The vibrational spectrum of Buckminsterfullerene

An application of symmetry reduction and computer algebra

Joris Mooij

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Preface

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Introduction

In 1996, the Nobel Prize for Chemistry was awarded to Curl, Kroto and Smalley for their discovery of Buckminsterfullerene. Buckminsterfullerenes, denoted C_{60}, or simply "buckyballs" are molecules consisting of 60 carbon atoms arranged in a highly symmetrical structure, similar to that of a soccer ball. In more technical terms, the carbon atoms are located at the vertices of a truncated icosahedron. The molecules are named after architect Buckminster Fuller known for his geodesic domes. Buckyballs are made when gaseous carbon mixed with helium gas is sent into a vacuum and the mixture is exposed to a high energy, high temperature carbon arc.

From a mathematical point of view, buckyballs are interesting because of their high symmetry (their symmetry group is $I_h \cong A_5 \times C_2$). A well-known application of group theory in physics is the study of small vibrations of molecules. These vibrations can be studied experimentally by means of spectroscopy. Group theory yields a classification of the eigenfrequencies and the corresponding eigenmodes. Furthermore, it is a powerful tool for the explicit calculation of these frequencies and modes. Especially if the symmetry of the molecules is high (which is the case for C_{60}) the techniques from group theory appear to full advantage.

In this thesis, we will explicitly calculate the eigenfrequencies for harmonic approximations of the potential energy of C_{60} in the neighbourhood of an equilibrium configuration. Group theory in combination with computer algebra will be used to postpone numerical calculations as much as possible, i.e. we try to get as far as possible with exact, symbolical computations. Only in the final stage we have to resort to numerical techniques for diagonalizing matrices of size 8×8 at most (without the use of group theory, one would need to diagonalize a 180×180 matrix). In this way, after a change of the parameters in the potential energy model it is not necessary to do the whole calculation all over again. This makes fitting of the model parameters against the experimental data a more efficient process and is an improvement over what has been done before by e.g. Weeks and Harter [4].

In the first chapter, the necessary techniques from group theory will be discussed and explained. The reader is assumed to have elementary knowledge of group and representation theory. The emphasis is on down-to-earth explicit formulations that can be used directly on a computer algebra system, in contrast to more abstract and elegant basis-independent formulations.

The second chapter gives a treatment of the general theory of small oscillations of classical conservative many-particle systems. A basic knowledge of classical mechanics is helpful in reading this chapter. Further, a discussion of the group-theoretical classification of vibration modes of molecules is presented and the selection rules for spectroscopy are mentioned.

The third and last chapter concerns the application to Buckminsterfullerene. The symmetry group is analyzed, models for the potential energy are proposed and the parameters of these models are fit against the experimental data for the optically active modes. The results are discussed and compared with literature.

Chapter 1

Elements of Group Theory

The techniques described in this chapter are not new, see e.g. [Mil] and [Cor]. In contrast to the references however, the formulation presented here makes no assumptions about unitarity of the matrix representations. This will turn out to be an advantage later on because normalization of high-dimensional vectors—which would lead to rather complicated expressions involving lots of square roots, drastically slowing down the symbolic computations—will be superfluous.

1.1 Projection operators

For completeness we state two theorems that should already be known to the reader. For proofs, see e.g. [Mil, pp. 69–70].

Theorem 1.1.1. *Let $T : G \to GL(V)$, $S : G \to GL(W)$ be irreducible representations of a finite group G on finite-dimensional vector spaces V, W, respectively and let A be an intertwiner for T and S, i.e. a linear transformation $V \to W$ such that*

$$S(g)A = AT(g) \quad \text{for all } g \in G.$$

Then either A is zero or A is invertible, in which case T and S are equivalent representations.

Theorem 1.1.2 (Schur's Lemma)**.** *Let $T : G \to GL(V)$ be a representation of the group G on the finite-dimensional* complex *vector space V. Then T is irreducible if and only if the only intertwiners for T with itself are of the form $A = \lambda \mathbb{1}_V$ with $\lambda \in \mathbb{C}$ and $\mathbb{1}_V$ the identity transformation on V.*

A useful consequence of these theorems is:

Theorem 1.1.3 (Orthogonality relations for matrix representations)**.** *Let T be an irreducible d_T-dimensional complex-valued matrix representation of a finite group G of order $\#(G)$. Then:*

$$\frac{1}{\#(G)} \sum_{g \in G} T_{kl}(g) T_{mn}(g^{-1}) = \frac{1}{d_T} \delta_{lm} \delta_{kn} \tag{1.1}$$

for $1 \leq k, l, m, n \leq d_T$. If S is another irreducible d_S-dimensional matrix representation of G which is inequivalent to T, then:

$$\frac{1}{\#(G)} \sum_{g \in G} T_{kl}(g) S_{mn}(g^{-1}) = 0 \tag{1.2}$$

for $1 \leq k, l \leq d_T$ and $1 \leq m, n \leq d_S$.

Proof. Let S, T be two irreducible matrix representations of G. Take $1 \leq l \leq d_T$ and $1 \leq m \leq d_S$. Let e_{lm} be the $d_T \times d_S$ matrix defined by $(e_{lm})_{ij} := \delta_{il}\delta_{jm}$. Then the matrix

$$A_{lm} := \frac{1}{\#(G)} \sum_{g \in G} T(g) e_{lm} S(g^{-1})$$

is an intertwiner for T and S, i.e. $T(h)A_{lm} = A_{lm}S(h)$ for all $h \in G$. Indeed:

$$T(h)A_{lm} = \frac{1}{\#(G)} \sum_{g \in G} T(h)T(g)e_{lm}S(g^{-1}) = \frac{1}{\#(G)} \sum_{g \in G} T(hg)e_{lm}S\big((hg)^{-1}\big)S(h) = A_{lm}S(h).$$

Now assuming that $T \not\cong S$, Theorem 1.1.1 implies that $A_{lm} = 0$, hence

$$\frac{1}{\#(G)} \sum_{g \in G} T_{kl}(g) S_{mn}(g^{-1}) = 0$$

for all $1 \leq k \leq d_T$, $1 \leq n \leq d_S$.

Alternatively, taking $S = T$ and applying Schur's lemma 1.1.2 implies that $A_{lm} = \lambda \mathbb{1}_{d_T}$ for some $\lambda \in \mathbb{C}$. Hence for all $1 \leq k \leq d_T$, $1 \leq n \leq d_S$:

$$\frac{1}{\#(G)} \sum_{g \in G} T_{kl}(g) T_{mn}(g^{-1}) = \lambda \delta_{kn}.$$

To evaluate λ, take $k = n$ and sum over k to obtain:

$$d_T \lambda = \sum_{k=1}^{d_T} \frac{1}{\#(G)} \sum_{g \in G} T(g)_{kl} T(g^{-1})_{mk} = \frac{1}{\#(G)} \sum_{g \in G} T(e)_{ml} = \delta_{ml}$$

hence $\lambda = \delta_{ml} d_T^{-1}$. □

In the rest of this chapter, G will be a finite group and T will be a fixed representation (not necessarily unitary) of G on a finite-dimensional complex vector space V. We will choose a fixed set $\mathcal{I}(G)$ of representatives for the similarity classes of irreducible representations of G. Further we will suppose all representations to be on complex vector spaces.

Definition 1.1.4. *Let π be a matrix representation of G of dimension d_π. For $m, n = 1, \ldots, d_\pi$, define the following linear operators on V:*

$$\mathcal{P}^\pi_{m,n} := \frac{d_\pi}{\#(G)} \sum_{g \in G} \pi_{n,m}(g^{-1}) T(g). \tag{1.3}$$

These operators have the following properties:

Theorem 1.1.5. *Let π and ρ be matrix representations of G of dimensions d_π and d_ρ, respectively. Then:*

1. *For $1 \leq m, n \leq d_\pi$ and all $g \in G$:*

$$T(g)\mathcal{P}^\pi_{m,n} = \sum_{j=1}^{d_\pi} \pi_{j,m}(g) \mathcal{P}^\pi_{j,n}, \tag{1.4}$$

i.e. for each n, the operators $\mathcal{P}^\pi_{1,n}, \ldots \mathcal{P}^\pi_{d_\pi,n}$ transform under T as if they were basis vectors for the representation π.

2. *If π and ρ are both irreducible and furthermore either $\pi \not\cong \rho$ or $\pi = \rho$, then for $1 \leq m, n \leq d_\pi$ and $1 \leq k, l \leq d_\rho$:*

$$\mathcal{P}^\pi_{k,l}\mathcal{P}^\rho_{m,n} = \delta_{\pi\rho}\delta_{lm}\mathcal{P}^\rho_{k,n}. \tag{1.5}$$

3. *Suppose that π and ρ are both irreducible and furthermore either $\pi \not\cong \rho$ or $\pi = \rho$. Suppose that $w_1, \ldots, w_{d_\rho} \in V$ transform under T as basis vectors for ρ, i.e.*

$$T(g)w_k = \sum_{l=1}^{d_\rho} \rho_{lk}(g)w_l \qquad \text{for all } g \in G \text{ and } k = 1, \ldots, d_\rho.$$

Then, for all $1 \leq m, n \leq d_\pi$ and all $1 \leq k \leq d_\rho$:

$$\mathcal{P}^\pi_{m,n}w_k = \delta_{\pi\rho}\delta_{nk}w_m$$

Proof. 1. This is trivial:

$$\begin{aligned} T(g)\mathcal{P}^\pi_{m,n} &= \frac{d_\pi}{\#(G)}\sum_{h\in G}\pi_{n,m}(h^{-1})T(gh) = \frac{d_\pi}{\#(G)}\sum_{h\in G}\sum_{j=1}^{d_\pi}\pi_{n,j}(h^{-1}g^{-1})\pi_{j,m}(g)T(gh) \\ &= \sum_{j=1}^{d_\pi}\pi_{j,m}(g)\frac{d_\pi}{\#(G)}\sum_{h\in G}\pi_{n,j}\big((gh)^{-1}\big)T(gh) = \sum_{j=1}^{d_\pi}\pi_{j,m}(g)\mathcal{P}^\pi_{j,n}. \end{aligned}$$

2. Using 1. and the orthogonality relations (Theorem 1.1.3):

$$\begin{aligned} \mathcal{P}^\pi_{k,l}\mathcal{P}^\rho_{m,n} &= \frac{d_\pi}{\#(G)}\sum_{g\in G}\pi_{l,k}(g^{-1})T(g)\mathcal{P}^\rho_{m,n} = \frac{d_\pi}{\#(G)}\sum_{g\in G}\pi_{l,k}(g^{-1})\sum_{j=1}^{d_\rho}\rho_{j,m}(g)\mathcal{P}^\rho_{j,n} \\ &= \sum_{j=1}^{d_\rho}\delta_{\pi,\rho}\delta_{l,m}\delta_{k,j}\mathcal{P}^\rho_{j,n} = \delta_{\pi,\rho}\delta_{l,m}\mathcal{P}^\rho_{k,n}. \end{aligned}$$

3. This is a direct consequence of the orthogonality relations:

$$\begin{aligned} \mathcal{P}^\pi_{m,n}w_k &= \frac{d_\pi}{\#(G)}\sum_{g\in G}\pi_{n,m}(g^{-1})T(g)w_k = \frac{d_\pi}{\#(G)}\sum_{g\in G}\pi_{n,m}(g^{-1})\sum_{l=1}^{d_\rho}\rho_{lk}(g)w_l \\ &= \delta_{\rho\pi}\sum_{l=1}^{d_\rho}\delta_{ml}\delta_{nk}w_l = \delta_{\rho\pi}\delta_{nk}w_m \end{aligned}$$

for all $1 \leq m, n \leq d_\pi$ and all $1 \leq k \leq d_\rho$. □

In particular, $\left(\mathcal{P}^\pi_{n,n}\right)^2 = \mathcal{P}^\pi_{n,n}$ for all irreducible matrix representations π of G and all $1 \leq n \leq d_\pi$, which explains why these operators are called *projection operators*.

