, as shown in Fig. 6.3. Due to the low intensity of this peak with respect to the zero-phonon line, relatively few phonons need to be added and the mask $\{10,6\}$ already gives a completely converged spectrum. Moreover for less coupled modes this effect is even less important and stricter cutoffs can be taken, as shown in Fig. 6.3 (right panel) for the system of $H_g1$ plus the weakly coupled $H_g5$.

Finally, in Fig. 6.4, we compare the $T = 0$ spectra calculated applying both the standard cutoff $v_{\text{max}} = 10$ quanta and our strict truncation, with the mask $\{10,6,3\}$, chosen on the basis of the 2-mode spectra of Fig. 6.3. With a basis of only 11079 states we get practically the same results as the standard truncation, involving a basis of 3268760 states. This confirms the validity of our truncation technique, at least at $T = 0$.

All these tests prove the validity of our mask-cutoff method, and provide the ingredients for the calculation of the $T = 0$ photoemission spectrum for the full system of all the $H_g$ and $G_g$ degenerates modes of $C_{60}$ to which we devote the next
6.3 Degenerate modes contribution to the C\textsubscript{60} photoemission spectrum

We come now to the actual calculation of the photoemission spectrum of C\textsubscript{60} at $T = 0$. In Table 6.1 we list the different masks used to cut off the basis. According to the analysis of the previous Section, we employ larger cutoff for the strongly coupled modes, in particular for the modes $H_g1$, $H_g3$, $H_g5$, $H_g7$, and $H_g8$. The modes $G_g$ and the modes $H_{gj}$ with an angle $\alpha_{H_j}$ close to 1.5, contribute weakly in the direction of the $D_3$ minimum and their cutoffs need not be so large.

In Fig. 6.5 we show the result of the calculations corresponding to the masks of Table 6.1. Already a basis of just about 25000 states, corresponding to mask E gives all the main structure, although with an excessive spectral weight in the main peak,
Figure 6.5: Convergence of the computed photoemission spectrum for the system of all degenerate $H_g$ and $G_g$ modes. Different spectra correspond to different cutoff masks listed in Table 6.1. Already with a basis including just about 25000 states (E), the main structures appear. The spectra evolve to full convergence in the largest calculation (A) based on $\sim 4.5$ million states.
Table 6.1: We show the mask used to investigate the convergence of the photoemission spectrum of C\textsubscript{60}, and the dimension of the corresponding basis. The results of the calculation are plotted in Fig. 6.5. In the third column we give the ground state energy E\textsubscript{0}, whose convergence indicate the convergence of the variational calculation.

<table>
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<tr>
<th>mask</th>
<th>dim</th>
<th>E\textsubscript{0}</th>
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<tbody>
<tr>
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<td>55</td>
<td>-102.5328</td>
</tr>
<tr>
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<td>4535498</td>
<td>-102.0102</td>
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<tr>
<td>15 5 4 4 3 4 4 4 3 4 4 3 3</td>
<td>214154</td>
<td>-98.8274</td>
</tr>
</tbody>
</table>

Figure 6.6: Total photoemission spectrum of C\textsubscript{60} at T = 0 K, including also the non degenerate modes, A\textsubscript{g}1 and A\textsubscript{g}2. The effect of the A modes is negligible because of their weak coupling (Table 3.1).
and with a rather poor ground-state energy $E_0$ (JT energy gain) (Table 6.1). As the calculation is variational with respect to an extension of the basis, the convergence of the ground state energy $E_0$ is an indicator of the goodness of the calculation. The values of $E_0$ plus the spectra of Fig 6.3 confirm the validity of the mask-cutoff technique employed and the good convergence of the spectrum A. We shall take spectrum A as the starting point of the analyzing of the spectrum in the following.

Finally, we complete the calculation of the $T = 0$ K photoemission spectrum of C$_{60}$ by the inclusion of the contribution of the A modes, as illustrated in Sect. 5.2. Because of their small coupling their effect is only to slightly broaden globally the spectrum, as shown in Fig 5.6.

