



2008-08-20

# Implementation of Optical Spectra Calculations in FIREBALL: A Local-Orbital Density Functional Theory Approach

Ivan Grigoryevich Okhrimenko  
*Brigham Young University - Provo*

Follow this and additional works at: <https://scholarsarchive.byu.edu/etd>

 Part of the [Astrophysics and Astronomy Commons](#), and the [Physics Commons](#)

---

## BYU ScholarsArchive Citation

Okhrimenko, Ivan Grigoryevich, "Implementation of Optical Spectra Calculations in FIREBALL: A Local-Orbital Density Functional Theory Approach" (2008). *All Theses and Dissertations*. 1592.  
<https://scholarsarchive.byu.edu/etd/1592>

This Dissertation is brought to you for free and open access by BYU ScholarsArchive. It has been accepted for inclusion in All Theses and Dissertations by an authorized administrator of BYU ScholarsArchive. For more information, please contact [scholarsarchive@byu.edu](mailto:scholarsarchive@byu.edu), [ellen\\_amatangelo@byu.edu](mailto:ellen_amatangelo@byu.edu).

IMPLEMENTATION OF OPTICAL SPECTRA CALCULATIONS IN FIREBALL:  
A LOCAL-ORBITAL DENSITY FUNCTIONAL THEORY APPROACH

by

Ivan Grigoryevich Okhrimenko

A dissertation submitted to the faculty of

Brigham Young University

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Department of Physics and Astronomy

Brigham Young University

December 2008

BRIGHAM YOUNG UNIVERSITY

GRADUATE COMMITTEE APPROVAL

of a dissertation submitted by

Ivan Grigoryevich Okhrimenko

This dissertation has been read by each member of the following graduate committee and by majority vote has been found to be satisfactory.

\_\_\_\_\_

Date

\_\_\_\_\_

Bret Hess, Chair

\_\_\_\_\_

Date

\_\_\_\_\_

John Colton

\_\_\_\_\_

Date

\_\_\_\_\_

Robert Davis

\_\_\_\_\_

Date

\_\_\_\_\_

Gus Hart

\_\_\_\_\_

Date

\_\_\_\_\_

Harold Stokes

BRIGHAM YOUNG UNIVERSITY

As chair of the candidate's graduate committee, I have read the dissertation of Ivan G. Okhrimenko in its final form and have found that (1) its format, citations, and bibliographical style are consistent and acceptable and fulfill university and department style requirements; (2) its illustrative materials including figures, tables, and charts are in place; and (3) the final manuscript is satisfactory to the graduate committee and is ready for submission to the university library.

---

Date

---

Bret Hess  
Chair, Graduate Committee

Accepted for the Department

---

J. Ward Moody, Graduate Coordinator  
Department of Physics and Astronomy

Accepted for College

---

Thomas W. Sederberg, Associate Dean  
College of Physical and Mathematical  
Sciences

## ABSTRACT

### IMPLEMENTATION OF OPTICAL SPECTRA CALCULATIONS IN FIREBALL: A LOCAL-ORBITAL DENSITY FUNCTIONAL THEORY APPROACH

Ivan G. Okhrimenko

Department of Physics and Astronomy

Doctor of Philosophy

We have expanded the capabilities of the *ab initio* tight-binding molecular dynamics package FIREBALL to include calculations of optical properties. Basic zero order approximation is based on transitions between Kohn-Sham states. Corrections for electron-electron interactions are based on time dependant density functional theory (TDDFT). Consistent with the FIREBALL approach, we use pre-calculated integrals and approximations to make the program faster.

## ACKNOWLEDGMENTS

I offer my heart-felt thanks to: Dr. Bret Hess for his patience during my dissertation efforts and for his review of the theory and mathematics supporting this paper. Likewise, Daniel Jensen provided invaluable assistance by handling a large portion of the four-integrals programming for CREATE, and by offering expertise related to debugging, testing and troubleshooting. Finally, Dr. James Lewis introduced FIREBALL to our research group and thus initiated the larger project from which this dissertation had its genesis.

I also express my greatest thanks to my family (especially my wife) and friends who supported me throughout this work.

## TABLE OF CONTENTS

TABLE OF CONTENTS.....	vi
TABLE OF FIGURES.....	viii
1 Introduction .....	1
1.1 Technology and nanoscience.....	1
1.2 Need for simulation.....	2
1.3 Tight-binding models .....	3
1.4 FIREBALL .....	4
2 Theory .....	5
2.1 The full Hamiltonian .....	5
2.2 The Born-Oppenheimer approximation .....	5
2.3 Exchange and Correlation .....	7
2.4 Hartree .....	8
2.5 Hartree-Fock.....	10
2.5.1 Hartree-Fock for free electron gas.....	11
2.6 Density functional theory (DFT) .....	12
2.6.1 The first Hohenberg and Kohn theorem.....	13
2.6.2 The second theorem.....	15
2.6.3 The Kohn-Sham equations.....	15
2.7 Time-dependent density functional theory (TDDFT).....	16
2.8 First order and full TDDTF .....	17
2.8.1 Oscillator strengths within TDDFT.....	18
2.9 Optical properties from energies and oscillator strengths .....	19
3 Implementation.....	20
3.1 General considerations .....	20
3.2 Optical absorption spectrum in zero order .....	21
3.2.1 Energies .....	21
3.2.2 Oscillator strengths.....	21
3.3 Implementation of first order and full TDDFT.....	21
3.4 Density projection approximation.....	24
4 Results and discussion .....	26
4.1 Benzene .....	27
4.2 C <sub>60</sub> .....	29
5 Conclusion and future work .....	35
6 APPENDICES .....	37
6.1 APPENDIX A TABLE OF $Y_L^M$ .....	37
6.2 APPENDIX B FIREBALL Functions as $Y_L^M$ .....	39
6.2.1 Definitions of FB orbitals .....	39
6.2.2 Derivations of relationships .....	39
6.2.3 Matrix form of FB and $Y_L^M$ 's relationship.....	42
6.3 APPENDIX C XYZ Dipole selection Rules .....	43
6.3.1 Derivations of the dipole selection rules. ....	43
6.3.2 Dipole selection rules for two identical atoms.....	44
6.3.3 Dipole selection rules for two different atoms.....	45

6.4	APPENDIX D Dipole rotations from CREATE to FIREBALL .....	46
6.5	APPENDIX E Rotations of p and d functions.....	48
6.5.1	Rotations summary .....	48
6.5.2	Derivation of rotational formulas.....	49
6.6	APPENDIX F Geometry of a perfect tetrahedron .....	58
6.6.1	Proofs of the identities mentioned.....	59
6.7	APPENDIX G Various Programs.....	65
6.7.1	Calculator.....	65
6.7.2	CrSlab .....	67
6.7.3	MicroCluster .....	68
6.7.4	Cluster.....	69
7	REFERENCES .....	72



## TABLE OF FIGURES

Figure 4.1 Optical absorption of benzene, full TDDFT, comparing two data sets .....	27
Figure 4.2 Optical absorption of benzene, DNP data set, TDDFT, comparing different approximations .....	28
Figure 4.3 Benzene absorption spectra, full TDDFT+DNP (below) superimposed with experimental [19] (above) .....	29
Figure 4.4 Optical absorption of C <sub>60</sub> , upper limit 7.5 ev, full TDDFT, comparing data sets .....	30
Figure 4.5 Absorption spectrum of C <sub>60</sub> ( <i>Ih</i> ) in <i>n</i> -hexane solution at room temperature. Superimposed are TDDFT calculations of optically allowed transition energies corrected for systematic errors by adding 0.35 eV. Oscillator strengths were normalized to experiment. [20] .....	31
Figure 4.6 Optical absorption of C <sub>60</sub> , single numeric data set, TDDFT, comparing approximations, full TDDFT limited to 7.5 ev .....	32
Figure 4.7 Optical absorption of C <sub>60</sub> , double numeric with polarization data set, comparing approximations. Full TDDFT is limited to the range of 0 to 7.5 ev .....	33
Figure 4.8 Free response of C <sub>60</sub> corresponding to Kohn-Sham levels, [21] .....	33
Figure 4.9 RPA response of C <sub>60</sub> [21] .....	34

# 1 Introduction

## *1.1 Technology and nanoscience*

Conventional technologies of microelectronics are limited not only by the resolution of the photolithographic process, but also by the physical limits of materials used. This limits the size of individual elements and the density of the elements on the crystal. The challenges encountered on the road toward miniaturization include power consumption, heat dissipation, the problem of the chemical heterogeneity of substrate and the problem of structure defects. Eventually, we will reach the physical limits of conventional silicon MOSFET (**Metal Oxide Semiconductor Field Effect Transistor**) devices technology. The search for a principally new type of device is therefore under way.

The single-electron tunneling (SET) transistor is one of the possible candidates thought capable of filling this future need [1, 2]. On the practical side, it was demonstrated that nanoclusters are good building blocks for those novel devices, even at room temperature [3-5]. A system of multiple nanoparticles participating in a tunneling transfer of charge between electrodes (an exact solution is provided for a double-particle system) is treated in [6].