The projection operators depend on a chosen basis. We can also define *character projection operators* that are basis independent:

Definition 1.1.6. *Let π be a d_π-dimensional matrix representation of G with character χ_π. Define:*

$$\mathcal{P}^\pi := \frac{d_\pi}{\#(G)}\sum_{g\in G}\chi_\pi(g^{-1})T(g). \tag{1.6}$$

The character projection operators have the following properties:

Theorem 1.1.7. *Let π, ρ be matrix representations of G.*

1. $\mathcal{P}^\pi = \sum_{n=1}^{d_\pi} \mathcal{P}^\pi_{nn}$.
2. $T(g)\mathcal{P}^\pi = \mathcal{P}^\pi T(g)$ *for all* $g \in G$.
3. *If π and ρ are both irreducible and furthermore either $\pi \not\cong \rho$ or $\pi = \rho$, then $\mathcal{P}^\pi \mathcal{P}^\rho = \delta_{\rho\pi}\mathcal{P}^\rho$.*
4. $\sum_{\pi \in \mathcal{I}(G)} \mathcal{P}^\pi = \mathbb{1}_V$.

Proof. 1. Trivial.
2. Because χ_π is constant on conjugacy classes, we have for $g \in G$:

$$T(g)\mathcal{P}^\pi = T(g)\frac{d_\pi}{\#(G)}\sum_{h\in G}\chi_\pi(h^{-1})T(h) = \frac{d_\pi}{\#(G)}\sum_{h\in G}\chi_\pi(gh^{-1}g^{-1})T(ghg^{-1})T(g) = \mathcal{P}^\pi T(g).$$

3. This follows immediately from Theorem 1.1.5.2.
4. Write $\mathcal{P} := \sum_{\pi\in\mathcal{I}(G)} \mathcal{P}^\pi$. From 3. it follows that $\mathcal{P}$ is a projection operator. Hence we have to show that $\ker \mathcal{P} := \{0\}$. Suppose on the contrary that $\dim \ker \mathcal{P} \geq 1$. The subspace $\ker \mathcal{P}$ of V is invariant under T; indeed, if $v \in \ker \mathcal{P}$ then also $T(g)v \in \ker \mathcal{P}$ for all $g \in G$ because $\mathcal{P}$ and $T(g)$ commute, which immediately follows from 2. Choose an irreducible subspace W of $\ker \mathcal{P}$. Then T restricted to W is equivalent to some $\pi \in \mathcal{I}(G)$. But Theorem 1.1.5.3 implies that $W \subseteq \operatorname{Im} \mathcal{P}^\pi \subseteq \operatorname{Im} \mathcal{P}$, hence $W = \{0\}$. Contradiction. □

1.2 Explicit decomposition of a representation

The projection operators enable us to explicitly perform a decomposition of the representation space V of the representation T in irreducible subspaces. The procedure is as follows (see also Fig. 1.1).

For each $\pi \in \mathcal{I}(G)$, apply the projection operator $\mathcal{P}^\pi_{11}$ to V and let $W^\pi_1 := \operatorname{Im} \mathcal{P}^\pi_{11}$ be the range of this operator. Choose a basis $\{f^\pi_{k1} \mid 1 \leq k \leq m_\pi\}$ of W^π_1 where $m_\pi := \dim W^\pi_1$ is called the *multiplicity of π in T*. For each $j = 2, \ldots, d_\pi$, define the m_π vectors $f^\pi_{kj} := \mathcal{P}^\pi_{j1} f^\pi_{k1}$ (for $k = 1, \ldots, m_\pi$) and let $W^\pi_j := \mathcal{P}^\pi_{j1} W^\pi_1$. It is not difficult to see that $W^\pi_j = \operatorname{Im} \mathcal{P}^\pi_{jj}$ (consider the isomorphism $\mathcal{P}^\pi_{1j}$ with inverse $\mathcal{P}^\pi_{j1}$). Hence $\bigoplus_j W^\pi_j = \operatorname{Im} \mathcal{P}^\pi$.

Define for each k the subspace $V^\pi_k := \operatorname{span}\{f^\pi_{kj} \mid 1 \leq j \leq d_\pi\} \subseteq V$. The spaces V^π_k are invariant under T and the restriction of T to V^π_k is equivalent to π, in fact for each $1 \leq k \leq m_\pi$:

$$T(g)f^\pi_{kj} = \sum_{i=1}^{d_\pi} \pi_{ij}(g) f^\pi_{ki} \quad \text{for all } 1 \leq j \leq d_\pi$$

as easily follows from Theorem 1.1.5.1. Furthermore,

$$V = \bigoplus_{\pi\in\mathcal{I}(G)} \bigoplus_{k=1}^{m_\pi} V^\pi_k = \bigoplus_{\pi\in\mathcal{I}(G)} V^\pi, \tag{1.7}$$

where $V^\pi := \operatorname{Im} \mathcal{P}^\pi$. This follows from Theorem 1.1.7.3 in combination with the fact that $\bigoplus_j W^\pi_j = \bigoplus_k V^\pi_k = V^\pi$. The spaces V^π are called *isotypical components for G*.

Since the decomposition of V into the subspaces V^π_k depends on the choice of basis vectors $\{f^\pi_{k1}\}$ and matrix representations π, it is not unique. Only if all multiplicities m_π are ≤ 1, this decomposition is unique.

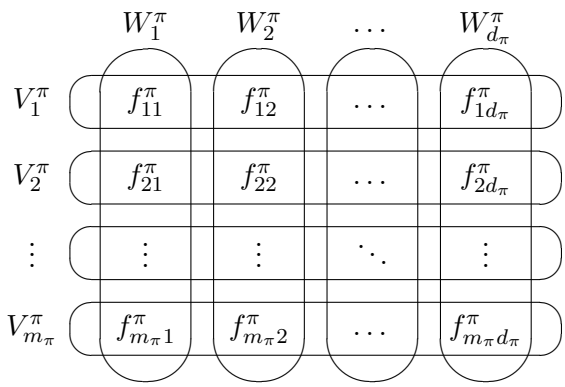

Figure 1.1: Various subspaces of $\operatorname{Im}\mathcal{P}^\pi$ with their bases. The rows are invariant under T, the columns are invariant under F.

1.3 Symmetry reduction

Let $F : V \to V$ be a linear transformation. The problem we want to solve is calculating the eigenvalues and eigenvectors of F. Suppose that G is a symmetry of F, more specifically that F is an intertwiner for the representation $T : G \to GL(V)$, i.e. $FT(g) = T(g)F$ for all $g \in G$. This simplifies the calculation of the eigenvalues and eigenvectors.

First note that F commutes with each operator $\mathcal{P}_{mn}^\pi$. Hence the spaces W_j^π are invariant under F. Furthermore, if $v \in W_1^\pi$ is an eigenvector of F with eigenvalue λ, then also $\mathcal{P}_{j1}^\pi v \in W_j^\pi$ is an eigenvector of F with the same eigenvalue:

$$F(\mathcal{P}_{j1}^\pi v) = \mathcal{P}_{j1}^\pi F v = \mathcal{P}_{j1}^\pi \lambda v = \lambda(\mathcal{P}_{j1}^\pi v)$$

and this holds for each $j = 1, \dots, d_\pi$. Hence, the multiplicity of each eigenvalue of an eigenvector in V^π is a non-negative integral multiple of d_π. This also implies that once we have diagonalized F on W_1^π, this immediately yields a diagonalization of F on the other spaces W_j^π with $j = 2, \dots, d_\pi$. Hence the original problem of diagonalizing a $(\dim V) \times (\dim V)$ matrix simplifies to diagonalizing $\#\mathcal{I}(G)$ matrices of dimensions $m_\pi \times m_\pi$ (for all $\pi \in \mathcal{I}(G)$). We can regard W_1^π as the "tensor quotient" of V^π with respect to the representation space of π: we have "divided out" the symmetry of G. We call the restriction $F_{|W_1^\pi}$ the *reduction of F at the irrep π*.

In conclusion, the eigenvalue spectrum of F is equal to the union of the spectra of the reductions of F at the irreps $\pi \in \mathcal{I}(G)$, each reduced spectrum counted with multiplicity d_π. If the spectra of the reduced operators $F_{|W_1^\pi}$ are multiplicity free and disjoint for all $\pi \in \mathcal{I}(G)$, then F is said to have *natural degeneracy* with respect to the representation T of the group G. It means that all degeneracy (i.e. collapse of eigenvalues) in the spectrum of F is accounted for by the symmetry group G. In most situations encountered in physics, it is reasonable to assume natural degeneracy. If F is not naturally degenerate, this can be an indication that the symmetry group is not the full symmetry group of the problem. Only if F is not naturally degenerate with respect to its *full* symmetry group, F is said to have *accidental degeneracy*. In that case we can get natural degeneracy by adding a small perturbation to F that commutes with T.

One final remark has to be made. If one only knows the characters χ_π of all irreducible representations $\pi \in \mathcal{I}(G)$ instead of all the matrix components, the only simplification of the original problem is that the matrix of F with respect to a basis that is compatible with the decomposition into isotypical components is block-diagonal with blocks of size $(m_\pi d_\pi) \times (m_\pi d_\pi)$. Hence knowledge of all the matrix components is a great advantage above merely knowing the

characters (which is the only information usually given in literature).

Chapter 2

Small oscillations

This chapter is based upon Chapter VII of [Hec] but occassionally goes into more detail.

2.1 Classical theory

We will first treat the general (classical) theory of small oscillations of conservative classical mechanical particle systems. Since we have an application to molecules in mind, we will talk about a "molecule" instead of a "system" and about "atoms" instead of "particles".