In the next Section we extend the present technique to the calculation of the photoemission spectrum at finite temperature, investigating the problems to be faced due to thermal excitation of the initial states.

### 6.4 Finite-temperature Lanczos

The calculation of the spectrum at finite temperature involves the contribution of many initial excitations, in accordance with Eq. (4.16). Besides the obvious problem of requiring a longer computational time, as seen for the nondegenerate modes, Eq. (5.14), high excitations involves many nonnegligible components on highly excited states in the finite state basis: a larger basis could be needed to obtain converging results.

In Fig 6.3, we investigate the convergence problem for a single 5-phonons initial excitation, for the strongly coupled modes, $H_g1, H_g2, H_g3, H_g7$, as we did in Fig. 5.2, for the 0-phonons initial state. Up to 20 phonons for $H_g1$, and to 8-10 for $H_g2, H_g3, H_g7$ are needed to get converging spectra, which requires a much larger basis than for $T = 0$ calculation.

The previous contribution of each given excited initial state to the total spectrum is weighted by the Boltzmann factor $e^{-\beta E_i}$, where $E_i$ is the energy of the initial excitation. Then, for high-frequency modes very few excitation give significant contribution. Unfortunately, the lowest-frequency mode in C$_{60}$, $H_g1$, is also the most strongly coupled one: these two fact end up making finite temperature calculations rather difficult. The mean number of quanta for an harmonic oscillator of frequency $\omega$, is given by the Planck’s relation:

$$\bar{n} = \frac{1}{e^{\beta \hbar \omega} - 1} \quad \beta = \frac{1}{k_B T}. \quad (6.17)$$

We can roughly estimate, that thermal statistics explores states with up to $(\bar{n} + \sqrt{\bar{n}})$-phonons at a given temperature $T$. Consequently, to make a converged quantum
Figure 6.7: Convergence of the spectra with starting excitation (1, 1, 1, 1, 1) and $M = 2$ for increasing cutoff of the oscillators basis. Note the appearance of the 4-phonons anti-Stokes satellite, besides the main line (5 phonons) and Stokes (6 phonons) satellite for all relatively weakly coupled modes $H_{g2}, H_{g3},$ and $H_{g7}$.
6.4. FINITE-TEMPERATURE LANCZOS

In Fig. 6.8 we plot the dependence of \( \bar{n} \) on temperature for the C\(_{60}\) oscillators, including only the degenerate modes involved in the computation. At \( T = 800 \) K, the temperature where molecular beam experiments have been carried out, about \((25 + \sqrt{25}) \approx 30\) phonons excitations are be excited, for which a cut-off of 60 quanta, giving a basis of \( \sim 10^{36} \) states, would be necessary. This is clearly only a rough, slightly pessimistic estimate, but it clarifies that there is no hope to compute photoemission spectrum of C\(_{60}\) at 800 K with this technique. We can only get converging spectra at temperature not higher than about 100 K.

In spite of this, the investigation of the thermal effects in a single-mode spectrum is perfectly feasible: together with the zero-temperature spectrum of C\(_{60}\) of Fig. 6.5, allows us to understand all the important features of the measured spectra, as we will see in Chap. 7.

For single-mode, the spectrum up to 1000 K can be quite easily computed. For the lowest frequency mode \( H_g1 \), which strongly feels the thermal effects, we have to consider up to roughly 15-phonons excitations, (see Fig. 6.8), for which a cut-off of 30 phonons is required. The right panel of Fig. 6.9 shows that indeed 30 phonons (i.e. a basis of 324632 states) gives a well converged thermal spectrum for \( H_g1 \). The sum of Eq. (4.16) involves an ensemble of more than 15000 states (i.e. 15000 spectra to compute).