Scientists are also researching the use of nanoparticles for medical applications [7-10]. Future drug delivery, where nanoparticles would transport attached drugs to specific cells or to specific locations in the body, and thereby activate the medication upon an encounter with a specific condition or signal, might well revolutionize the future pharmaceutical industry. Future medical providers may one day consider current medical

practice to be a primitive, indiscriminate “nuking” of the entire patient’s body with a drug that really only need to kill a few germs, and instead treat the patients of the future with local treatment delivery precisely where needed. An advance drug delivery would presumably lead to better performance and fewer side effects.

The nanoparticles can be engineered to bond to specific types of cells (for example cancer cells) by choosing specific antibodies or peptides as nanoparticle ligands. Nanoparticles with high luminescence can be used as visible biological markers. When activated (excited by ultraviolet radiation for example) the glowing nanoparticles attached to targeted cells would be a great help for future surgeons. Another possible application is a photodynamic therapy, during which nanoparticles attached to targeted cells would act on cells when triggered to do so. For example, this could be used to destroy cancerous cells inside the tissue without cutting away “a pound of flesh” to achieve the excision.

## ***1.2 Need for simulation***

With modern chemistry, or patterning technologies, one can synthesize nanostructures with engineered structure and surface. One would like to know or model physical properties before beginning the tremendous and almost impossible task of experimentally trying and testing all possible structures. There is a definite need for simulation and modeling of physical properties in order to narrow down the list of potentially promising structures prior to any physical experimentation.

Calculation of optical properties is one of the critical aspects of modeling. Optical analysis affords insight into the electronic levels structure, which in turn is quite

important for acquiring an accurate knowledge about the likely optical and electronic properties of a material.

This dissertation describes the implementation of calculation of optical properties within the computational FIREBALL package. Calculation of a decent size quantum system cannot be exact and will always require inclusion of some approximations. The complexity of the calculation task rapidly increases with the increasing size of the system under investigation. Simulating nanosystems requires the ability to work with the systems with one hundred atoms or more.

### ***1.3 Tight-binding models***

The tight-binding model is an approximate method for determining the electronic structure of a system. Because most of tight-binding models are so loosely defined in terms of the fundamental theory, there is no unique tight-binding model. One common characteristic among all tight-binding models is that they all use the local orbital approach, meaning that only interactions with neighbors which are closer than a certain distance are taken into account.

One can define two general classes of tight-binding models: *semi-empirical* and *ab-initio*. While *ab-initio* models are based on a first principles approach, *semi-empirical* models use a set of parameters fitted to experimental data or first principle theory results.

The need to fit parameters within a *semi-empirical* model severely limits reliability, and restricts the results to a very specific case for which the parameters were fitted. Also, imposed parameters are typically not transferable between systems through the use of simple distance scaling [11].

## 1.4 FIREBALL

FIREBALL (“FB”) is a suite of programs designed to perform molecular dynamics calculations using the *ab initio* tight-binding model. The program can calculate a variety of characteristics including, but not limited to, structure (atomic positions), energy levels and charge distribution. The main parts of the FB suite are called CREATE and FIREBALL.

The program achieves great time performance due to its use of pre-calculated integrals. The part of the package called CREATE calculates all data files for a user-selected set of atoms. During the work of the FIREBALL part, it need only to assemble required integrals out of pre-calculated ones recorded in data files, interpolate, rotate as necessary and keep track of the various indexing.

FB is based on Sankey-Niklewski (SN) *ab-initio* formalism [11], with significant improvements such as going beyond the  $sp^2$  basis set of SN allowing for double-numeric basis sets with *d*-orbitals, and accommodating future provisions for *f*-orbitals. The atomic cores are represented by pseudopotentials. This means that we are working only with valence electrons, an approach which further improves time performance. FB operates with slightly excited atomic-like local orbitals because of the cut-offs [11, 12].

Note that our work with FB has been focused on developing the capacity to calculate optical properties within the package.

## 2 Theory

### 2.1 The full Hamiltonian

Speaking very generally, the Schrödinger equation we need to solve has the form

$$H\psi = E\psi . \quad (2.1)$$

For the general purpose of solid state application, we can define the Hamiltonian in the following terms:

$$H = T + V + V_{ee} , \quad (2.2)$$

where

$$T = \sum_{i=1}^N \left( -\frac{\sum \nabla_i^2}{2} \right) , \quad (2.3)$$

$$V = -\sum_{i=1}^N \sum_{\alpha} \frac{e^2 Z_{\alpha}}{r_{i\alpha}} , \quad (2.4)$$

$$V_{ee} = \sum_{i<j}^N \frac{e^2}{r_{ij}} . \quad (2.5)$$

The primary difficulty here is that this is a many-particle equation with all associated variables entangled. This equation is unsolvable for a general system. We must therefore resort to approximations.

### 2.2 The Born-Oppenheimer approximation

Our first step toward a solution is the Born-Oppenheimer approximation, because the mass of electrons is so much smaller than that of the nuclei, we can say that the

electrons respond instantaneously to changes in the positions of nuclei. As an approximation we can separate the electronic and nuclear degrees of freedom, while nuclei are in static, classical potential derived from the total energy of the electrons. It is then a good approximation to say that the electrons are always in their ground state, responding immediately to any changes of the nuclear positions. It further follows that evaluation of the energies involved in moving nuclei depend upon the solution of the electron problem. This is a good example of adiabatic approximation.

As an analogy, imagine a swarm of flies (representing electrons) that is steadily buzzing around a boat (representing atomic nuclei) that is slowly floating adrift in the middle of a lake. Imagine further an attempt to mathematically characterize the collective movement of the flies and the boat. Instead of attempting the difficult task of describing the flies and boat together, the analysis could be deconstructed into an examination of the boat separate from the flies. From the perspective of the tiny and fast-moving flies, the much larger boat is effectively stationary at any given moment. As a result, flies achieve their equilibrium positions very quickly, adjusting virtually instantaneously to every new position of the boat.

Carrying this “boat-fly Hamiltonian” analogy forward, we would separate “boat” terms and will need to solve “fly Hamiltonian” where “state of the boat” would only enter as a generator of a “fly potential” in which flies are moving. The assertion is that the process of flies achieving their equilibrium positions for a given “boat state” is instantaneous and does not affect the state of the boat. An approximation of this kind breaks down with respect to any non-adiabatic events like non-adiabatic electron jumps in chemical reactions or nonradiative transitions in solids. The latter breaks the

approximation because it involves phonons, and thus explicitly requires coupling between electrons and nuclei.

Note that the Born-Oppenheimer approximation does not prohibit electrons in excited states.

### ***2.3 Exchange and Correlation***

Electrons are charged particles. As such, they are constantly interacting with each other. Each electron repels others for two reasons. The first one is Coulomb. The second is exchange interaction due to the exclusion principle. Physically, both considerations arise from the same Coulomb potential. The presence of an electron in a particular locale depletes the probability of finding another electron within a certain vicinity of that same locale. The region defined by the depleted probability of an additional electron is called the exchange-correlation hole.

If we start thinking about electron-electron interactions, we would quickly realize that a given electron is interacting with all other electrons. Consequently, we should not be able to wholly describe electronic properties in terms of single electron states. Nevertheless, single-electron theories and models do exist and do yield reasonable results. The reason single-electron models works is because electrons are screening each other, so a given electron is predominantly influenced by a limited number of electrons in its immediate vicinity [13].

To summarize, the avoidance of other electrons due to Coulomb repulsion is known as correlation. The avoidance of other electrons due to exclusion is known as exchange.



## 2.4 Hartree

Even after the Born-Oppenheimer approximation is applied, the Schrödinger equation is a many-body problem and extremely difficult to solve.

The electronic problem is

$$H_{el} \Phi_n^{el}(\{\mathbf{R}\}, \{\mathbf{r}\}) = \epsilon_n(\{\mathbf{R}\}) \Phi_n^{el}(\{\mathbf{R}\}, \{\mathbf{r}\}), \quad (2.6)$$

where  $\{\mathbf{R}\}$  and  $\{\mathbf{r}\}$  are the nuclei and electron coordinates respectively, and the Hamiltonian of this electronic problem is

$$H_{el} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{2} \sum_{l,i} \frac{ze^2}{|\mathbf{r}_i - \mathbf{R}_l|}. \quad (2.7)$$

The first term of this latter equation is kinetic energy, the second term is electron-electron interaction and the third term is electron-ion Coulomb interaction.

The Schrödinger equation has  $3N$  degrees of freedom and a non-separable electronic part.

The electron-electron interaction, if approached directly, entails a computational burden that is often unacceptable from a practical standpoint. To resolve this, Hartree (1928) developed approximation replacing the true electron-electron interaction with an effective potential. In this approach, each electron moves in a field which is a superposition of the fields produced by all other electrons. In other words, electrons are moving in a mean field produced by the sum of all other electrons.