Consider a molecule consisting of N atoms numbered $1, \ldots, N$. We will assume that the potential energy $\mathcal{V} : \mathbb{R}^{3N} \to \mathbb{R}$ only depends on $\mathbf{x} = (\mathbf{x}_1, \ldots, \mathbf{x}_N) = (x_1, \ldots, x_{3N})$ where $\mathbf{x}_i = (x_{3i-2}, x_{3i-1}, x_{3i}) \in \mathbb{R}^3$ is the position of atom i (for $i = 1, \ldots, N$). Suppose that at position $\mathbf{r} = (\mathbf{r}_1, \ldots \mathbf{r}_N) \in \mathbb{R}^{3N}$, the molecule is in equilibrium, i.e. the force on each atom i, given by:

$$\mathbf{F}_i := -\frac{\partial \mathcal{V}}{\partial \mathbf{x}_i} := -\left(\frac{\partial \mathcal{V}}{\partial x_{3i-2}}, \frac{\partial \mathcal{V}}{\partial x_{3i-1}}, \frac{\partial \mathcal{V}}{\partial x_{3i}}\right),$$

vanishes. We will investigate small displacements $\mathbf{q}$ about the equilibrium position, defining the new coordinates $\mathbf{q} \in \mathbb{R}^{3N}$ by $\mathbf{x} = \mathbf{r} + \mathbf{q}$. We can then make a Taylor series expansion of the potential energy $\mathcal{V}$ about the equilibrium position $\mathbf{r}$:

$$\mathcal{V}(\mathbf{r} + \mathbf{q}) = \mathcal{V}(\mathbf{r}) + \sum_{n=1}^{3N} \frac{\partial \mathcal{V}}{\partial x_n}\bigg|_{\mathbf{x}=\mathbf{r}} q_n + \frac{1}{2} \sum_{n,m=1}^{3N} \frac{\partial^2 \mathcal{V}}{\partial x_m \partial x_n}\bigg|_{\mathbf{x}=\mathbf{r}} q_m q_n + \cdots \approx \frac{1}{2}\langle \mathbf{q}, F\mathbf{q}\rangle, \tag{2.1}$$

where $\langle \cdot, \cdot \rangle$ is the standard inner product on $\mathbb{R}^{3N}$. Here we exploited the freedom of choice in the zero of $\mathcal{V}$ to make $\mathcal{V}(\mathbf{r}) = 0$. Further, the linear part vanishes because we assumed the molecule to be in equilibrium at $\mathbf{r}$. The linear transformation $F : \mathbb{R}^{3N} \to \mathbb{R}^{3N}$ defined by its matrix coefficients

$$F_{mn} := \frac{\partial^2 \mathcal{V}}{\partial x_m \partial x_n}\bigg|_{\mathbf{x}=\mathbf{r}}$$

is called the *force constant matrix* or *Hessian of* $\mathcal{V}$ and is obviously symmetric (i.e. $\langle F\mathbf{x}, \mathbf{y}\rangle = \langle \mathbf{x}, F\mathbf{y}\rangle$ for all $\mathbf{x}, \mathbf{y} \in \mathbb{R}^{3N}$). Apparently under these assumptions the potential energy is a quadratic polynomial in $\mathbf{q}$. Higher order terms are being neglected in this approximation.

The kinetic energy $\mathcal{K}$ of the molecule is given by:

$$\mathcal{K} = \frac{1}{2} \sum_{j=1}^{N} m_j \langle \dot{\mathbf{q}}_j, \dot{\mathbf{q}}_j \rangle$$

where $\dot{\mathbf{q}}_j := \frac{d}{dt}\mathbf{q}_j(t) = \frac{d}{dt}\mathbf{x}_j(t)$ is the velocity of atom j at time t, m_j is its mass and $\langle \cdot, \cdot \rangle$ is the standard inner product on $\mathbb{R}^3$.

Define the linear transformation $S : \mathbb{R}^{3N} \to \mathbb{R}^{3N}$ by

$$Se_{3(i-1)+\alpha} := \sqrt{m_i} e_{3(i-1)+\alpha} \quad \text{for all } i = 1, \ldots, N \text{ and } \alpha = 1, 2, 3.$$

We can then write the equations of motion as:

$$S^2 \ddot{\mathbf{q}} + F\mathbf{q} = 0,$$

or equivalently

$$S\ddot{\mathbf{q}} + \tilde{F} S\mathbf{q} = 0$$

where $\tilde{F} := S^{-1} F S^{-1}$. Since F and S^{-1} are symmetric, $\tilde{F}$ is symmetric as well and hence it can be diagonalized. Let $\mathbf{f}_1, \ldots, \mathbf{f}_{3N}$ be an orthonormal basis of $\mathbb{R}^{3N}$ with respect to which $\tilde{F}$ is diagonal with eigenvalues $k_1, \ldots, k_{3N}$. Writing $S\mathbf{q} = \left(\sum_{j=1}^{3N} z_j \mathbf{f}_j\right)$, the equations of motion decouple:

$$\ddot{z}_j + k_j z_j = 0 \quad \text{for } j = 1 \ldots 3N.$$

The coordinates z_j are called *normal coordinates*. Formulated in normal coordinates, the system is seen to be equivalent to $3N$ uncoupled harmonic oscillators (assuming the k_j to be positive).

In the next section we will see that under certain rather natural assumptions, 6 of the eigenvalues k_j (namely those corresponding to translations and rotations of the molecule as a whole) vanish. Assuming that the equilibrium position $\mathbf{q} = 0$ is *stable*, the other $3N - 6$ eigenvalues k_j are positive. If the molecule does not rotate and does not have an overall speed, the general solution of the equations of motion is then a superposition of $3N - 6$ harmonic *normal modes* with frequencies $\nu_j := \sqrt{k_j}$ (for those j with $k_j > 0$).

2.2 Translational and rotational invariance

We will now make extra assumptions regarding the nature of the potential energy $\mathcal{V}$. We assume that the mass is characteristic of the chemical properties of the atoms, i.e. atoms with the same mass are chemically indistinguishable. Further we assume the potential energy to be invariant under translations and orthogonal transformations of the molecule as a whole. These assumptions can be expressed as follows:

$$\left[\begin{array}{ll} \mathcal{V}(\mathbf{x}_{\sigma(1)}, \ldots, \mathbf{x}_{\sigma(N)}) = \mathcal{V}(\mathbf{x}_1, \ldots, \mathbf{x}_N) & \text{for all } \sigma \in S_N \text{ with } \forall_{i \in \{1,\ldots,N\}} [m_i = m_{\sigma(i)}] \\ \mathcal{V}(\mathbf{x}_1 + \mathbf{a}, \ldots, \mathbf{x}_N + \mathbf{a}) = \mathcal{V}(\mathbf{x}_1, \ldots, \mathbf{x}_N) & \text{for all } \mathbf{a} \in \mathbb{R}^3 \\ \mathcal{V}(A\mathbf{x}_1, \ldots, A\mathbf{x}_N) = \mathcal{V}(\mathbf{x}_1, \ldots, \mathbf{x}_N) & \text{for all } A \in O(\mathbb{R}^3) \end{array}\right. \tag{2.2}$$

for all $\mathbf{x} \in \mathbb{R}^{3N}$.

The translation invariance of $\mathcal{V}$ implies that the forces $-\frac{\partial \mathcal{V}}{\partial \mathbf{x}_i}$ are also translation invariant; indeed for all $\mathbf{a} \in \mathbb{R}^3$:

$$\frac{\partial \mathcal{V}}{\partial x_m}(\mathbf{r}_1 + \mathbf{a}, \ldots, \mathbf{r}_N + \mathbf{a}) = \frac{\partial \mathcal{V}}{\partial x_m}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \quad \text{for all } m = 1, \ldots, 3N.$$

Setting $\mathbf{a} = \lambda \mathbf{w}$ for $\lambda \in \mathbb{R}$ and $\mathbf{w} \in \mathbb{R}^3$, defining $\mathbf{W} := (\mathbf{w}, \ldots, \mathbf{w}) \in \mathbb{R}^{3N}$, differentiating with respect to λ and setting $\lambda = 0$ yields:

$$\sum_{n=1}^{3N} \left. \frac{\partial^2 \mathcal{V}}{\partial x_n \partial x_m} \right|_{\mathbf{x}=\mathbf{r}} W_n = 0 \quad \text{for all } m = 1, \ldots, 3N,$$

or equivalently $F\mathbf{W} = 0$. Thus the translation invariance of $\mathcal{V}$ implies that $F = 0$ on the subspace W_T of $\mathbb{R}^{3N}$ defined by

$$W_T := \{(\mathbf{w}, \ldots, \mathbf{w}) \in \mathbb{R}^{3N} \,|\, \mathbf{w} \in \mathbb{R}^3\}.$$

In the same way, the invariance of $\mathcal{V}$ under orthogonal transformations implies that the forces $-\frac{\partial \mathcal{V}}{\partial \mathbf{x}_i}$ are invariant under $O(\mathbb{R}^3)$. In particular, for a rotation $D_{\mathbf{w},\phi} \in O(\mathbb{R}^3)$ around the axis $\mathbb{R}\mathbf{w}$ over an angle ϕ (with $\mathbf{w} \in \mathbb{R}^3$, $\phi \in \mathbb{R}$):

$$\frac{\partial \mathcal{V}}{\partial x_m}(D_{\mathbf{w},\phi}\mathbf{r}_1, \ldots, D_{\mathbf{w},\phi}\mathbf{r}_N) = \frac{\partial \mathcal{V}}{\partial x_m}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \quad \text{for all } m = 1, \ldots, 3N.$$

Using the identity

$$D_{\mathbf{w},\phi}(\mathbf{v}) := \cos\phi \cdot \mathbf{v} + \sin\phi \cdot \mathbf{w} \wedge \mathbf{v} + (1 - \cos\phi)\langle \mathbf{v}, \mathbf{w}\rangle \cdot \mathbf{w} \quad \text{for all } \mathbf{v}, \mathbf{w} \in \mathbb{R}^3,\ \phi \in \mathbb{R},$$

with $\wedge$ the outer product on $\mathbb{R}^3$, this time defining $\mathbf{W} := (\mathbf{w} \wedge \mathbf{r}_1, \ldots, \mathbf{w} \wedge \mathbf{r}_N)$, differentiating with respect to ϕ and setting $\phi = 0$ yields:

$$\sum_{n=1}^{3N} \frac{\partial^2 \mathcal{V}}{\partial x_n \partial x_m}\bigg|_{\mathbf{x}=\mathbf{r}} W_n = 0 \quad \text{for all } m = 1, \ldots, 3N,$$

or equivalently $F\mathbf{W} = 0$. Thus[1] the rotation invariance of $\mathcal{V}$ implies that $F = 0$ on the subspace W_R of $\mathbb{R}^{3N}$ defined by

$$W_R := \{(\mathbf{w} \wedge \mathbf{r}_1, \ldots, \mathbf{w} \wedge \mathbf{r}_N) \in \mathbb{R}^{3N} \,|\, \mathbf{w} \in \mathbb{R}^3\}.$$

If $\mathbf{r}_1, \ldots, \mathbf{r}_N$ do not lie on one line in $\mathbb{R}^3$ then one can show that $\dim W_R = 3$ and $W_T \cap W_R = \{\mathbf{0}\}$ hence $\dim(W_T + W_R) = 6$.

2.3 Group theoretical analysis

If the equilibrium position $\mathbf{r}$ of the molecule has a sufficiently rich point group symmetry, we can apply group theory to draw some remarkable qualitative conclusions, for which no additional detailed knowledge of the potential energy $\mathcal{V}$ is required. In addition, given the potential energy $\mathcal{V}$, the symmetry group can be used to simplify the calculation of the frequencies of the eigenmodes and to classify the eigenfrequencies according to the corresponding representations, as we will see.

Take the centre of mass $\sum_{k=1}^N m_k \mathbf{r}_k / \sum_{k=1}^N m_k$ of the molecule to be the origin of $\mathbb{R}^3$.