This huge number of diagonalization can be drastically reduced by random sampling. The idea of random sampling is to substitute the sum over the initial excitations with a sum over a suitable sample granting the correct partition function.
Figure 6.9: Left: sampling convergence. The photoemission spectra at $T = 800$ K, for sampling with 100 and 300 states, are compared to the calculation without sampling on an ensemble of 15504 states, including all states up to 15-phonons initial excitations. Right: basis cutoff dependence.

\[
Z = \sum_i e^{-\beta E_i} \rightarrow Z^s = \sum_{r \in \text{sample}} A(r)
\]  

(6.18)

where $A(r)$ is the correct weight to give to each state $\Psi^r$ of the sample. For each possible initial state we generate a random number $\zeta$ between 0 and $\xi$

\[
0 < \zeta < \xi
\]

(6.19)

where $\xi$ is a number taken in the (0,1] interval in such a way to obtain a sampling of a given size. A state $\Psi^r$ is kept in the sample only if $e^{-\beta E_r} > \zeta$. The probability of keeping a state $\Psi^r$, is then

\[
\frac{e^{-\beta E_r}}{\xi} \quad \text{if} \quad \xi > e^{-\beta E_r}
\]

\[
1 \quad \text{if} \quad \xi < e^{-\beta E_r}.
\]

Then $A(r)$ is simply the $\max(e^{-\beta E_r}, \xi)$ and the photoemission spectrum (4.16) is given in term of the sample states by

\[
I(E) = \frac{1}{Z^s} \sum_{r \in \text{sample}} \max(e^{-\beta E_r}, \xi) I_r(E)
\]

(6.20)

The number of states of the sample depends on the choice of $\xi$ according to

\[
N_s \approx \sum_i \frac{e^{-\beta E_i}}{\xi} n(E_i)
\]

(6.21)
6.4. FINITE-TEMPERATURE LANCZOS

Figure 6.10: Temperature dependence of the $H_g1$ (on the left) and $H_g7$ (on the right) spectra. All spectra have a Lorentzian broadening of 10 meV. Notice the different effect of temperature. On the lowest frequency modes $H_g1$ a large broadening appears, while for the highest frequency one $H_g7$ only little spectral weight displaces from the main peak to the satellites.

where $n(E_i)$ is the number of states of the ensemble with energy $E_i$. Inverting Eq. (6.21) we then get a relation to obtain the correct $\xi$ giving the needed sample dimension $N_s$. A measure of the goodness of the sample is given by the partition function error $Z^s - Z$: an error of few per cent indicates a good sample. The left panel of Fig. 6.9 ($H_g1$ at $T = 800$ K) shows that a sample of few hundred states is sufficient, with a computational time gain of 50-100 times or more.

Finally, notice the much stronger effect of temperature on the lowest-frequency modes $H_g1$ with respect to the highest frequency one $H_g7$ as shown in Fig. 6.10. For $H_g1$, a large broadening appears, giving to the spectrum a Gaussian-like shape, much different from that at $T = 0$ K. For $H_g7$ instead the spectrum at $T = 800$ K remains practically unchanged than at $T = 0$ K. The only effect of thermal excitations is a minor displacement of spectral weight from the main peak to the satellite. In particular we can see a weak anti-Stokes structure at about 200 meV below the zero-phonon line. This is enlightening and suggests where the origin of the large broadening of the measured spectra is.

In the final Chapter we use the present results to interpret the main features of the measured spectra.
Chapter 7

Analysis and discussion

Figure 7.1: The experimental PES by Bruhwiler et al. [1] and by Canton et al. [2].

Photoemission from a closed-shell high-symmetry molecule, involving JT-effect in the final states, is by necessity accompanied by characteristic vibronic structure in the measured spectra. In this chapter we employ our theoretical $T = 0$ photoemission spectrum from the HOMO of $C_{60}$, computed in the previous chapter (Fig. 6.6), to understand and assign single-molecule photoemission spectrum, measured by two separate groups [1, 2] and shown in Fig. 7.1. Unfortunately, both spectra are measured at $T \approx 800$ K in a molecular beam. They show a strong satellite at 230 meV and a weak shoulder around 400 meV above the main peak, and
Figure 7.2: The computed spectrum at $T = 0$ compared with the experimental spectrum (T=800 K). The HOMO, prior to JT coupling is taken at 0 energy on this scale and the experimental spectrum is shifted accordingly. In spite of the large broadening of the measured spectrum, the strong satellite at 230 meV from the main peak, is the dominant features of both spectra. This makes the $T = 0$ photoemission spectrum, stripped of thermal effects, the correct starting point for the understanding of these typical JT features.

a characteristic large asymmetric broadening. This 230 meV separation is some 20% larger than the highest characteristic frequency of C$_{60}$, and thus cannot be understood in terms of a simple non-JT electron-phonon model (see Sect. 5.4 and Ref. [1]).