We are solving a set of single-particle equations

$$-\frac{\hbar^2}{2m} \nabla_i^2 \psi_i(\mathbf{r}_i) + U_i(\mathbf{r}_i) \psi_i(\mathbf{r}_i) = \varepsilon_i \psi_i(\mathbf{r}_i) \quad (2.8)$$

or

$$h_i \psi_i(\mathbf{r}_i) = \varepsilon_i \psi_i(\mathbf{r}_i), \quad (2.9)$$

which are N separated Schrödinger equations and the wavefunction is a simple product:

$$\Phi_n(\{\mathbf{R}\}, \{\mathbf{r}\}) = \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N). \quad (2.10)$$

The corresponding potential must be

$$U_i(\mathbf{r}_i) = \int d\mathbf{r}' \frac{e^2 n(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}'|}, \quad (2.11)$$

where  $n$  is the number density of electrons:

$$n(\mathbf{r}) = \sum_j |\psi_j(\mathbf{r})|^2. \quad (2.12)$$

The corresponding potential of electron-electron interaction then can be written as

$$U^{ee}(\{\mathbf{r}\}) = \sum_i \sum_{\substack{j \neq i \\ occ}} e^2 \int \frac{|\psi_j(\mathbf{r}_i)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}. \quad (2.13)$$

The Hamiltonian of full electronic problem is a sum of single-electron

Hamiltonians:

$$H^{el} = \sum_i h_i, \quad (2.14)$$

so the electronic problem turns into

$$\left( \sum_i h_i \right) \left[ \prod_i \psi_i(\mathbf{r}_i) \right] = \sum_i \varepsilon_i \left[ \prod_i \psi_i(\mathbf{r}_i) \right], \quad (2.15)$$

which is N separate and decoupled single-electron equations. The energy is a sum of one-electron energies:

$$E_{el} = \langle \psi | H | \psi \rangle = \langle \psi | \sum_i h_i | \psi \rangle = \sum_i \epsilon_i . \quad (2.16)$$

## 2.5 Hartree-Fock

The main fault of Hartree approximation is that it does not take the exclusion principle into account. Fock and Slater (1930) realized that if one renders the wavefunctions antisymmetric, the exclusion principle will be enforced. It is easy to see, that if we have an exchange operator X, then if we apply it twice, we should get back where we started, with maybe a sign change:

$$XX|\psi\rangle^2 = (\pm 1)|\psi\rangle^2 . \quad (2.17)$$

Positive eigenvalue would land us in Bose-Einstein statistics, while negative eigenvalue would lead to Fermi-Dirac.

The Fock and Slater approximation represents the wave function as an antisymmetrized product of one-particle wave functions:

$$\begin{aligned} \psi(r_1\sigma_1 \dots r_N\sigma_N) &= \frac{1}{\sqrt{N!}} \sum_s (-1)^s \psi_{s_1}(r_1\sigma_1) \dots \psi_{s_N}(r_1\sigma_1) \\ &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1\sigma_1) & \cdot & \cdot & \psi_1(r_N\sigma_N) \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \psi_N(r_1\sigma_1) & \cdot & \cdot & \psi_N(r_N\sigma_N) \end{vmatrix} \end{aligned} \quad (2.18)$$

This is called a Slater determinant. In this approximation all particles depend on each other in an antisymmetric way and thus enforce the Pauli principle. This makes the positions of electrons anticorrelated, meaning the acknowledged probability of finding an electron close to another electron is lowered.

If we employ variational principle we should end up with new  $h_i$  :

$$\varepsilon_i \psi_i = h_i^{prev} \psi_i + \sum_j^N \delta_{x_i x_j} \psi_j(\mathbf{r}) \int d\mathbf{r}_j \frac{e^2 \psi_j^*(\mathbf{r}) \psi_i(\mathbf{r})}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (2.19)$$

Overall this poses an  $N^4$  problem.

This integral (Fock term) is exact exchange energy assuming we have exact  $\psi_i$ .

### 2.5.1 Hartree-Fock for free electron gas

A free electron has a known wavefunction, represented by a plane wave:

$$h_i \psi_i \rightarrow \psi_i(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (2.20)$$

Each wave-vector less than  $k_F$  occurs twice (one for each spin orientation) in the Slater determinant. These wave functions give a solution to the H-F equation for free electrons.

The potential term due to ions is cancelled by the potential term from electrons:

$$U^{ion} + U^{el} = 0 \quad (2.21)$$

Only the exchange and kinetic energy terms survive, and they are easily evaluated by writing them in terms of their Fourier transforms:

$$\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \rightarrow 4\pi e^2 \frac{1}{V} \sum_q \frac{1}{q^2} e^{iq(\mathbf{r}_i - \mathbf{r}_j)} = 4\pi e^2 \int \frac{dq}{(2\pi)^3} \frac{1}{q^2} e^{iq(\mathbf{r}_i - \mathbf{r}_j)} \quad (2.22)$$

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m} - \int \frac{d^3 k'}{(2\pi)^3} \frac{4\pi e^2}{|k - k'|^2} = \frac{\hbar^2 k^2}{2m} - \frac{2e^2}{\pi} k_F F\left(\frac{k}{k_F}\right), \quad (2.23)$$

where

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right| \quad (2.24)$$

For  $k < k_F$ , sum is over all  $k$  (N electrons)

$$E_{tot} = N \left( \frac{3}{5} \varepsilon_F - \frac{3}{4} \frac{e^2 k_F}{\pi} \right) \quad (2.25)$$

or

$$\frac{E}{N} = \frac{e^2}{2a_0} \left[ \frac{3}{5} (k_F a_0)^2 - \frac{3}{2\pi} (k_F a_0) \right], \quad (2.26)$$

where  $a_0 = 0.529A$  is a Bohr radius. Using Fermi wave vector for free electrons:

$$k_F = (3\pi^2 n)^{1/3}, \quad (2.27)$$

where  $n$  is number density, one can easily see that energy can be written completely as a function of density.

## 2.6 Density functional theory (DFT)

Density functional theory asserts that electron density as a function of coordinates will contain all the information needed to solve the many-electron problem. This concept was observed and proved by Hohenberg and Kohn (1964). One can think of expressing every function (e.g. kinetic energy, ground-state energy and so on) as a function of the density function. Hence the name, density functional theory (DFT).

Thomas-Fermi (Dirac) theory, which precedes DFT, can only give total energy of the ground state. The significant break-through associated with DFT is two theorems proven by Hohenberg and Kohn which laid the theoretical justification for the density function as a state function. This sub-chapter is a result of compilation between [11, 12, 14] and some personal lecture notes.

### 2.6.1 *The first Hohenberg and Kohn theorem*

*“For a given electron density which is the density of the ground state for some system, there cannot be two different external potentials.”*

Put another way, since external potential uniquely defines the state of the system, every observable quantity of a (stationary) system is determined by ground-state density alone. By external potential in the context of the theorem, we mean everything but kinetic and electron-electron parts.

The forward proof – the dependence of density on the potential – is rather straightforward: wavefunction dependence on potential is explicit in equation (2.1) and dependence of density on the wavefunction is explicit from equation (2.12).

The proof for the other direction (that density uniquely defines potential) is a classical contradiction proof.

a) If two potentials,  $V_1$  and  $V_2$  are different by more than a constant, they will not produce the same wavefunction.

b) Two different *ground* states  $\Psi_1$  of  $H_1$  and  $\Psi_2$  of  $H_2$  cannot lead to the same density.

Let's assume that the *same* wavefunctions lead to different potentials. Then we can write

$$(T + V_{ee} + V_1)|\Psi_1\rangle = E_1|\Psi_1\rangle \quad (2.28)$$

$$(T + V_{ee} + V_2)|\Psi_2\rangle = E_2|\Psi_2\rangle. \quad (2.29)$$

Setting wavefunctions equal to each other we can write

$$(V_1 - V_2)|\Psi\rangle = (E_1 - E_2)|\Psi\rangle, \quad (2.30)$$

which leads to the conclusion that two potentials are different by no more than a constant, in direct contradiction of assumption (a). Thus the opposite is true and potentials different by a constant necessarily lead to the same wavefunction.

The second part of the relationship is based on the variational principle and the fact that we are working with ground state:

$$\begin{aligned} E_1 &= \langle \Psi_1 | H_1 | \Psi_1 \rangle < \langle \Psi_2 | H_1 | \Psi_2 \rangle = \langle \Psi_2 | H_2 + V_1 - V_2 | \Psi_2 \rangle = \\ &= E_2 + \int n_2(\vec{r}) [v_1(\vec{r}) - v_2(\vec{r})] d\vec{r} \end{aligned} \quad (2.31)$$

$$\begin{aligned} E_2 &= \langle \Psi_2 | H_2 | \Psi_2 \rangle < \langle \Psi_1 | H_2 | \Psi_1 \rangle = \langle \Psi_1 | H_1 + V_2 - V_1 | \Psi_1 \rangle = \\ &= E_1 + \int n_1(\vec{r}) [v_2(\vec{r}) - v_1(\vec{r})] d\vec{r} \end{aligned} \quad (2.32)$$

Now if we set two densities equal, it will lead to this:

$$E_1 + E_2 < E_1 + E_2, \quad (2.33)$$

which is an obvious contradiction.