Definition 2.3.1. *The symmetry group G of the molecule in equilibrium position $\mathbf{r} \in \mathbb{R}^{3N}$ is defined as:*

$$G := \{g \in O(\mathbb{R}^3) \,|\, \forall_{i \in \{1,\ldots,N\}} \exists_{j \in \{1,\ldots,N\}} [m_i = m_j \text{ and } g\mathbf{r}_i = \mathbf{r}_j]\}.$$

As a subgroup of $O(\mathbb{R}^3)$, G has a natural representation $\rho : G \mapsto GL(\mathbb{C}^3)$ with character χ_ρ. Every element $g \in G$ defines a permutation $\sigma_g \in S_N$ by $\sigma_g(i) = j$ if $g\mathbf{r}_i = \mathbf{r}_j$. We define the natural representation (also called *displacement representation*) T of G on $V := \mathbb{C}^{3N}$ by[2]

$$T(g)(\mathbf{q}_1, \ldots, \mathbf{q}_N) := \big(\rho(g)\mathbf{q}_{\sigma_g^{-1}(1)}, \ldots, \rho(g)\mathbf{q}_{\sigma_g^{-1}(N)}\big) \tag{2.3}$$

for $g \in G$ and $\mathbf{q} = (\mathbf{q}_1, \ldots, \mathbf{q}_N) \in V$. Note that the displacement representation is unitary. We have the following obvious theorem due to Wigner:

[1] The derivation of this property of the force constant matrix presented in [Cor, Ch. 7 Thm. IV] is misleading and strictly spoken incorrect.

[2] Because we need complex representation spaces, we will complexify everything in this section, sometimes implicitly. In particular, we will not make a difference in notation for linear operators defined on $\mathbb{R}^{3N}$ and their complexifications defined on V.

Theorem 2.3.2 (Wigner's rule)**.** *The character χ_T of the displacement representation $T : G \to GL(\mathbb{C}^{3N})$ is given by:*

$$\chi_T(g) = \#\{i \in \{1, \dots, N\} \,|\, \sigma_g(i) = i\} \cdot \chi_\rho(g) \qquad \textit{for } g \in G.$$

Define the *translational subspace* $V_\mathcal{T}$ of V by:

$$V_\mathcal{T} := \big\{\big(\sqrt{m_1}\mathbf{w}, \dots, \sqrt{m_N}\mathbf{w}\big) \in V \,\big|\, \mathbf{w} \in \mathbb{C}^3\big\}.$$

It is invariant under T: for $g \in G$ and $\mathbf{w} \in \mathbb{C}^3$:

$$\begin{aligned} T(g)\big(\sqrt{m_1}\mathbf{w}, \dots, \sqrt{m_N}\mathbf{w}\big) &= \Big(\sqrt{m_{\sigma_g^{-1}(1)}}\rho(g)\mathbf{w}, \dots, \sqrt{m_{\sigma_g^{-1}(N)}}\rho(g)\mathbf{w}\Big) \\ &= \big(\sqrt{m_1}\rho(g)\mathbf{w}, \dots, \sqrt{m_N}\rho(g)\mathbf{w}\big) \in V_\mathcal{T} \end{aligned}$$

since σ only permutes atoms with the same mass. We also see from the formula above that the subrepresentation $T_{V_\mathcal{T}}$ is equivalent with ρ and therefore has character χ_ρ.

Define the *rotational subspace* $V_\mathcal{R}$ of V by:

$$V_\mathcal{R} := \big\{\big(\sqrt{m_1}\mathbf{w} \wedge \mathbf{r}_1, \dots, \sqrt{m_N}\mathbf{w} \wedge \mathbf{r}_N\big) \in V \,\big|\, \mathbf{w} \in \mathbb{C}^3\big\}$$

where $\wedge$ is the obvious generalization of the outer product on $\mathbb{R}^3$ to $\mathbb{C}^3$. The rotational subspace is also invariant under T: for $g \in G$ and $\mathbf{w} \in \mathbb{C}^3$:

$$\begin{aligned} &T(g)\big(\sqrt{m_1}\mathbf{w} \wedge \mathbf{r}_1, \dots, \sqrt{m_N}\mathbf{w} \wedge \mathbf{r}_N\big) \\ &\quad= \Big(\sqrt{m_{\sigma_g^{-1}(1)}}\rho(g)\big(\mathbf{w} \wedge \mathbf{r}_{\sigma_g^{-1}(1)}\big), \dots, \sqrt{m_{\sigma_g^{-1}(N)}}\rho(g)\big(\mathbf{w} \wedge \mathbf{r}_{\sigma_g^{-1}(N)}\big)\Big) \\ &\quad= \det\big(\rho(g)\big)\Big(\sqrt{m_1}\big(\rho(g)\mathbf{w}\big) \wedge \mathbf{r}_1, \dots, \sqrt{m_N}\big(\rho(g)\mathbf{w}\big) \wedge \mathbf{r}_N\Big) \in V_\mathcal{R} \end{aligned}$$

because the identity

$$g(\mathbf{u} \wedge \mathbf{v}) = \det(g)(g\mathbf{u} \wedge g\mathbf{v}) \qquad \text{for } g \in O(\mathbb{R}^3) \text{ and } \mathbf{u}, \mathbf{v} \in \mathbb{R}^3$$

is also valid in the above slightly more general case (where $\mathbf{w} \in \mathbb{C}^3$). Further we see that the subrepresentation $T_{V_\mathcal{R}}$ is equivalent with $\det \otimes \rho$ (where det is the one-dimensional representation of $O(\mathbb{R}^3)$ that assigns to an orthogonal transformation its determinant) and hence has character $\det \cdot \chi_\rho$.

Since we have taken the centre of mass at the origin, $V_\mathcal{T}$ and $V_\mathcal{R}$ are orthogonal subspaces, as one readily verifies. We define the *vibrational subspace* to be the orthogonal complement $V_\mathcal{V} := (V_\mathcal{T} \oplus V_\mathcal{R})^\perp$. Thus we get a decomposition (called the *Eckart decomposition*) into mutually orthogonal G-invariant subspaces:

$$V = V_\mathcal{V} \oplus V_\mathcal{T} \oplus V_\mathcal{R}.$$

Since $F = 0$ on $W_T \oplus W_R$, it follows that $\tilde{F} = 0$ on $V_\mathcal{T} \oplus V_\mathcal{R}$. Because of the assumptions made at the end of section 2.1, the vibration subspace $V_\mathcal{V}$ is spanned by the basis vectors $\mathbf{f}_j$ with $k_j > 0$. The character of the subrepresentation $T_{V_\mathcal{V}}$ is given by

$$\chi\mathcal{V} := \chi_T - \chi_\rho - \det \cdot \chi_\rho.$$

The assumptions (2.2) about the potential energy $\mathcal{V}$ imply that $\mathcal{V}$ is invariant under the action T of the symmetry group G, i.e.

$$\mathcal{V}\big(\mathbf{r} + T(g)\mathbf{q}\big) = \mathcal{V}(\mathbf{r} + \mathbf{q}) \qquad \text{for all } \mathbf{q} \in \mathbb{R}^{3N} \text{ and all } g \in G.$$

Hence also its harmonic approximation (2.1) is invariant under T, which implies that

$$T(g)F = FT(g) \quad \text{for all } g \in G.$$

Because each $T(g)$ also commutes with S^{-1} we get

$$T(g)\tilde{F} = \tilde{F}T(g) \quad \text{for all } g \in G. \tag{2.4}$$

Thus the eigenspaces $V_k := \{\mathbf{v} \in V \mid \tilde{F}\mathbf{v} = k\mathbf{v}\}$ are invariant under T and the vibration subspace $V_{\mathcal{V}}$ decomposes as follows:

$$V_{\mathcal{V}} = \bigoplus_{k>0} V_k.$$

Because of (2.4), we can apply the symmetry reduction procedure described in section 1.3 to explicitly perform this decomposition.

Concluding, the *vibration spectrum* of the molecule is $\left\{\sqrt{k} \,\middle|\, k > 0, V_k \neq \{0\}\right\}$ which is the square root of the positive part of the eigenvalue spectrum of $\tilde{F}$. Each eigenfrequency $\nu = \sqrt{k}$ corresponds with one or more irreducible representations of G, namely the irreducible components of $T_{V_{\mathcal{V}}}$ occurring in the eigenspace V_k. In case we have natural degeneration, each eigenfrequency corresponds with exactly one irreducible representation of G. In this way, the symmetry group yields a classification of the eigenmodes. Also, the number of frequencies in the vibration spectrum cannot be larger than the number of irreducible components of the representation $T_{V_{\mathcal{V}}}$, which can be significantly smaller than $3N - 6$.

2.4 Quantum mechanical theory

Once the classical mechanical problem has been solved, the corresponding quantum mechanical problem presents no further difficulties. Indeed, as is easily seen when formulated in normal coordinates, the quantum mechanical system is equivalent to $3N - 6$ uncoupled (quantum) harmonic oscillators with force constants k_j. The solutions of such a system are well-known.

Because of the nature of the quantum mechanical interactions between the molecule and incident photons not all frequencies in the vibration spectrum can be observed using spectroscopy. Which frequencies can be observed is described by *selection rules* that depend on the particular form of spectroscopy.

In particular, the selection rule for *IR spectroscopy* (in which the infrared absorption spectrum is measured) states that only those frequencies $\nu = \sqrt{k}$ are observed for which the corresponding irreducible representation T_{V_k} occurs in the natural representation. Assuming natural degeneracy, this requirement can be formulated using character theory as $\langle \chi_k, \chi_\rho \rangle \geq 1$, where χ_k is the character of T_{V_k}.

Another form of spectroscopy is *Raman spectroscopy*, discovered by Raman in 1928. The selection rule for Raman spectroscopy states that only those frequencies $\nu = \sqrt{k}$ are observed for which the irreducible representation T_{V_k} occurs in the second symmetrical tensor power $S^2(\rho)$ of the natural representation ρ. Again assuming natural degeneracy, this can be shown to be equivalent to $\langle \chi_k, \chi_\rho^2 - \det \cdot \chi_\rho \rangle \geq 1$ with χ_k the character of T_{V_k}.

The reader is referred to [Ste] and [Wil] for a more detailed discussion of the selection rules. There are other experimental techniques to measure the vibration spectrum of molecules, e.g. inelastic neutron scattering [6]. However, the resolution of such techniques is low. Further, the selection rules are not always strictly valid: under certain circumstances[3] it is possible to measure (using IR or Raman spectroscopy) other frequencies than those satisfying the selection

[3]For the case of C_{60}, see e.g. [10]

rules. However, the intensities of these "optically inactive modes" are relatively low and hence these modes are difficult to detect.

The classification of the eigenfrequencies can be obtained by using character theory alone. In the next chapter we will go beyond this and explicitly calculate the eigenfrequencies for the case of Buckminsterfullerene by diagonalizing $\tilde{F}$, making use of its symmetry by the procedure of symmetry reduction.

Chapter 3

Application: Buckminsterfullerene

The *Buckminsterfullerene* C_{60} molecule (or simply *buckyball*), illustrated in Fig. 3.1, consists of 60 carbon atoms located at the vertices of a truncated (regular) icosahedron. Its structure is similar to that of the well-known soccer ball. It has twenty hexagonal faces and twelve pentagonal faces; on the soccer ball, these are usually coloured white and black respectively. There are two types of bonds: bonds separating a hexagon from a pentagon ("single" bonds) and bonds separating two hexagons (the "double" bonds). Hence each carbon atom has a total number of four bonds, in accordance with the Lewis octet rule.