The gigantic vibrational Hilbert space size called for at this high temperature prevents us from getting converging spectra with the technique described in the previous chapter. However, the $T = 0$ spectrum already shows the main satellite at the right position, plus several other structures hidden by thermal effects in the observed spectrum. Analyzing in detail the different contributions to the computed spectrum, and investigating thermal effects on the more accessible single-mode systems, we account satisfactorily for the experimental lineshape.

7.1 $T = 0$ analysis

In Fig. 7.2 we compare the $T = 0$ computed spectrum, with the measured one (Ref. [1]). In spite of the impossibility of an all-modes finite-temperature calcu-
7.1. $T = 0$ ANALYSIS

Figure 7.3: Analysis of the different contribution to the $T = 0$ computed spectrum. The investigation shows that the main features of the complete spectrum are accounted for by the two high-frequency modes, $H_g^7$ and $H_g^8$, responsible of the strong 230 meV structure and the weak 400 meV shoulder in the measured spectra, and by $H_g^1$, responsible for the $\sim 30$ meV close to the main peak.

We analyze now the different contributions, in order to extract a more general qualitative understanding of the spectrum. As a first step, we remove sequentially the contributions of the weakly coupled modes, and of the modes which do not participate directly to the 230 meV structure. In Fig. 7.3, we show the sequence of this analysis. We ignore the reduction in JT energy gain, which takes contributions from all modes, by shifting the ground-state energy of all the spectra to zero energy. The investigation shows that the main features of the complete spectrum are accounted for by the two high-frequency modes, $H_g^7$ and $H_g^8$, responsible for the
Figure 7.4: Analysis of the specific contributions of the $H_g 1$ and of $H_g 7$ plus $H_g 8$. When only the $H_g 1$ mode is considered all satellite structures above 200 meV disappear demonstrating that the 230 meV spectral structure in C$_{60}$ is to be associated to vibrons connected with the high-frequency modes $H_g 7$ and $H_g 8$. Note the blue-shift of the satellites in the $H_g 7 + H_g 8$ spectrum.

strong 230 meV structure and the weak 400 meV shoulder in the measured spectra, and by $H_g 1$, responsible for the $\sim 30$ meV sequence close to the main peak. The other modes contribute weakly in the intermediate range of energy $50 - 150$ meV (mainly $H_g 2$ and $H_g 3$). The exclusion of all the $A_g$, $G_g$, and of $H_g 4$, $H_g 5$, $H_g 6$ modes leaves the spectrum almost unaffected, because of their very weak couplings.

In Fig. 7.4 we show the specific contributions of the $H_g 1$ and of $H_g 7$ plus $H_g 8$: $H_g 7$ and $H_g 8$ affect the same region of the spectrum, because of their comparable frequencies and couplings. When only the $H_g 1$ mode is considered, all satellite structures above 200 meV disappear demonstrating that the 230 meV spectral structure in C$_{60}$ is to be associated to vibrons connected with the high-frequency modes $H_g 7$ and $H_g 8$. The spectrum computed including these two modes alone, shows a narrow satellite above 200 meV, This main satellite appears significantly (10%) blue-shifted with respect to $h\omega_{H_g 8}$. This increase in vibron excitation energy above the purely vibrational $h\omega$ for the 1-phonon excitation of a trivial displaced oscillator is in fact a characteristic signature of dynamic JT effect, and can be understood on the basis
7.2. 1-PHONON VIBRONIC MULTIPLET INTERPRETATION

The blue-shifted peak of the $H_g^7 + H_g^8$ spectrum of Fig. 7.3, is readily explained on the basis of symmetry. We will argue in the next Section that the conclusions we arrive to here extend to finite temperature $T = 800$ K.