Thus the first theorem proves uniqueness (up to a constant for potential) and bi-directionality with respect to the relationship between potential and density:

$$V \leftrightarrow \Psi \leftrightarrow n. \quad (2.34)$$

The ultimate consequence is an ability to write any observable system variable as a function of density alone instead of as a function of wavefunction.

### 2.6.2 The second theorem

*“Given an electron density, the energy is bound from below.”*

This means that an exact solution of the electronic part of the Hamiltonian yields the minimum energy. Any approximation will be approaching this exact energy as a limit from above. This theorem ensures that we can deploy variational methods and principles, leading to the Kohn-Sham equations.

### 2.6.3 The Kohn-Sham equations

*“The ground state density of the interacting particle system can be calculated as the ground state density of an auxiliary non-interacting system.”*

Basically, we are to solve the one-electron Hohenberg-Kohn-Sham equations in a self-consistent way [11]:

$$\left[ \frac{p^2}{2m} + \sum_l [V_{ion}(r - R_l) + V_{NL}(r - R_l)] + e^2 \int \frac{n(r')}{|r - r'|} d^3 r' + V_{XC}(n(r)) \right] \psi_i(r) = \epsilon_i \psi_i(r) \quad (2.35)$$

where  $V_{XC} = \left( \frac{d}{dn} \right) n \epsilon_{XC}(n)$  is the XC potential. Total energy can be written as

$$E_{tot} = 2 \sum_{iocc} \epsilon_i + \frac{e^2}{2} \left[ \sum_{ll'} \frac{Z_l Z_{l'}}{|R_l - R_{l'}|} - \int n(r) d^3 r \int \frac{n(r')}{|r - r'|} d^3 r' \right] + \int n(r) [\epsilon_{XC}(n) - V_{XC}(n)] d^3 r \quad (2.36)$$



Self-consistency is achieved when resulting density  $n_{out}(r) = \sum_{i-occ} \psi_i^*(r) \psi_i(r)$  is

essentially the same as the input one or within certain limits.

The only problem is that there is no exact form of  $V_{xc}$ . This is where we absolutely must go into approximation. There are a variety of different methods available. For example, local density approximation (LDA) deploys some functional form of  $V_{xc}$  as a function of density within a vicinity of a point, and generalized gradient approximation adds first order (and sometimes second order) gradients of a density to a functional form.

## 2.7 Time-dependent density functional theory (TDDFT)

Time dependent Hohenberg-Kohn-Sham formalism and its derivation is drastically more complicated than DFT. First formulated in 1984 by Runge and Gross, it is similar to the formalism of Hohenberg-Kohn-Sham except for the “little” change of a Schrödinger equation to a time-dependent one. The derivation or proof of TDDFT formalism will not be presented here. For full formalism and proof, the reader is referred to [15].

In simple terms, the aim of TDDFT (consistent with the aim of other theories for excited states) is to find energies of transitions. Assume a transition between two states, described by two wavefunctions  $\psi_i$  and  $\psi_a$ . During the transition, the current state of the system will be linear superposition of those two:

$$\psi(t) = c_1 \psi_i \exp(i\omega_i t) + c_2 \psi_a \exp(i\omega_a t). \quad (2.37)$$

Inspecting the density represented by this wavefunction, we will get

$$\rho(t) \propto |\psi|^2 = |c_1 \psi_i|^2 + |c_2 \psi_a|^2 + c_1^* c_2 \psi_i^* \psi_a \exp(i[\omega_i - \omega_a]t) + c.c. \quad (2.38)$$

The first two terms are constants, but the last terms represent “oscillating” density functional, which represents the transition.

The  $\psi_i^* \psi_a$  term represents an oscillating charge density. When we add electron-electron interactions to the excited states, we will encounter integrals of the form

$$\int \psi_i(\mathbf{r}) \psi_a(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}') \psi_a(\mathbf{r}'). \quad (2.39)$$

This “four-psi” type of integral presented in (2.39) is needed when one is utilizing TDDFT. This integral presents a great computational challenge, and a straight-forward approach to it is unreasonable due to time cost for a system of decent size.

## 2.8 First order and full TDDTF

For each of the transitions  $q \equiv i \rightarrow a$  and  $q' \equiv j \rightarrow b$  between initial states  $i$  ( $j$ ) and final states  $a$  ( $b$ ), we calculate a Hartree term:

$$\langle q | f_H | q' \rangle = \int d^3 r \int d^3 r' (\psi_i^*(\mathbf{r}) \psi_a(\mathbf{r}))^* \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_j^*(\mathbf{r}') \psi_b(\mathbf{r}') \quad (2.40)$$

and exchange-correlation term  $\langle q | f_{XC} | q' \rangle$  done with LDA, one-center integrals:

$$f_{XC} = \left[ \frac{d^2}{dn^2} n \mathcal{E}_{XC}(n) \right]_{n=n_0(\mathbf{r})} \quad (2.41)$$

$$\langle q | f_{XC} | q' \rangle = \int d^3 r (\psi_i^*(\mathbf{r}) \psi_a(\mathbf{r}))^* \left[ \frac{d^2}{dn^2} n \mathcal{E}_{XC}(n) \right]_{n=n_0(\mathbf{r})} (\psi_j^*(\mathbf{r}) \psi_b(\mathbf{r})). \quad (2.42)$$

Casida [16, 17] showed that energies and oscillator strengths could be obtained by solving

$$\Gamma\Psi = \omega^2\Psi, \quad (2.43)$$

where on-diagonal elements are:

$$\Gamma_{qq} = \left(E_q^{(0)}\right)^2 + 2E_q^{(0)}\left(\langle q|f_H|q\rangle + \langle q|f_{XC}|q\rangle\right) \quad (2.44)$$

and off-diagonal elements are:

$$\Gamma_{qq'} = 2\sqrt{E_q^{(0)}E_{q'}^{(0)}}\left(\langle q|f_H|q'\rangle + \langle q|f_{XC}|q'\rangle\right). \quad (2.45)$$

Here  $E_q^{(0)}$  denotes energy corresponding to transition  $q \equiv i \rightarrow a$  between two Kohn-Sham states  $i$  and  $a$ .

The eigenvalues are the squares of the corrected energies. If we just want a first order TDDFT (i.e. no coupling between transitions), than we can simply take

$$E^{(1)} = \left[\left(E_q^{(0)}\right)^2 + 2E_q^{(0)}\left(\langle q|f_H|q\rangle + \langle q|f_{XC}|q\rangle\right)\right]^{1/2} \quad (2.46)$$

as our corrected energies, which is essentially a square root of the diagonal elements of matrix  $\Gamma$  (2.44).

### 2.8.1 Oscillator strengths within TDDFT

We can calculate oscillator strengths by solving (2.43) for eigenvectors

$$\Psi_{q_{new}} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \dots \\ a_{N_a} \end{pmatrix}. \quad (2.47)$$

Then the corrected oscillator strengths are

$$f_{q_{new}} = \frac{2m}{\hbar} \left[ \left( \sum_{q=1}^{N_q} a_q^{q_{new}} x_q \sqrt{E_q^{(0)}} \right)^2 + \left( \sum_{q=1}^{N_q} a_q^{q_{new}} y_q \sqrt{E_q^{(0)}} \right)^2 + \left( \sum_{q=1}^{N_q} a_q^{q_{new}} z_q \sqrt{E_q^{(0)}} \right)^2 \right], \quad (2.48)$$

where

$$x_q = \langle i|x|a \rangle, \quad y_q = \langle i|y|a \rangle, \quad z_q = \langle i|z|a \rangle \quad (2.49)$$

## 2.9 Optical properties from energies and oscillator strengths

The dynamic polarizability [16, 17]:

$$\alpha(\omega) = \sum_i \frac{f_i}{\omega_i^2 - \omega^2 + i\eta\omega}, \quad (2.50)$$

where  $\eta$  is a broadening parameter. From this we can calculate the optical absorption

cross-section:

$$\sigma(\omega) = -\frac{4\pi\omega}{c} \text{Im} \alpha \quad (2.51)$$

## 3 Implementation

### 3.1 General considerations

The design feature of FIREBALL (“FB”) which makes it very fast is the pre-calculation of all tables of integrals that are used to assemble all necessary integrals during the FB calculation phase. For a given structure (or set of structures), there are only so many different types of atoms involved. Consider, for example, two-center integrals. For every different pair of types of atoms, we will pre-calculate given two-center integrals for all the distances from zero up to the sum of chosen cut-offs with a certain distance step. During this pre-calculation process, those atoms will be positioned a certain way (along the z-axis). A similar method is used with all other integrals. The results of the calculations of the integrals are then written into files collectively denoted as a “data set”. Only non-zero data is stored. Choices about the kind of atoms to work with, what orbitals those atoms will have etc., are done at the stage of creating a data set. The part of FB package which deals with data set creation is called CREATE. This is the part of the FB package that takes the longest to run, but the data sets produced after the CREATE step is completed can be used and re-used many times over.