3.1 Icosahedral symmetry

A regular icosahedron, illustrated in Fig. 3.2, has 12 vertices, 30 edges and 20 regular triangular faces. In Fig. 3.3 a buckyball is shown together with the corresponding icosahedron. Each of the 30 edges of the icosahedron is divided into three parts by two vertices of the buckyball. The relative lengths of those parts are $l : (1 - 2l) : l$ where $0 \leq l \leq 1/2$ is a truncation parameter. The regular buckyball (which has regular hexagonal faces) has truncation parameter $l = 1/3$.[1] The symmetry group of the buckyball is clearly the same as that of the icosahedron.

[1]Measurements give a value of $l = 0.3289$ for Buckminsterfullerene (see [12]).

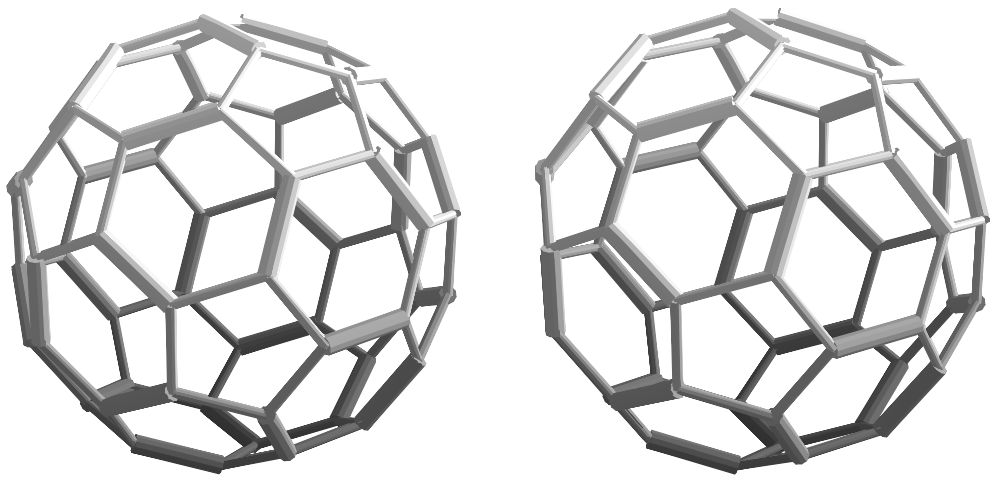

Figure 3.1: Stereoscopic view of the buckyball. The double bonds are accentuated. To see the three-dimensional structure, look with your left eye at the left part and at the same time with your right eye at the right part of the image.

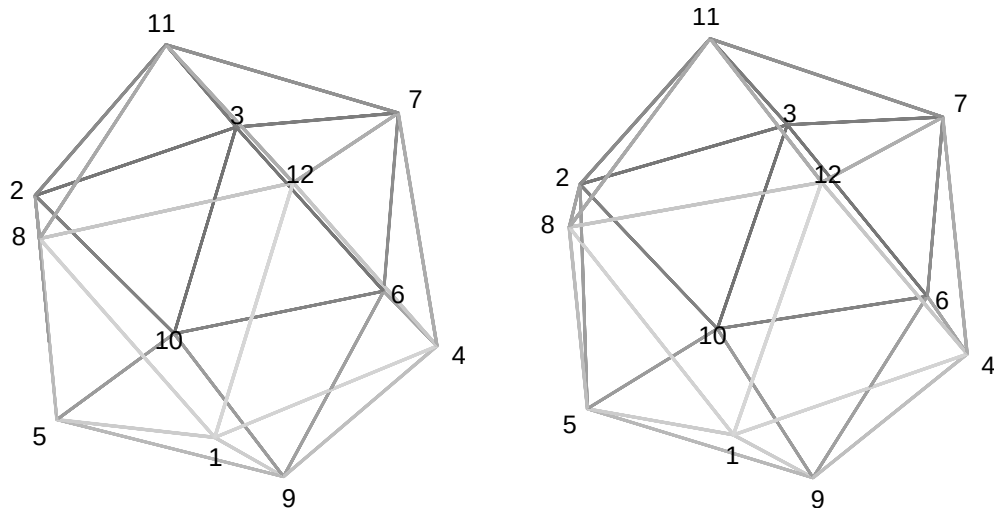

Figure 3.2: Stereoscopic view of an icosahedron.

Definition 3.1.1. *Choose a fixed icosahedron centered at the origin. The rotations under which the icosahedron is transformed into itself form a subgroup of $SO(3)$, called the* icosahedral rotation group I.

This group has generators a, b, c such that $a^2 = b^3 = c^5 = e$ and $cba = e$ and it consists of 60 elements. Note that $c = ab^2$ so I can also be presented as the group with two generators a and b and relations $a^2 = b^3 = (ab^2)^5 = e$.

The icosahedral rotation group is isomorphic to A_5, the alternating group of five elements (namely the 5 orthogonal triplets of lines through the midpoints of opposite edges), with as isomorphism e.g. the one defined by $a \mapsto (12)(34)$, $b \mapsto (135)$.

The icosahedral rotation group can also be seen as a subgroup of S_{12}, the permutation group of 12 elements (namely the vertices of the icosahedron). A particular embedding of I in S_{12} is given by

$$\begin{cases} a \mapsto (1,4)(2,3)(5,7)(6,8)(9,12)(10,11) \\ b \mapsto (1,4,12)(2,10,3)(5,6,11)(7,8,9), \end{cases}$$

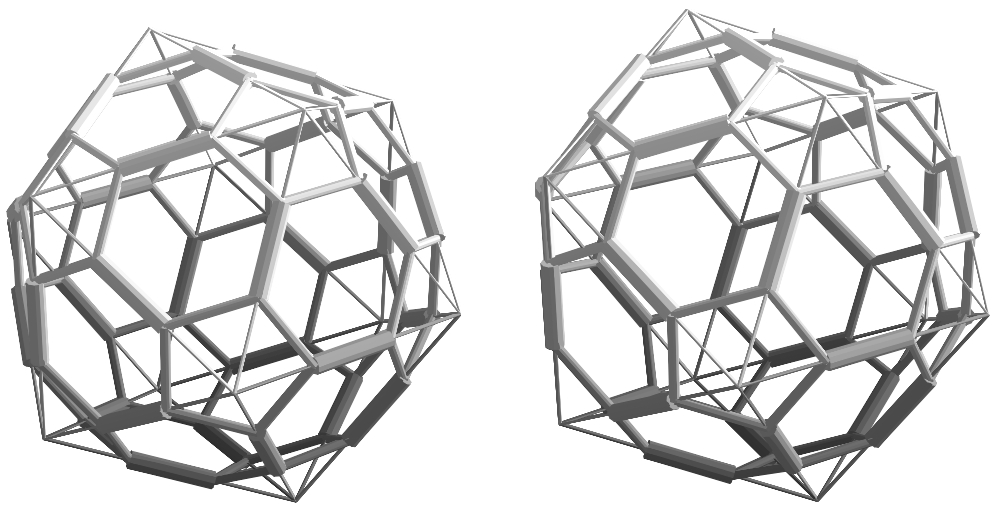

Figure 3.3: Stereoscopic view of a buckyball inside its surrounding icosahedron.

	e	a	b	c	c^2	s	sa	sb	sc	sc^2
	E	C_2	C_3	C_5	C_5^2	i	σ	S_6	S_{10}^3	S_{10}
	1	15	20	12	12	1	15	20	12	12
$\pi_{1+} = \mathrm{A_g}$	1	1	1	1	1	1	1	1	1	1
$\pi_{2+} = \mathrm{T_{1g}}$	3	-1	0	τ	τ'	3	-1	0	τ	τ'
$\pi_{3+} = \mathrm{T_{2g}}$	3	-1	0	τ'	τ	3	-1	0	τ'	τ
$\pi_{4+} = \mathrm{G_g}$	4	0	1	-1	-1	4	0	1	-1	-1
$\pi_{5+} = \mathrm{H_g}$	5	1	-1	0	0	5	1	-1	0	0
$\pi_{1-} = \mathrm{A_u}$	1	1	1	1	1	-1	-1	-1	-1	-1
$\pi_{2-} = \mathrm{T_{1u}}$	3	-1	0	τ	τ'	-3	1	0	$-\tau$	$-\tau'$
$\pi_{3-} = \mathrm{T_{2u}}$	3	-1	0	τ'	τ	-3	1	0	$-\tau'$	$-\tau$
$\pi_{4-} = \mathrm{G_u}$	4	0	1	-1	-1	-4	0	-1	1	1
$\pi_{5-} = \mathrm{H_u}$	5	1	-1	0	0	-5	-1	1	0	0

Table 3.1: Character table of the icosahedral symmetry group I_h. Here $\tau = \frac{1}{2}(1+\sqrt{5})$ and $\tau' = \frac{1}{2}(1-\sqrt{5})$. The first two rows contain representatives of the conjugation classes, the first row using the notation employed in this work and the second row using a notation that is more conventional in theoretical chemistry.

where the numbers of the vertices correspond with the labeling in Fig. 3.2, in coordinates:

$$\begin{array}{llllll}
1: & (1,\tau,0) & 5: & (\tau,0,-1) & 9: & (0,1,-\tau) \\
2: & (1,-\tau,0) & 6: & (-\tau,0,-1) & 10: & (0,-1,-\tau) \\
3: & (-1,-\tau,0) & 7: & (-\tau,0,1) & 11: & (0,-1,\tau) \\
4: & (-1,\tau,0) & 8: & (\tau,0,1) & 12: & (0,1,\tau)
\end{array}$$

Here $\tau := \frac{1}{2}(1+\sqrt{5})$ is the *Golden Ratio*. Define $\tau' := \frac{1}{2}(1-\sqrt{5})$, the Galois conjugate of τ. These numbers satisfy the relations $\tau^2 = \tau + 1$, $\tau'^2 = \tau' + 1$ and $\tau^{-1} = \tau' = \tau - 1$.

The *central inversion* of $\mathbb{R}^3$ is the transformation $s : \mathbb{R}^3 \to \mathbb{R}^3 : x \mapsto -x$. The full symmetry group of the icosahedron, i.e. the elements of $O(\mathbb{R}^3)$ that transform the icosahedron into itself, is the direct product $I_h := I \cup Is \cong A_5 \times C_2$. Since the buckyball has the same symmetry as the icosahedron and all the constituting carbon atoms have identical mass, the symmetry group of the buckyball is $G := I_h$.

Table 3.1 contains the character table of I_h, which is easily found from the character table of $I \cong A_5$. The notation of the representations ($\mathrm{A_g}$, $\mathrm{T_{1g}}$, etc.), called the *Mulliken notation* is conventional in spectroscopy.[2] The representation $\mathrm{T_{1u}}$ is the natural representation of $I_h < O(\mathbb{R}^3)$. A simple calculation using Wigner's rule and the character table yields that the $\mathrm{T_{1u}}$ modes satisfy the IR selection rule and the $\mathrm{A_g}$ and $\mathrm{H_g}$ modes satisfy the Raman selection rule. The other modes are optically inactive. With the characters we can also easily calculate the multiplicities of the irreps in the displacement representation; there are $2\,\mathrm{A_g}$, $4\,\mathrm{T_{1g}}$, $4\,\mathrm{T_{2g}}$, $6\,\mathrm{G_g}$, $8\,\mathrm{H_g}$, $1\,\mathrm{A_u}$, $5\,\mathrm{T_{1u}}$, $5\,\mathrm{T_{2u}}$, $6\,\mathrm{G_u}$ and $7\,\mathrm{H_u}$ modes. Subtracting the translational ($1\,\mathrm{T_{1u}}$) and rotational ($1\,\mathrm{T_{1g}}$) modes, this yields a total of $46 = 48 - 2$ eigenmodes.