At $T = 0$ the only contribution to the spectrum (1.16) comes from the ground state $|\Psi^{i=0}\rangle$, and the bare excitation $c^\dagger |\Psi^0\rangle$ has the orbital $h_u$ symmetry of the HOMO. This state has nonzero overlap strictly only with final states of the same symmetry $h_u$. This single symmetry channel thus represents the only contributor to the zero-temperature photoemission spectrum.

In the left panel of Fig. 7.3 we depict the vibron excitation energy with special attention to the $h_u$ states, for the simplest case of a single $H_g$ mode, as a function of the coupling strength $g$. The average of the multiplet of states derived from

Figure 7.5: Left panel: Vibronic excitation energies for a single $H_g$ mode coupled to the $h_u$ level, as a function of coupling $g$. The value $\alpha = 0.5$ is characteristic of the $H_g^7$ and $H_g^8$ modes. The average refers to the multiplet originating from the 1-phonon states. $h_u$ states, the only visible states in $T = 0$ PES, are highlighted as thick solid lines. Right panel: detail of the $H_g^7$, $H_g^8$ 1-phonon structures (Lorenzian $\epsilon = 1$ meV). Note the blue-shift of the average of the $h_u$ vibrons, and their cooperation to the shifted peak in $H_g^7 + H_g^8$.
Figure 7.6: $\alpha$ dependence of 1-vibron multiplet pattern. The $h_u$ states are blue-shifted for any value of $\alpha$. However, $\alpha$ is crucial in determining the precise splitting pattern of the 1-vibron multiplet.

the 1-vibration manifold is, to second order in the electron-phonon coupling $g$, independent of $g$, because the JT coupling is a traceless perturbation within that manifold. Within this multiplet (made of $H_g \times h_u = a_u + t_{1u} + t_{2u} + 2g_u + 2h_u$), the $h_u$ vibronic states are the sole that have another $h_u$ state (the GS itself) lower in energy and “pushing” them upward. As a result, for small but increasing coupling, the $h_u$ states shift in average necessarily upward in energy above $\hbar \omega$. The amount of this shift reflects the strength of the coupling.

In the right panel of Fig. 7.5 we show the 1-phonon vibronic structure of the two high-frequency modes $H_{g7}, H_{g8}$ (at $\hbar \omega = 181$ and 197 meV) and of their simultaneous action $H_{g7} + H_{g8}$. The couplings for these two modes alone accounts for a 10%, or roughly 20 meV shift of the important $H_{g7} + H_{g8}$ vibron satellite above $\hbar \omega$. This is about half of the total observed and calculated shift of $\sim 40$ meV.
7.3 THERMAL EFFECTS

of the 230 meV satellite relative to $\hbar \omega = 181 \div 197$ meV. The crucial observation here is the asymmetry of the spectral weight distribution between the pair of $h_u$ vibronic states, for both the two modes $H_g7, H_g8$. This manifests itself as a blue-shifted main satellite also above the multiplet average. Moreover, the cooperation of the two modes amplifies this effect in the $H_g7 + H_g8$ photoemission spectrum (Fig. 7.5). The remaining 10% blue shift is then a collective effect of all other modes simultaneously interacting with the HOMO, and pushing their respective 1-vibration satellite upward. All goes as if effectively the coupling of the high frequency $H_g7, H_g8$ modes were larger, i.e. effectively moving to the right of the vertical dashed line in the left panel of Fig. 7.5.