The part of the FB package which deals with actual structure is likewise called FIREBALL, and it handles the final step of the computation. Again, returning to the example of two-center integrals, FIREBALL can determine the types, relative positions and distances of a pair of atoms in the structure. FIREBALL can then read appropriate data out of the data set, interpolate, and perform appropriate integral rotation.

The FB package works with real spherical harmonic functions; refer to the APPENDIX B for an overview of the relationships between FB functions and spherical harmonics.

### ***3.2 Optical absorption spectrum in zero order***

#### *3.2.1 Energies*

The Kohn-Sham energy levels are known from the ground state calculation within the FIREBALL. Taking all possible pairs of levels where one level is occupied and another is not, and then computing the difference yielded zero order (Kohn-Sham) transition energies.

#### *3.2.2 Oscillator strengths*

In zero order, the oscillator strengths are based on the dipole moments and thus simple

$$f_q = \frac{2m\omega_q}{\hbar} (x_q^2 + y_q^2 + z_q^2). \quad (3.1)$$

A lot of effort was required to program dipoles into the preexisting structure of FIREBALL. For further reference, see APPENDIX C, APPENDIX D and APPENDIX E.

### ***3.3 Implementation of first order and full TDDFT***

In FIREBALL, wavefunctions are a linear combination of atomic-like orbitals

$$\psi_i(\mathbf{r}) = \sum_{\alpha l} c_{\alpha l}^i \phi_{\alpha l}(\mathbf{r}) \quad (3.2)$$

and are represented by a set of coefficients  $c_{\alpha l}^i$ , where

$$c_{\alpha l}^i = \langle \varphi_{\alpha l}(\mathbf{r}) | \psi_i \rangle \quad (3.3)$$

$$\varphi_{\alpha l}(\mathbf{r}) = \varphi_l(\mathbf{r} - \mathbf{R}_\alpha), \quad (3.4)$$

and where  $\varphi$  is a rotated orbital in FIREBALL. Applying the aforementioned to (2.40),

we obtain a general representation in FIREBALL:

$$\begin{aligned} & \langle \psi_m(\mathbf{r}) \psi_n(\mathbf{r}) | \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} | \psi_p(\mathbf{r}') \psi_s(\mathbf{r}') \rangle = \\ & = \int d^2 r d^3 r' \sum_{\alpha \mu} c_{\alpha \mu}^m \varphi_{\alpha \mu}^*(\mathbf{r}) \sum_{\alpha' \mu'} c_{\alpha' \mu'}^n \varphi_{\alpha' \mu'}(\mathbf{r}) \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \times \\ & \quad \times \sum_{\alpha'' \mu''} c_{\alpha'' \mu''}^p \varphi_{\alpha'' \mu''}^*(\mathbf{r}') \sum_{\alpha''' \mu'''} c_{\alpha''' \mu'''}^s \varphi_{\alpha''' \mu'''}(\mathbf{r}') \\ & = \sum_{\alpha \mu} \sum_{\alpha' \mu'} \sum_{\alpha'' \mu''} \sum_{\alpha''' \mu'''} c_{\alpha \mu}^m c_{\alpha' \mu'}^n c_{\alpha'' \mu''}^p c_{\alpha''' \mu'''}^s \times \\ & \quad \times \int d^2 r d^3 r' \varphi_{\alpha \mu}^*(\mathbf{r}) \varphi_{\alpha' \mu'}(\mathbf{r}) \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \varphi_{\alpha'' \mu''}^*(\mathbf{r}') \varphi_{\alpha''' \mu'''}(\mathbf{r}') \end{aligned} \quad (3.5)$$

Adding the rotations from the CREATE coordinates to the “molecular”

coordinates in FIREBALL represented by coefficients  $a$  the above equation becomes

$$\begin{aligned} & \langle \psi_m(\mathbf{r}) \psi_n(\mathbf{r}) | \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} | \psi_p(\mathbf{r}') \psi_s(\mathbf{r}') \rangle = \\ & \sum_{\alpha \mu} \sum_{\alpha' \mu'} \sum_{\alpha'' \mu''} \sum_{\alpha''' \mu'''} c_{\alpha \mu}^m c_{\alpha' \mu'}^n c_{\alpha'' \mu''}^p c_{\alpha''' \mu'''}^s \times \\ & \quad \times \sum_u a_{\mu u} \sum_{u'} a_{\mu' u'} \sum_{u''} a_{\mu'' u''} \sum_{u'''} a_{\mu''' u'''} \times \\ & \quad \times h_{\alpha u, \alpha' u', \alpha'' u'', \alpha''' u'''} \end{aligned} \quad (3.6)$$

where  $h_{\alpha u, \alpha' u', \alpha'' u'', \alpha''' u'''}$  is a pre-calculated Hartree term.

CREATE calculates  $f_{XC}$  integrals for the neutral atoms. However, in FIREBALL we do have a charge transfer  $\Delta q_s \equiv q_s - q_{s0}$  representing a charge change in each shell (s,p,d). To calculate XC, we expand  $f_{XC}$  from (2.41) in power series:

$$f_{XC} \approx f_{XC}|_{q_0} + \sum_{shells\ s} \Delta q_s \frac{\partial f_{XC}}{\partial q_s} + \dots \quad (3.7)$$

Then (2.42) in FIREBALL terms:

$$\begin{aligned} & \sum_{atoms} \sum_{orb} \sum_{on\ at\ orb} \sum_{on\ at\ orb} \sum_{on\ at} c_1^* c_2^* c_3^* c_4 (v_{XC4}(1234) + \\ & + \sum_{shells\ s} [\Delta q_s \times (dv)_{XC4}^{(s)}(1234)] + \dots) \end{aligned} \quad (3.8)$$

where

$$\begin{aligned} v_{XC4}(1234) &= \int d^3 r \varphi_1(\vec{r}) \varphi_2(\vec{r}) \varphi_3(\vec{r}) \varphi_4(\vec{r}) v_{XC} [\rho_{in}(\vec{r})]^2 = \\ &= \int d^3 r \varphi_1(\vec{r}) \varphi_2(\vec{r}) \varphi_3(\vec{r}) \varphi_4(\vec{r}) f_{XC}(\vec{r})|_{q_0} \end{aligned} \quad (3.9)$$

$$\begin{aligned} (dv)_{XC4}^{(s)}(1234) &= \frac{1}{2\Delta q_s} \int (d^3 r \varphi_1(\vec{r}) \varphi_2(\vec{r}) \varphi_3(\vec{r}) \varphi_4(\vec{r}) \times \\ & \times [f_{XC}(\vec{r})|_{q=q_0+\delta q_s} - f_{XC}(\vec{r})|_{q=q_0-\delta q_s}]) \end{aligned} \quad (3.10)$$

We drop derivatives that are higher than the first one, due to computational instabilities.

Full TDDFT, which accounts for transitions coupling, operates in the following way. The transition matrix  $\Gamma$  with dimensions  $N_{transitions} \times N_{transitions}$  can be huge, unwieldy, and impractical to deal with. We addressed this challenge by choosing a smaller set of sub-matrices positioned on the main diagonal of the original matrix. Members of each sub-matrix are transitions that are separated from each other by no more than a user-defined value. The assertion here is that only transitions of sufficient



proximity will couple with each other effectively. Proceeding on this basis, we then fill those sub-matrices according to (2.44) and (2.45) and diagonalize them. First order approximation simply does not compute and fill off-diagonal elements and thus does not couple transitions.

### 3.4 Density projection approximation

So far we have not described the approximations we used for calculation of the four-integrals  $\langle q | f_H | q \rangle$ . Using (3.6) in its full form would impose unreasonable time demands for very large systems: sum over  $c$ 's represent  $N^4$  calculations for each of the  $\sim N^2$  transitions. And this is just the first order! At this juncture, therefore, we explain our approximation to maximize the speed of TDDFT calculation.

We project  $(\psi_i^*(r)\psi_a(r))$  not onto  $\{\varphi_\mu^*(r)\varphi_\nu(r)\}$  but rather on  $\{|\varphi_\mu(r)|^2\}$ , using a Mulliken charge-like projection [18]. For each transition we pre-calculate the projection coefficients  $\gamma_\mu^{ia}$  which we call gamma charges:

$$\gamma_\mu^{ia} = \sum_\nu \frac{1}{2} (c_\mu^{i*} c_\nu^a S_{\mu\nu} + c_\nu^{i*} c_\mu^a S_{\mu\nu}). \quad (3.11)$$

Here,  $S_{\mu\nu}$  stands for an overlap between two corresponding orbitals. One way to think about this approximation is that one-half of a true bond charge between two orbitals is being assigned to the “left” atom and another half of a bond charge is being assigned to the “right” atom.

With this approximation, our four-integrals become

$$\begin{aligned}
& \int d^3 r \int d^3 r' (\psi_i^*(\mathbf{r}) \psi_a(\mathbf{r}))^* \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_j^*(\mathbf{r}') \psi_b(\mathbf{r}') \approx \\
& \sum_{\mu} \sum_{\nu} \gamma_{\mu}^{ia} \gamma_{\nu}^{jb} \int d^3 r \int d^3 r' |\varphi_{\mu}(\mathbf{r})|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\varphi_{\nu}(\mathbf{r}')|^2
\end{aligned} \tag{3.12}$$

Here we do not explicitly show the approximation in FIREBALL terms, so as to avoid unnecessary clutter.