To perform the symmetry reduction, we need the full matrix representations of I_h. These are given in Table 3.2. We have tried to choose the bases in such a way that the matrix coefficients are as simple as possible, since this will significantly speed up the computations to be performed by the computer algebra system. The natural representation $\mathrm{T_{1u}}$ was found by explicit calculation using the embedding of I into S_{12} and the explicit coordinates of the

[2] Although different versions have been observed in literature, e.g. "F" is used instead of "T" in [1]. Also the use of "F" instead of "G" has been observed.

	a	b	s
$\pi_{1+} = \mathrm{A_g}$	(1)	(1)	(1)
$\pi_{2+} = \mathrm{T_{1g}}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} -1 & \tau' & \tau \\ -\tau' & \tau & 1 \\ -\tau & 1 & \tau' \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
$\pi_{3+} = \mathrm{T_{2g}}$	$\frac{1}{2}\begin{pmatrix} -\tau & 1 & \tau' \\ 1 & -\tau' & -\tau \\ \tau' & -\tau & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
$\pi_{4+} = \mathrm{G_g}$	$\begin{pmatrix} -1 & -1 & -1 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ -1 & -1 & -1 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$
$\pi_{5+} = \mathrm{H_g}$	$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & \omega & 0 & 0 \\ 0 & \omega^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \omega^2 \\ 0 & 0 & 0 & \omega & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & \omega & 0 & 0 \\ 0 & \omega^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \omega^2 \\ 0 & 0 & 0 & \omega & 0 \\ 1 & 0 & 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$
$\pi_{1-} = \mathrm{A_u}$	(1)	(1)	(-1)
$\pi_{2-} = \mathrm{T_{1u}}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} -1 & \tau' & \tau \\ -\tau' & \tau & 1 \\ -\tau & 1 & \tau' \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
$\pi_{3-} = \mathrm{T_{2u}}$	$\frac{1}{2}\begin{pmatrix} -\tau & 1 & \tau' \\ 1 & -\tau' & -\tau \\ \tau' & -\tau & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
$\pi_{4-} = \mathrm{G_u}$	$\begin{pmatrix} -1 & -1 & -1 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ -1 & -1 & -1 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$
$\pi_{5-} = \mathrm{H_u}$	$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & \omega & 0 & 0 \\ 0 & \omega^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \omega^2 \\ 0 & 0 & 0 & \omega & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & \omega & 0 & 0 \\ 0 & \omega^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \omega^2 \\ 0 & 0 & 0 & \omega & 0 \\ 1 & 0 & 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & -1 \end{pmatrix}$

Table 3.2: Convenient choices of generators for the irreducible matrix representations of I_h. Here $\omega = e^{2\pi i/3}$, $\tau = \frac{1}{2}(1+\sqrt{5})$ and $\tau' = \frac{1}{2}(1-\sqrt{5})$.

vertices of the icosahedron as given above. The representation $\mathrm{T}_{2\mathrm{u}}$ can be obtained from $\mathrm{T}_{1\mathrm{u}}$ by replacing $\sqrt{5}$ by $-\sqrt{5}$, which amounts to exchanging τ and τ' (this operation is called *Galois conjugation* in the ring $\mathbb{Q}(\tau)$). The four-dimensional representation G_u was obtained by restricting the five-dimensional representation of A_5 as permutation matrices to the subspace $\{(x_1, x_2, x_3, x_4, x_5) \in \mathbb{C}^5 \mid \sum_k x_k = 0\}$. As a basis of this subspace we took $(1, -1, 0, 0, 0)$, $(1, 0, -1, 0, 0)$, $(1, 0, 0, -1, 0)$, $(1, 0, 0, 0, -1)$. Finally, the five-dimensional representation H_u was obtained by inducing a one-dimensional non-trivial representation of $A_4/V_4 \cong C_3$ to A_5, taking the powers of (12345) as representatives of the left cosets. The five other "gerade" representations are obtained by omitting the minus signs from the matrices representing the central inversion s.

3.2 Potential energy models

Our models of the buckyball will be mass-spring models consisting of 60 masses (the carbon atoms) connected by a multitude of springs.

3.2.1 Parallel springs

The potential energy of a spring of length L with force constant k at displacement x is given by $\mathcal{V}(x) = \frac{1}{2}k(L-x)^2$. Expanding the potential energy for a spring connecting two atoms at positions $\mathbf{r}_1 + \mathbf{q}_1$ and $\mathbf{r}_2 + \mathbf{q}_2$ as a Taylor series in $\mathbf{q}_1$ and $\mathbf{q}_2$ yields, up to second order terms:

$$\mathcal{V}(\mathbf{q}_1, \mathbf{q}_2) = \tfrac{1}{2}k\big(\|\mathbf{r}_2 + \mathbf{q}_2 - \mathbf{r}_1 - \mathbf{q}_1\| - \|\mathbf{r}_2 - \mathbf{r}_1\|\big)^2 \approx \tfrac{1}{2}k\frac{\langle \mathbf{q}_2 - \mathbf{q}_1, \mathbf{r}_2 - \mathbf{r}_1\rangle^2}{\|\mathbf{r}_2 - \mathbf{r}_1\|^2} = \tfrac{1}{2}k(\mathbf{q}_2 - \mathbf{q}_1)_\parallel^2,$$

the notation $\mathbf{v}_\parallel$ (for $\mathbf{v} \in \mathbb{R}^3$) meaning the part of $\mathbf{v}$ that is parallel to the vector $\mathbf{r}_2 - \mathbf{r}_1$.

The total potential energy (approximated up to second order) for the general mass-spring model of the buckyball can hence be written as:

$$\mathcal{V}(\mathbf{q}) = \frac{1}{2}\sum_{i=1}^{60}\sum_{\substack{j=1\\ j>i}}^{60} k_{ij}(\mathbf{q}_i - \mathbf{q}_j)_\parallel^2 = \frac{1}{2}\sum_{i=1}^{60}\sum_{\substack{j=1\\ j>i}}^{60} k_{ij}\frac{\langle \mathbf{q}_i - \mathbf{q}_j, \mathbf{r}_i - \mathbf{r}_j\rangle^2}{\|\mathbf{r}_i - \mathbf{r}_j\|^2}$$

with k_{ij} the force constant of the string connecting atom i and j. Written out in a form convenient for reading off the matrix coefficients of the Hessian of V:

$$\mathcal{V} = \frac{1}{2}\sum_{i=1}^{60}\sum_{j=1}^{60}\sum_{\mu=1}^{3}\sum_{\nu=1}^{3} q_{i\mu}q_{j\nu}\left(\delta_{ij}\sum_{m=1}^{60} k_{im}\frac{(r_{m\mu} - r_{i\mu})(r_{m\nu} - r_{i\nu})}{\|\mathbf{r}_m - \mathbf{r}_i\|^2} - k_{ij}\frac{(r_{j\mu} - r_{i\mu})(r_{j\nu} - r_{i\nu})}{\|\mathbf{r}_j - \mathbf{r}_i\|^2}\right).$$

3.2.2 Transversal springs

In [7] a potential energy is used (called by the authors the *Born potential*) that has also "transversal springs", i.e. components perpendicular to the difference vector of the equilibrium positions. Since it will turn out that this model gives good results we will extend our parallel model above as follows:

$$\begin{aligned}\mathcal{V}(\mathbf{q}) &= \frac{1}{2}\sum_{i=1}^{60}\sum_{\substack{j=1\\ j>i}}^{60}\left(k_{ij}^{\parallel}(\mathbf{q}_i - \mathbf{q}_j)_\parallel^2 + k_{ij}^{\perp}(\mathbf{q}_i - \mathbf{q}_j)_\perp^2\right)\\ &= \frac{1}{2}\sum_{i=1}^{60}\sum_{\substack{j=1\\ j>i}}^{60}\left((k_{ij}^{\parallel} - k_{ij}^{\perp})(\mathbf{q}_i - \mathbf{q}_j)_\parallel^2 + k_{ij}^{\perp}(\mathbf{q}_i - \mathbf{q}_j)^2\right).\end{aligned} \tag{3.1}$$

where $\mathbf{v}_\perp$ (for $\mathbf{v} \in \mathbb{R}^3$) means the part of $\mathbf{v}$ that is perpendicular to the equilibrium difference vector $\mathbf{r}_j - \mathbf{r}_i$. Writing this out yields:

$$\mathcal{V}(\mathbf{q}) = \frac{1}{2}\sum_{i=1}^{60}\sum_{j=1}^{60}\sum_{\mu=1}^{3}\sum_{\nu=1}^{3} q_{i\mu}q_{j\nu}\left(\delta_{ij}\sum_{m=1}^{60}(k_{im}^{\parallel} - k_{im}^{\perp})\frac{(r_{m\mu}-r_{i\mu})(r_{m\nu}-r_{i\nu})}{\|\mathbf{r}_m - \mathbf{r}_i\|^2}\right.$$
$$\left. -(k_{ij}^{\parallel} - k_{ij}^{\perp})\frac{(r_{j\mu}-r_{i\mu})(r_{j\nu}-r_{i\nu})}{\|\mathbf{r}_j - \mathbf{r}_i\|^2} + \delta_{\mu\nu}\left(\delta_{ij}\sum_{m=1}^{60} k_{im}^{\perp} - k_{ij}^{\perp}\right)\right). \quad (3.2)$$

We will choose the parallel force constants $k_{i,j}^{\parallel}$ $(i, j = 1, \ldots, 60)$ as follows:

$$k_{i,j}^{\parallel} := \begin{cases} k_5^{\parallel} & \text{if } i,j \text{ are nearest neighbours within a pentagon} \\ k_{5n}^{\parallel} & \text{if } i,j \text{ are next-nearest neighbours within a pentagon} \\ k_6^{\parallel} & \text{if } i,j \text{ are nearest neighbours separating two hexagons} \\ k_{6n}^{\parallel} & \text{if } i,j \text{ are next-nearest neighbours within a hexagon} \\ 0 & \text{otherwise.} \end{cases} \quad (3.3)$$

where $k_5^{\parallel}$, $k_{5n}^{\parallel}$, $k_6^{\parallel}$ and $k_{6n}^{\parallel}$ are adjustable parameters that can be chosen in such a way as to give optimal agreement with the experimental data. The orthogonal force constants $k_{i,j}^{\perp}$ will be taken as:

$$k_{i,j}^{\perp} := \begin{cases} k_5^{\perp} & \text{if } i,j \text{ are nearest neighbours within a pentagon} \\ k_{5n}^{\perp} & \text{if } i,j \text{ are next-nearest neighbours within a pentagon} \\ k_6^{\perp} & \text{if } i,j \text{ are nearest neighbours separating two hexagons} \\ k_{6n}^{\perp} & \text{if } i,j \text{ are next-nearest neighbours within a hexagon} \\ 0 & \text{otherwise.} \end{cases} \quad (3.4)$$

with $k_5^{\perp}$, $k_{5n}^{\perp}$, $k_6^{\perp}$ and $k_{6n}^{\perp}$ additional adjustable parameters.