So far, we referred just to the $H_g7, H_g8$ coupling strength as the main parameter. However, as discussed in Sect. 3.4, the $H \otimes h$ problem is characterized by a second parameter, namely the value of the mixing angle $\alpha$. As it turns out, we find that in C$_{60}$ this parameter is far from irrelevant and in fact very important. In static JT, it determines the symmetry of the distortion ($D_5$ vs $D_3$). In dynamic JT, it also determines the ground state symmetry, namely $h_u$ for $\alpha \approx 0$, and $a_u$ for $\alpha \approx \pi/2$. In PE spectroscopy, $\alpha$ is crucial in determining the precise splitting pattern of the 1-vibron multiplet, even though the general feature that on average the $h_u$ states shift upward holds for any value of $\alpha$, as shown in Fig. 7.6 for $\alpha = 0.1, 0.5, 1,$ and $1.5$. En passant, note that for $D_5$ minima ($\alpha < 3/\sqrt{5}$) only an $h_u$ and an $a_u$ state move to low energy at strong coupling: these become the tunneling states among the 6 $D_5$ wells. For the 10 $D_3$ wells ($\alpha > 3/\sqrt{5}$), an extra $g_u$ state also moves to low energy at strong coupling: that one completes the tunneling picture. Note, however, that the tunneling regime ($g \geq 4$) is not relevant for the intermediate coupling of C$_{60}$, contrary to the assignment of Ref. [2, 50].

7.3 Thermal effects

Will the considerations of the previous Section on the 1-phonon states remain valid at finite-temperature? We claim that this is the case. For the two high-frequency modes $H_g7$ and $H_g8$, at $T = 800$ K, the thermal energy $k_B T$ is only about one third of $\hbar \omega$: the main contribution to the spectrum still comes from the ground-state. Indeed their spectrum lineshape is practically unchanged upon turning temperature up to 800 K, as shown in the left panel of Fig. 7.7. The $T = 0$ conclusions of the previous Sections, still hold at $T = 800$ K: the main peak at 230 meV comes from the splitting of the 1-phonon excitation of $H_g7$ plus $H_g8$. Thermal effects only affect significantly the low frequency modes, especially $H_g1$. for which many initial excitations have to be included. The broadening of its $T = 800$ K spectrum accounts for most of the observed broadening of the band, as shown in Fig. 7.7 (right). This broadening is responsible for hiding the minor structures of the spectrum. Many
Figure 7.7: Left panel: \( T \)-dependence of the \( H_g^7 \) plus \( H_g^8 \) spectrum. At \( T = 800 \) K the main contribution to the photoemission spectra still comes from the ground state: no substantial change in the spectrum lineshape appears. Right panel: \( T = 800 \) K \( H_g^1 \) spectrum (Lorenzian broadening \( \epsilon = 10 \) meV compared to the width of the experimental band).

7.4 Conclusions and outlook

The results of the present calculations confirm that the linear JT model \( (3.6) \) based on the DFT-LDA parameters of Ref. \[3\] describes well the electron-phonon dynamics of \( C_{60}^+ \). The difficulties of the present technique to address high temperature can be overcome by a combined use of random sampling (Sect 6.4) and a variable-basis method, where the quantum basis adapts itself to each sampled initial state, including only those states most strongly coupled to it. The implementation of such technique is currently being pursued, with good preliminary results, not included in this work.

A quantitative understanding of the photoemission spectrum from a degenerate molecular shell, with its characteristic vibronic features, is mandatory if the all-important electron-vibration coupling parameters are to be extracted from this kind of experiment, often the only reliable source of pertinent information available on the molecular ion. The method employed here has wide potential application either based, as in this work, on \textit{ab initio} parameters, or, for simple enough molecules, used to determine electron-phonon parameters by means of suitable fitting of experimental data.
Bibliography


[6] E. Bright Wilson, J. C. Decius, and P. C. Cross, Molecular Vibrations, The Theory of Infrared and Raman Vibrational Spectra (Dover, New York, 1955). In the table of characters of the icosahedral group, the character of $C_2$ for representation $H$ is 1 (not 0 as in the first edition). Notice also that the threefold representations of the icosahedral group are labeled by $f_1$ and $f_2$, in the traditional, and somewhat more coherent, molecular notation, while here we adopt for them the solid-state symbols $t_1$ and $t_2$.