Out of all possible classes of four-integrals we are choosing the biggest contribution: one and two center ones, where “left” and “right” functions are residing on no more than two separate atoms.

Within gamma-charges approximation, the loop to compute  $\langle q | f_H | q' \rangle$  is simply this:

```

for all atoms K
  for orbitals  $\mu$  on atom K
    for all atoms L
      for orbitals  $\nu$  on atom L
         $I = I + \gamma_{\mu}^{ia} \gamma_{\nu}^{jb} I_{no-overlap}(\mu\mu | \nu\nu)$ 
      end for
    end for
  end for
end for
end for

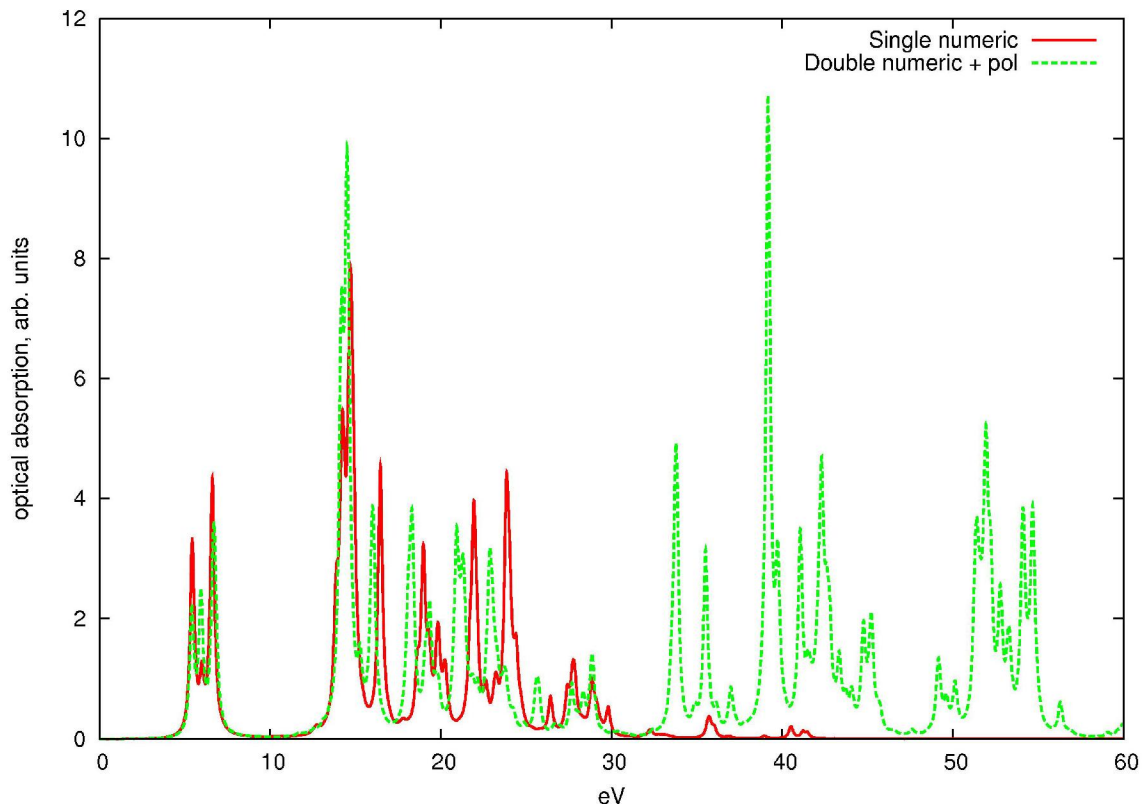
```

Here  $I_{no-overlap}(\mu\mu | \nu\nu)$  is already rotated integral. This loop structure is by far faster than the full loop structure in (3.6).

## 4 Results and discussion

We have calculated the optical absorption of benzene ( $C_6H_6$ ) and  $C_{60}$ . Two different orbital data sets were used for calculation: single numeric (SN) and double numeric with polarization (DNP). The single numeric set consists of the following orbitals (element(orbitals)): H(s), C(s, p). The double numeric with polarization (DNP) set consists of: H(s, s<sup>\*</sup>), C(s, s<sup>\*</sup>, p, p<sup>\*</sup>, d). Both structures were first relaxed down to an average kinetic energy below 5K using the DNP data set. After that, the optical branch of FIREBALL was turned on. The resulting discrete set of oscillator strength vs. energy  $f_q(E_q)$  was then used to calculate optical absorption  $\sigma(\omega)$  in accordance with (2.50) and (2.51). A broadening parameter  $\eta = 0.30 eV$  was employed, which is close to the broadening utilized in experimental optical absorption.