3.2.3 Bending springs

We can also consider "bending springs", springs attached to *bonds* modeling the contribution to the potential energy arising from the angle between two bonds. Consider three particles at positions $\mathbf{x}_1$, $\mathbf{x}_2$ and $\mathbf{x}_3$ with bonds between the pairs $(1, 2)$ and $(2, 3)$. We will write $\mathbf{v}_{\alpha-\beta} := \mathbf{v}_\alpha - \mathbf{v}_\beta$ for two vectors $\mathbf{v}_\alpha$ and $\mathbf{v}_\beta$ in $\mathbb{R}^3$. Denoting the angle between bonds $(1, 2)$ and $(2, 3)$ by:

$$\phi := \cos^{-1}\frac{\langle \mathbf{x}_{1-2}, \mathbf{x}_{3-2}\rangle}{\|\mathbf{x}_{1-2}\|\|\mathbf{x}_{3-2}\|},$$

and writing ϕ_0 for the equilibrium angle, the contribution to the potential energy is given by:

$$\tfrac{1}{2}k^{\angle}(\phi - \phi_0)^2 = \frac{1}{2}k^{\angle}\left(\cos^{-1}\frac{\langle \mathbf{r}_{1-2} + \mathbf{q}_{1-2}, \mathbf{r}_{3-2} + \mathbf{q}_{3-2}\rangle}{\|\mathbf{r}_{1-2} + \mathbf{q}_{1-2}\|\|\mathbf{r}_{3-2} + \mathbf{q}_{3-2}\|} - \cos^{-1}\frac{\langle \mathbf{r}_{1-2}, \mathbf{r}_{3-2}\rangle}{\|\mathbf{r}_{1-2}\|\|\mathbf{r}_{3-2}\|}\right)^2,$$

where $k^{\angle}$ is the angular spring constant. The harmonic approximation of this term is as follows:

$$\frac{1}{2}k^{\angle}\frac{1}{\sin^2\phi_0}\left(\left\langle \mathbf{e}_{3-2} - \cos\phi_0\mathbf{e}_{1-2}, \frac{\mathbf{q_{1-2}}}{\|\mathbf{r}_{1-2}\|}\right\rangle + \left\langle \mathbf{e}_{1-2} - \cos\phi_0\mathbf{e}_{3-2}, \frac{\mathbf{q_{3-2}}}{\|\mathbf{r}_{3-2}\|}\right\rangle\right)^2,$$

where $\mathbf{e}_{\alpha-\beta} := \mathbf{r}_{\alpha-\beta}/\|\mathbf{r}_{\alpha-\beta}\|$. The total contribution to the potential energy consists of the sum of these terms for all possible bond angles. There are two types of angles in the buckyball:

angles inside a pentagon (for which we take $k^{\angle} = k_5^{\angle}$) and angles inside a hexagon (with another spring constant $k^{\angle} = k_6^{\angle}$). We will not write this expression out in a form that is convenient for reading off the matrix coefficients of the force constant matrix, since the resulting expressions are rather cumbersome.

In total, together with the truncation parameter l, the number of adjustable model parameters is 11.

3.3 Computational details and results

All the calculations have been done with the computer algebra system *Maple* 8.00. The full Maple source can be found online [13]; here we will only give a short description of the calculational procedures.

The first step was to represent the symmetry group G and its representations within Maple. We represented the group elements by "words" in the generators (a,b,c and s). To represent a matrix representation of the group in Maple, it then suffices to prescribe the matrices corresponding to these generators—Maple can calculate the other $120 - 4$ matrices by itself. The second step was to calculate the projection operators. For each irrep π we need d_π projection operators, so in total we have to calculate 32 projection operators. This takes about three hours on a modern 2.5 GHz Pentium IV processor, which is actually rather long. The next step was constructing the basis vectors $\{f_{jk}^{\pi}\}$. The built-in `basis` function of Maple turned out to be not useful for this purpose, because after waiting for several hours we ran out of patience before it would finish the calculation. Instead, we constructed a basis by subsequentially adding vectors to the collection of already chosen basis vectors whenever the rank of the matrix consisting of these vectors would increase. After a convenient basis had been constructed, the reductions of $\tilde{F}$ were calculated and expressed in our basis by using the `linsolve` function. The final step was to substitute the parameter values and to numerically calculate the eigenvalues and eigenvectors of the reductions of $\tilde{F}$ (using the `eigenvals` and `eigenvectors` functions).

To find the optimal parameter values for the various models, we used a numerical least-squares fit against the experimental data on the (optically active) $\mathrm{T_{1u}}$, $\mathrm{A_g}$ and $\mathrm{H_g}$ modes taken from [5] and reproduced in Table 3.4. We have chosen not to use experimental data on the optically inactive modes because these are less trustworthy, since their assignment to the vibrational modes is still a matter of ongoing discussion [10]. To solve the multidimensional minimization problem, we used the *Downhill Simplex method of Nelder and Mead*, as described in [NRC, pp. 408–411] which we implemented in Maple.

To investigate the importance of the various parameters we have organized these into a hierarchy of model families according to their complexity. One can choose some of the parameters to be adjustable during the fit and keep the others at fixed default values (e.g. $l = 1/3$). The different resulting model families can be described using a 5-bit digit $d_1d_2d_3d_4d_5$ in which the bits have the following meaning:

Bit	Value	Meaning
d_1	0	l is kept fixed at $l = 1/3$
	1	l adjustable within its range $0 < l < \frac{1}{2}$
d_2	0	no difference between single and double bonds, i.e. $k_5^{\parallel} = k_6^{\parallel}, k_{5n}^{\parallel} = k_{6n}^{\parallel}, k_5^{\perp} = k_6^{\perp}, k_{5n}^{\perp} = k_{6n}^{\perp}, k_5^{\angle} = k_6^{\angle}$
	1	the single and double bond force constants can be chosen independently each other
d_3	0	no next-nearest neighbour interaction, i.e. $k_{5n}^{\parallel} = 0$, $k_{6n}^{\parallel} = 0$, $k_{5n}^{\perp} = 0$ and $k_{6n}^{\perp} = 0$
	1	the next-nearest neighbour parameters can be nonzero
d_4	0	no transversal interactions, i.e. $k_5^{\perp} =$, $k_6^{\perp} = 0$, $k_{5n}^{\perp} = 0$ and $k_{6n}^{\perp} = 0$
	1	transversal parameters can be nonzero
d_5	0	no bending springs, i.e. $k_5^{\angle} = k_6^{\angle} = 0$
	1	angular spring constants can be nonzero

Since the truncation parameter l cancels out if there is no next-nearest neighbour interaction and no angular interaction, we can neglect 4 models, namely those with $d_1 = 1$, $d_3 = 0$ and $d_5 = 0$. Also we did not consider models with $d_1 = 1$ and $d_5 = 1$ because the algebra would really become cumbersome in this case, even for a computer algebra system. For the remaining model families, the free parameters have been adjusted by the least-squares fitting procedure to give optimal agreement with the 14 experimental eigenfrequencies of the optically active modes. The results are shown in Table 3.3. In addition, we have done two fits (those marked with a *) using all available experimental frequency data (i.e. also for optically inactive modes). These data were taken from [10] and are reproduced in Table 3.4.

3.4 Discussion and conclusion

Several, somewhat surprising, conclusions can be drawn from Table 3.3.

- First of all, the truncation parameter l cannot be inferred from the vibrational frequencies. In general, "setting the first bit" does not yield significantly better fits. This may be surprising since l might in the first instance be thought of as the most basic model parameter. Instead it turns out to be only a higher order correction. Some reflection leads to the conviction that the electronic structure of carbon atoms is indispensable information for a theoretical calculation of the value of l. The harmonic oscillator approximation around the equilibrium configuration employed here is too rudimentary for this purpose.

- The two-parameter model 01000 in which we distinguish single and double bonds does not give a better result than the one-parameter model 00000 in which single and double bonds have identical force constants. Only when combined with next-nearest neighbour interaction does distinguishing between single and double bonds give significant improvements.

- Taking into account next-nearest neighbour interaction (setting the third bit) gives in all cases a significant improvement.

- Out of the four two-parameter models (01000, 00100, 00010, 00001), model 00010 performs extremely well. Unfortunately, however, all models with transversal interactions turn out

Model	χ^2	%	l	$k_5^{\parallel}$	$k_6^{\parallel}$	$k_{5n}^{\parallel}$	$k_{6n}^{\parallel}$	$k_5^{\perp}$	$k_6^{\perp}$	$k_{5n}^{\perp}$	$k_{6n}^{\perp}$	$k_5^{\angle}$	$k_6^{\angle}$
00000	1120	32		766	idem								
01000	1120	32		809	711								
00100	280	15.6		463	idem	206	idem						
01100	170	12.5		161	266	48	643						
00010	29.0	5.3		677	idem			147	idem				
01010	27.1	5.0		693	655			167	108				
00110	15.5	4.2		643	idem	35	idem	196	idem	-25	idem		
01110	13.1	4.0		572	665	85	29	205	228	-25	-34		
10100	156	10.5	0.5	161	idem	425	idem						
11100	149	9.3	0.49	388	45	333	423						
10110	14.8	4.2	0.22	626	idem	40	idem	204	idem	-28	idem		
11110	12.5	3.9	0.46	526	696	105	46	202	219	-25	-35		
00001	134	10.1		627	idem							15.9	idem
01001	132	9.7		631	615							12.7	18.2
00101	45	4.3		478	idem	95	idem					15.2	idem
01101	11.8	2.6		236	347	311	95					8.8	21.9
01111	5.9	2.7		305	315	366	74	136	223	-25	-33	12.8	3.2
01111*	46	2.6		489	666	61	73	97	62	-15	-2.4	5.6	4.8
01101*	274	7.6		345	525	212	61					12.1	11.4

Table 3.3: Results of the least-squares fitting for all possible model families. The first column describes the model family, as explained in the main text. The second column, labeled "χ^2", contains the sum of the squares of the residuals after fitting (in units of 10^3) and indicates the goodness-of-fit, a lower value meaning a better fit. The third column, labeled "%" gives the average percentual error of the fitted frequencies, which is another measure for the goodness-of-fit that is somewhat easier to interpret than χ^2. The fourth column contains the optimal value for the truncation parameter; if it is missing then the value $l = 1/3$ has been kept fixed. The remaining columns contain the optimal values for the force constants (in 10^3 dyn/cm, except the angular ones, these are in units of 10^3 dyn cm); if a value is missing this means that the parameter was kept fixed at the value 0 during the fit. "Idem" means that the parameter for the double bond $k_{6?}^{?}$ is kept equal to the corresponding parameter $k_{5?}^{?}$ for the single bond. The last two rows (with model names marked with a *) are fits using all 46 modes, i.e. also optically inactive ones.

to have an additional T_{1u} mode since the Hessian is not zero on the rotational subspace. This means that on principal grounds, we should reject these models because they are not harmonic approximations of rotationally invariant potential energies. This result is rather disappointing regarding the excellent performance of the models with transversal interactions. One could fix this problem by subtracting a compensating part from the force constant matrix. Or alternatively, one could ignore the extra mode (it has a low frequency and is easily visually identified, since its eigenspace is reminiscent of the rotational subspace, see Figure 3.7). Either way however, the situation remains unsatisfactory.

- The parameters $k_{5n}^{\perp}$ and $k_{6n}^{\perp}$ can be safely omitted from the models since they are almost zero. The fact that the optimal values of these parameters are *negative* should be of no concern since they form only a small correction on the other large and positive force constants.

- Initially, we hoped that increasing the complexity of the model would only lead to minor modifications of the force constants. This turns out to be a little naive. A redefinition of the force constants might help. Indeed, a variation in the value of $k_{6n}^{\parallel}$ e.g. should be

compensated with a variation in $k_6^{\|}$, since they have similar contributions to particular elements of the force constant matrix.

It should be noted that it is not difficult to construct a model that perfectly reproduces all 46 eigenfrequencies (this model is most easily formulated in normal coordinates). However, this model does not survive application of Ockham's Razor.

The resulting eigenfrequencies for the best performing model without transversal interactions, namely 01101, are shown in Table 3.4. For comparison, also the resulting frequencies of model 01101*, i.e. where we have used all experimental data for the fit, are given. Also shown in this table are the results of calculations of other groups as well as experimental results. The first column contains early theoretical results from [4], who also use the symmetry reduction method but use a less sophisticated potential energy with fixed force constants (namely the corresponding values for benzene). The second column contains the results of modern Density Functional Theory calculations from [10], the most accurate theoretical method currently available for the case of C_{60}. Here the mathematical model is much more subtle: one uses that each carbon atom has a nucleus with 6 electrons and finds the force constant matrix by extensive numerical calculations based on a detailed quantum mechanical model of the system. The third column contains conventional IR and Raman spectroscopy data taken from [5]. The fourth column contains all available experimental data, collected using different experimental methods, reproduced from the "supporting information" of [10]. The experimental errors for these data are not known.

Concluding, the results of this work are a significant improvement over [4] but cannot compete with the DFT results of e.g. [10]. However, in contrast with the DFT results, the potential energy model for the buckyball found here is easily written down analytically.

A final remark has to be made concerning the computer algebra system. We have chosen to use *Maple* because this program is used in the education of mathematics students at the KUN. However, the next time that the author undertakes such a large project with a computer algebra system he will definately not use Maple again. Working with Maple (version 8.00) turned out to be a frustrating experience because of Maple's instability, the bugs that were encountered, its slowness and its user-unfriendliness. For example, in general one does not know how much time a calculation will take—whether it is a question of seconds or hours—and there is no auditory signal when a calculation finishes. The author also would have liked to produce some animations of vibrating buckyballs, but because of a memory leak in Maple this was not possible. Instead, some of the modes have been illustrated in Figures 3.4–3.7.

Mode	Calculated		Experimental		Calculated (this work)	
	[4]	[10]	[5]	[10]	01101	01101*
T_{1u}	478	528	527 ± 1	525	538	422
	618	577	577 ± 1	578	598	576
	1462	1189	1183 ± 1	1182	1165	1125
	1868	1431	1428 ± 1	1433	1418	1451
A_g	510	487	496 ± 2	496	512	491
	1830	1474	1470 ± 2	1468	1442	1477
H_g	274	261	273 ± 2	264	274	250
	413	429	437 ± 2	430	416	369
	526	705	710 ± 2	709	630	529
	828	772	774 ± 2	773	755	738
	1292	1104	1099 ± 2	1101	1110	1129
	1575	1251	1250 ± 2	1251	1290	1166
	1910	1426	1428 ± 2	1425	1438	1420
	2085	1585	1575 ± 2	1576	1603	1576
T_{1g}	513	562		560	565	448
	1045	823		825	1029	897
	1662	1276		1260	1602	1294
T_{2g}	615	555		552	667	586
	724	724		713	809	651
	951	789		796	1178	1015
	1900	1344		1345	1504	1347
G_g	433	480		485	412	379
	593	565		567	657	538
	657	741		751	731	678
	1327	1072		1078	980	1017
	1813	1308		1309	1492	1385
	2006	1507		1497	1660	1510
A_u	1243	946		956	1549	1138
T_{2u}	358	337		341	370	339
	526	709		706	650	535
	1122	958		963	985	1013
	1543	1177		1166	1269	1185
	1954	1536		1540	1556	1553
G_u	360	351		354	346	309
	663	738		741	795	639
	876	751		756	851	841
	1086	962		972	973	950
	1845	1307		1307	1362	1336
	2004	1434		1428	1571	1425
H_u	405	400		403	400	356
	470	531		533	464	435
	569	665		665	680	559
	849	729		738	844	747
	1464	1219		1215	1302	1161
	1797	1343		1341	1578	1365
	2086	1576		1566	1655	1564

Table 3.4: Vibrational frequencies of Buckminsterfullerene: theoretical and experimental results (all values in cm^{-1}). A description of the contents of each column is given in the main text.

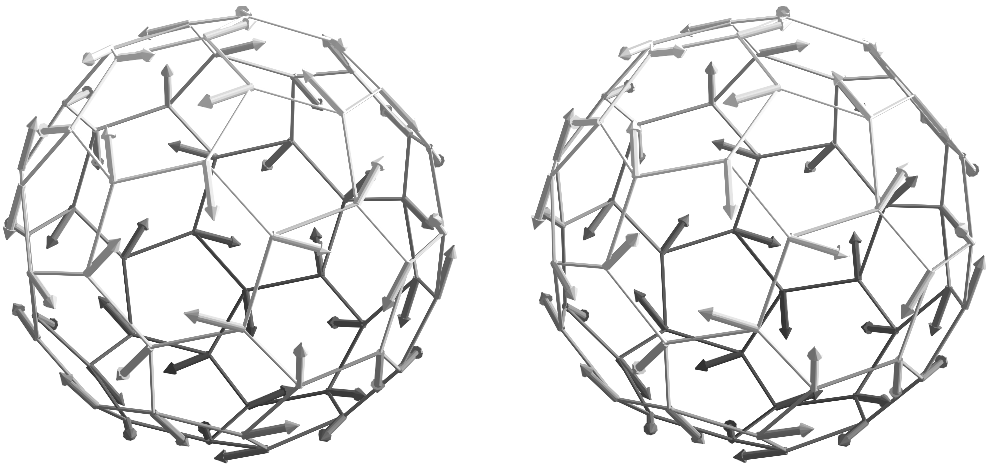

Figure 3.4: Stereoscopic view of the A_u mode.

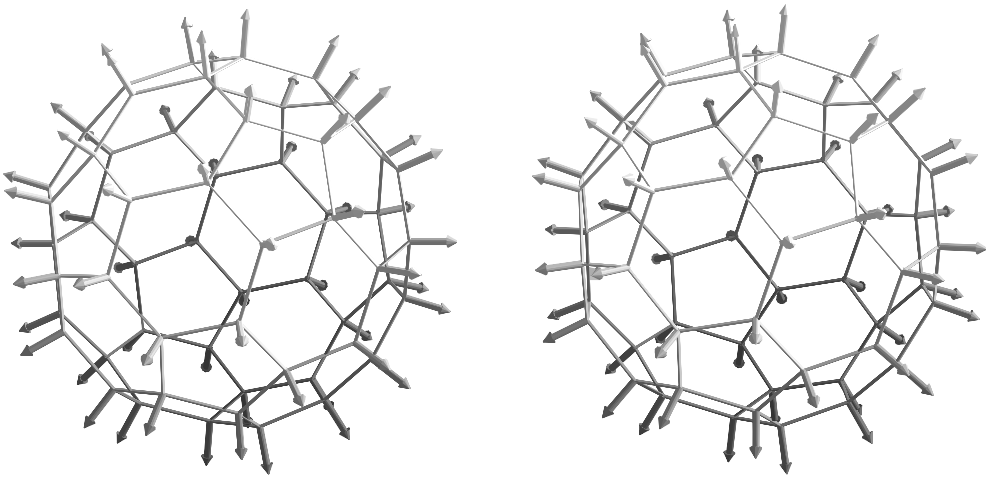

Figure 3.5: Stereoscopic view of the low-frequency A_g mode.

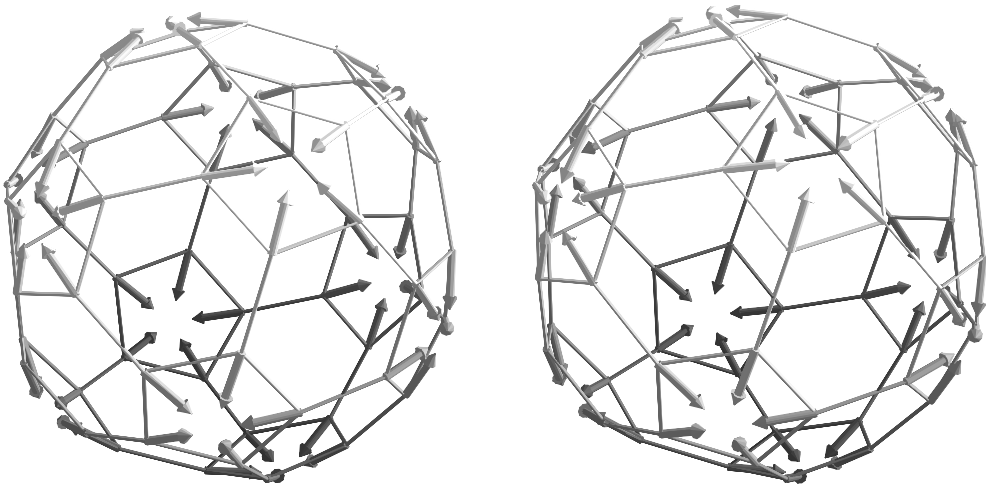

Figure 3.6: Stereoscopic view of the high-frequency A_g mode.

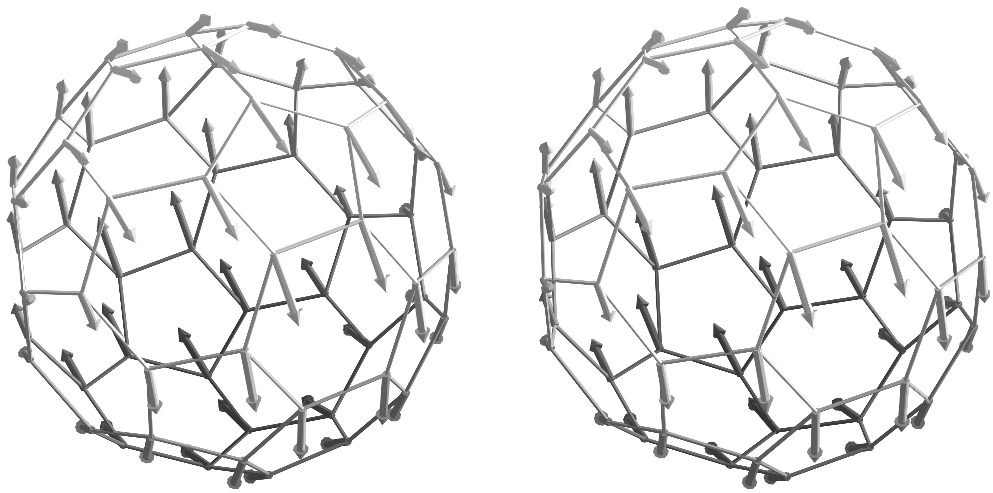

Figure 3.7: Stereoscopic view of the unphysical rotational T_{1g} mode.

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