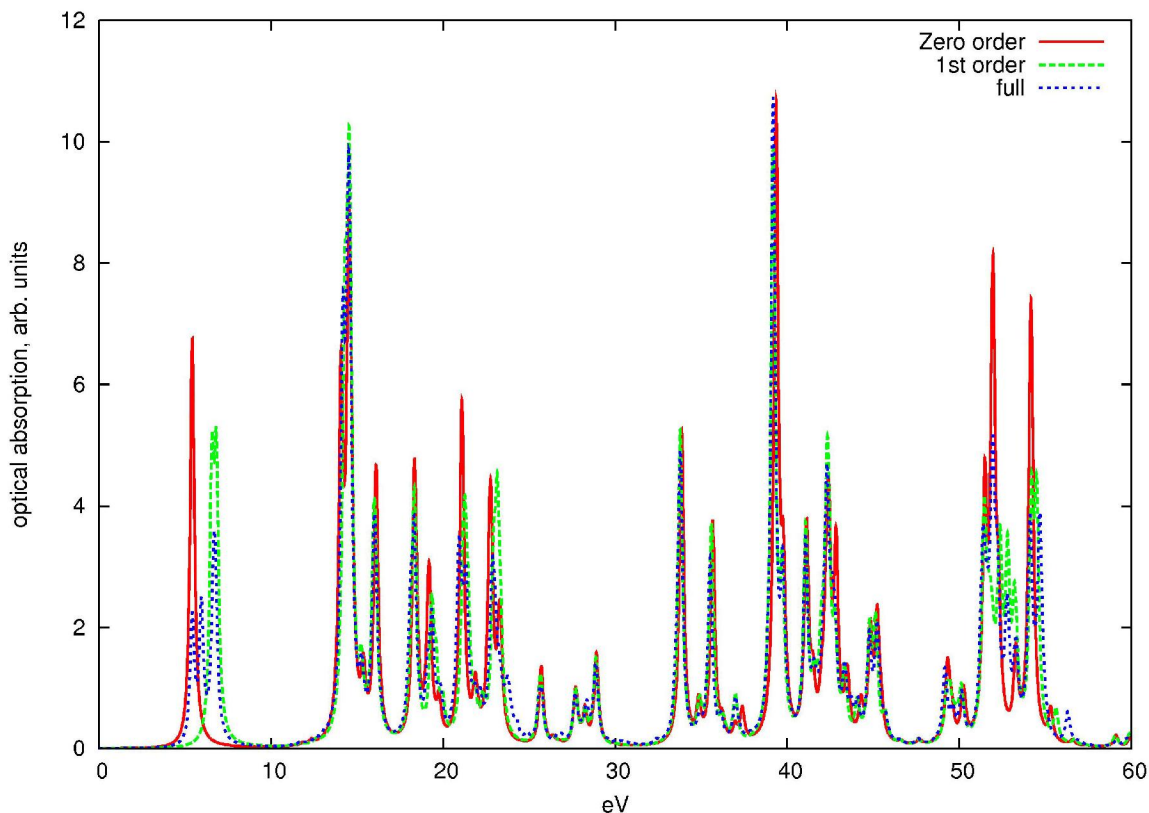
## 4.1 Benzene



**Figure 4.1** Optical absorption of benzene, full TDDFT, comparing two data sets

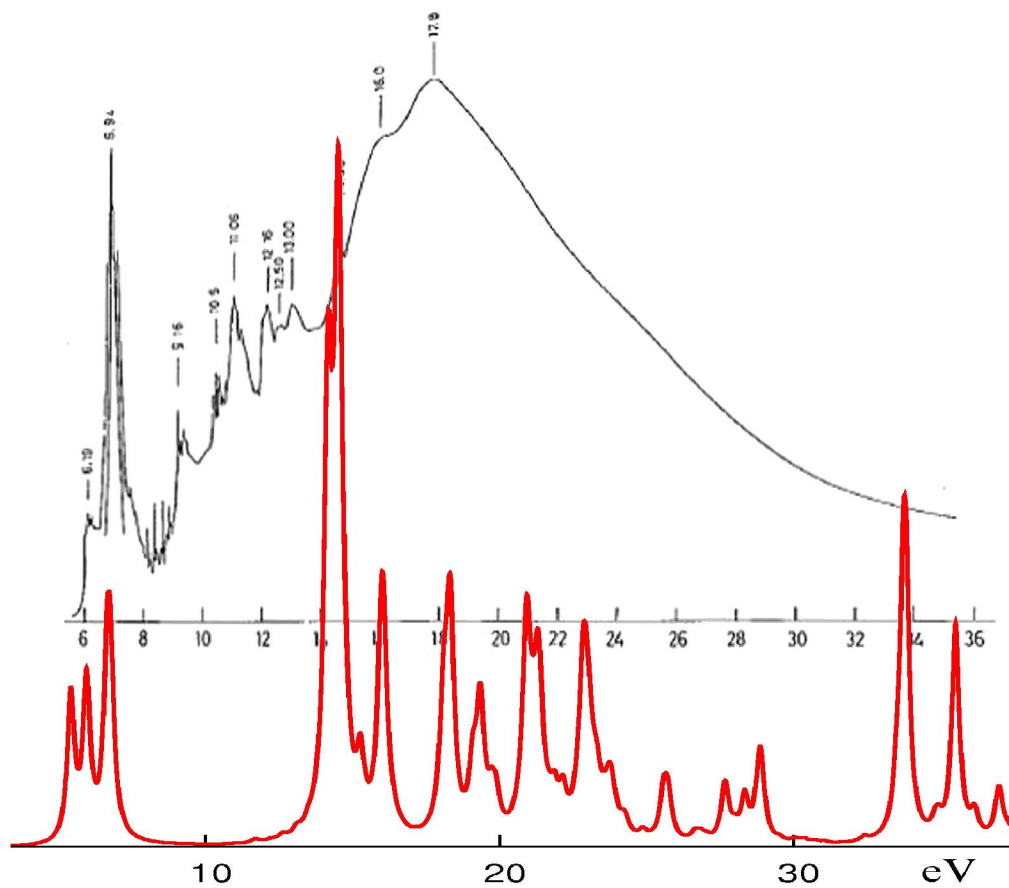
Figure 4.1 demonstrates the importance of the data set choice. Restricting amount, types of orbitals and empty orbitals makes calculation faster, but having too small data set could lead a researcher to miss important transitions. Transition oversights would occur due to the fact that the participating orbitals are not in the data set. In addition, it is apparent that transition coupling strongly affects the lowest transitions.

Figure 4.2 takes a DNP data set and examines three approximations: zero order (which is based on Kohn-Sham states), first order TDDFT (no coupling between transitions) and full TDDFT. Clearly, all three approximations agree pretty well, except for the transitions below 10 eV.



**Figure 4.2 Optical absorption of benzene, DNP data set, TDDFT, comparing different approximations**

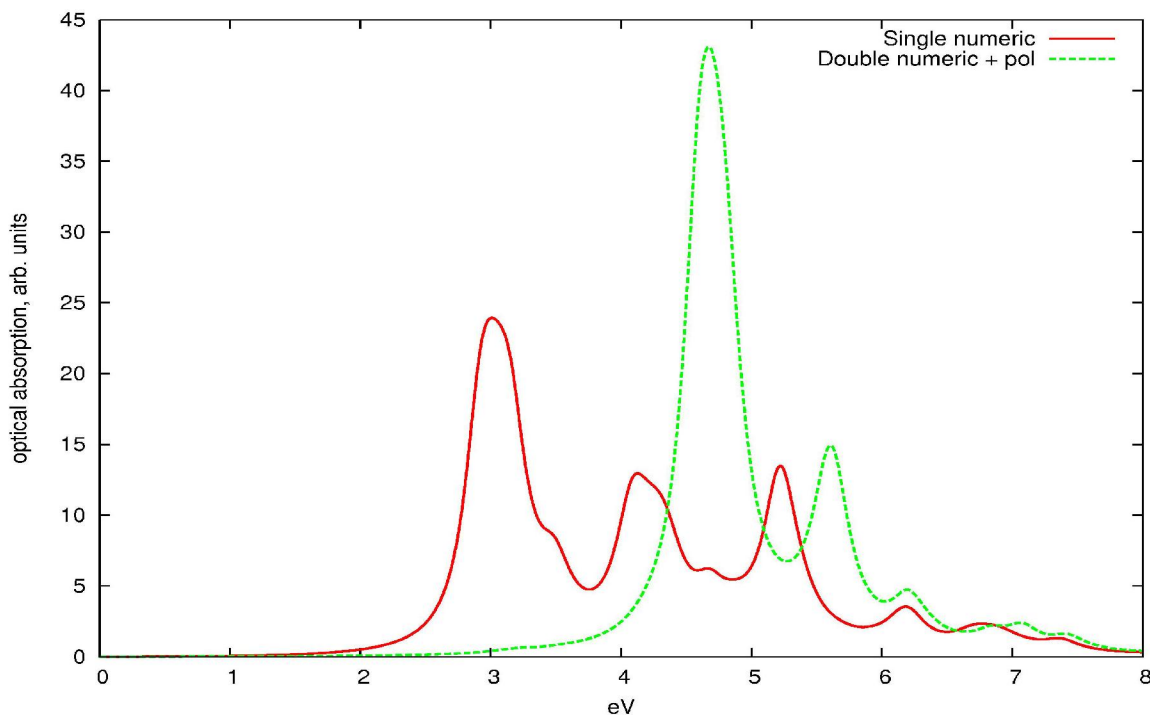
The comparison with experiment (Fig. 4.3) shows very good agreement for energies and good agreement for oscillator strengths. Experiment [19] shows a strong excitation at 6.9 eV and broad continuum-like absorption with a maximum at about 17.8 eV. Superimposing our computational result made with full TDDFT+DNP, and experimental data, one can clearly see common features like a triple peak in the lowest energy transitions. One may also notice the experimental peaks at around 10 eV are missing from our calculation. We speculate that the peak discrepancies resulted from a data set that was not sufficiently large.



**Figure 4.3 Benzene absorption spectra, full TDDFT+DNP (below) superimposed with experimental [19] (above)**

## 4.2 $C_{60}$

The calculations of  $C_{60}$  were performed similar to benzene, but with addition of a block parameter of 0.2 eV. As a reminder, a given block includes a sequence of transitions which are separated by each other by no more than a given block parameter.



**Figure 4.4 Optical absorption of  $C_{60}$ , upper limit 7.5 eV, full TDDFT, comparing data sets**

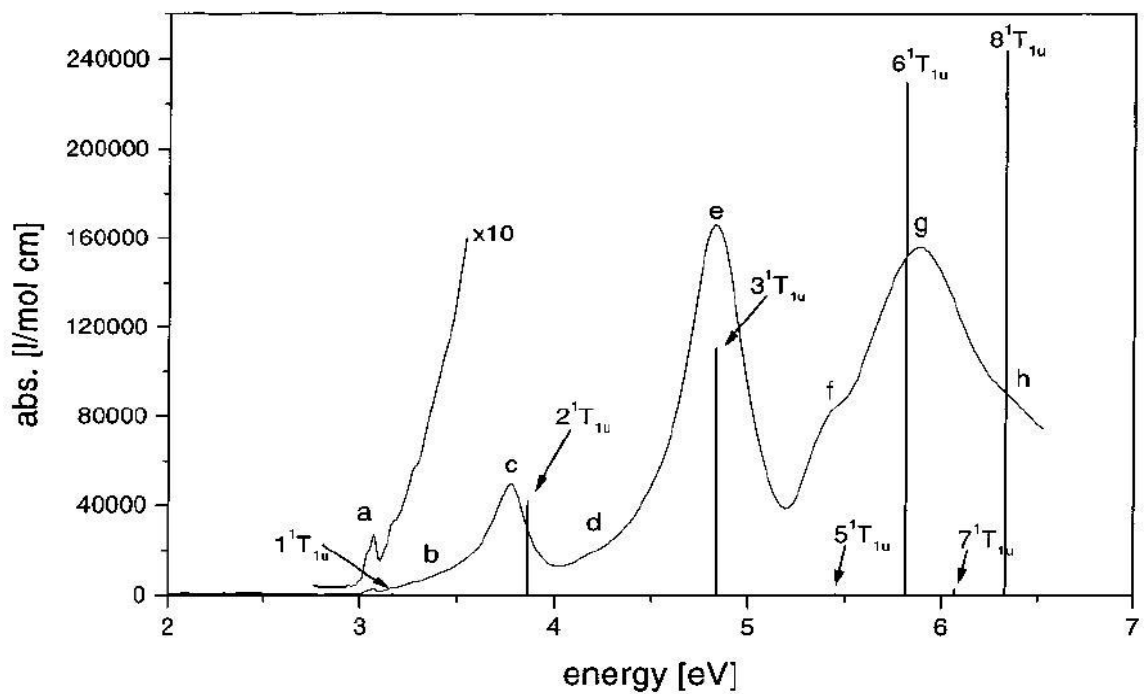
Let's do some comparison with the experimental data presented in Fig. 4.5.

Experimentally, the lowest energy peaks are at about 3.8, 4.8, 5.4 and 5.9 eV. [20].

Calculations with SN data set yield peaks at about 3.0, 3.5, 4.2, 4.8, 5.2, 5.5 and 6.2 eV.

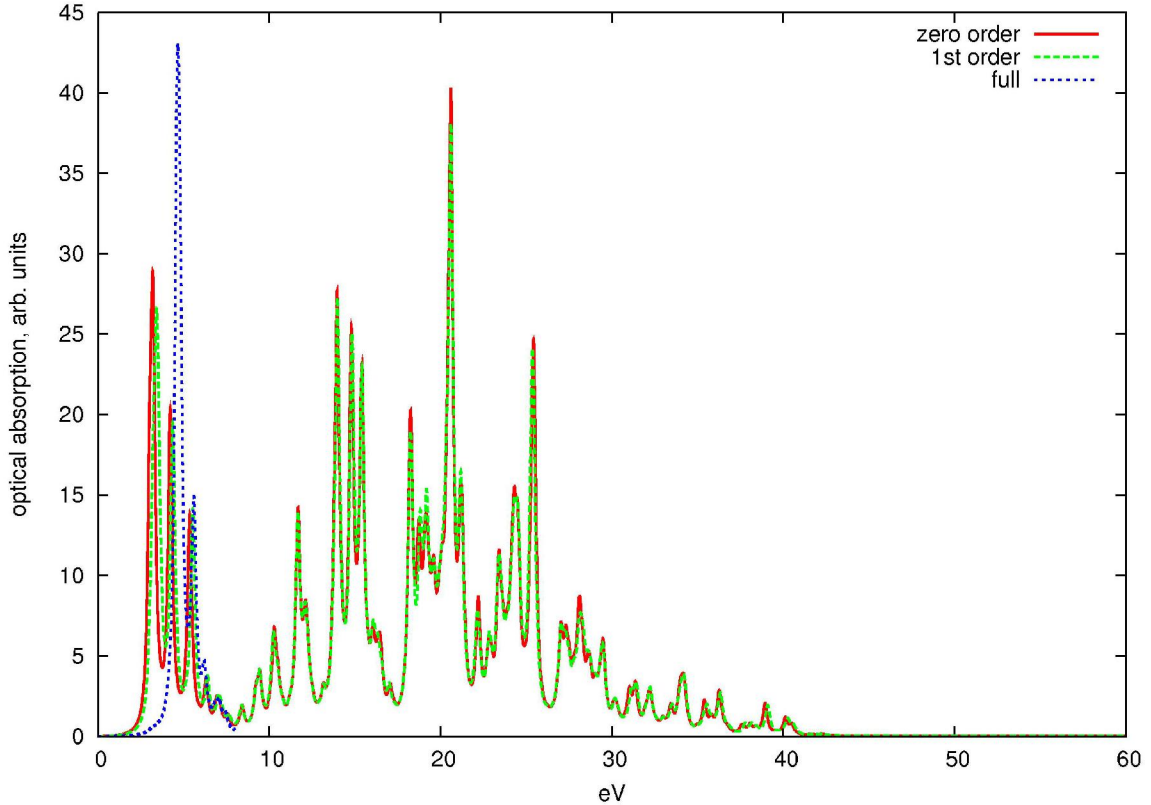
The DNP data set shows peaks at about 3.2 (small), 4.8, 5.6 and 6.2 eV. The DNP data set shows better energy matching and the comparison reflects the importance of transition coupling for the lowest transitions. A block parameter set to 0.2 eV resulted in blocks of about 1.5 to 2.0 eV size.

A trade-off between accuracy and speed is in play here. Setting the block parameter to a big value and opening the resulting matrix of transitions coupling to a full size (and thus taking into account more coupling effects) would make the calculation too long. On the other hand, setting block parameter to a value too small gives results close to the first order TDDFT.



**Figure 4.5** Absorption spectrum of C<sub>60</sub> (I<sub>h</sub>) in *n*-hexane solution at room temperature. Superimposed are TDDFT calculations of optically allowed transition energies corrected for systematic errors by adding 0.35 eV. Oscillator strengths were normalized to experiment. [20]

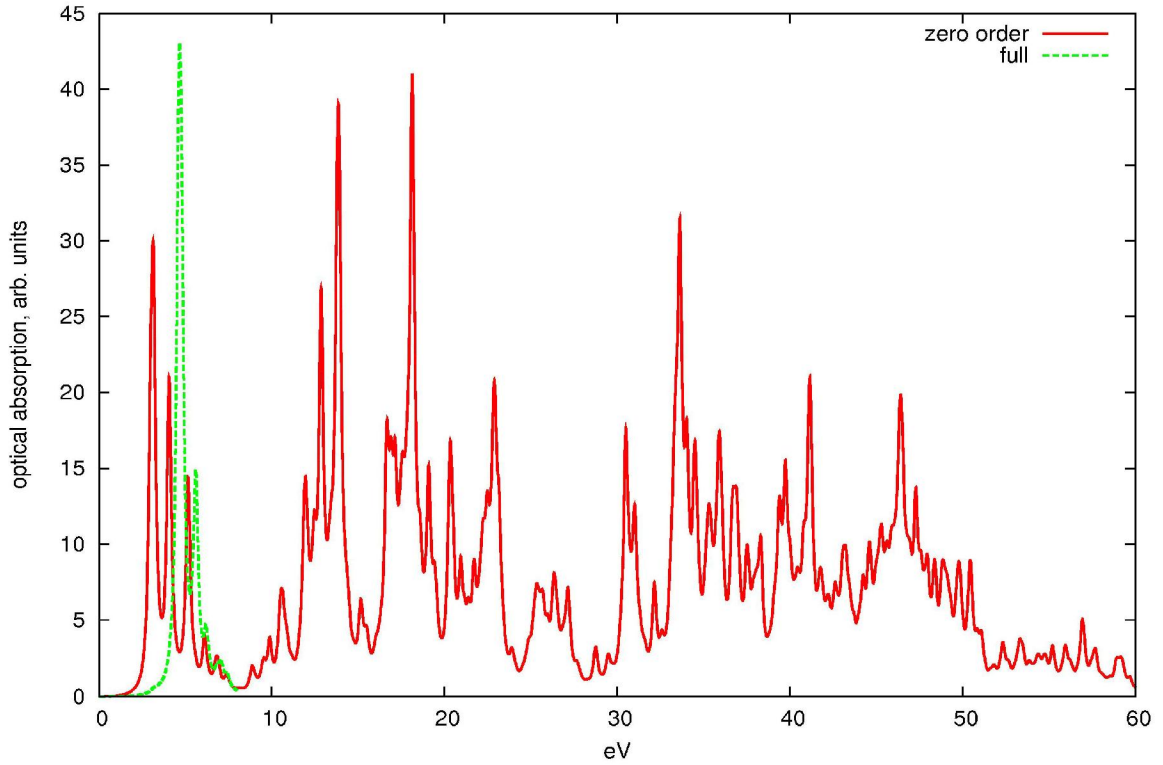




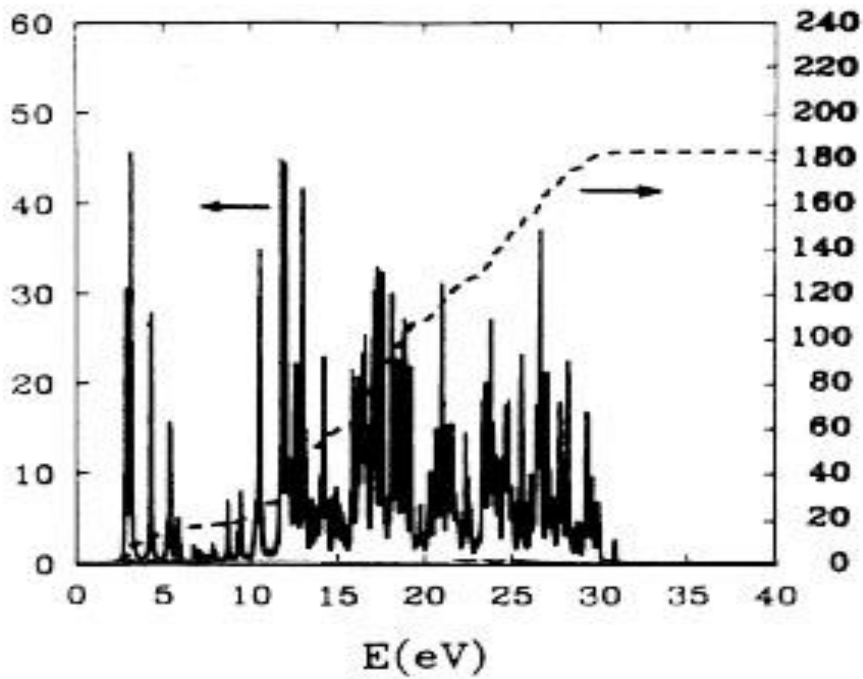
**Figure 4.6** Optical absorption of  $C_{60}$ , single numeric data set, TDDFT, comparing approximations, full TDDFT limited to 7.5 eV

When comparing Fig. 4.6, Fig. 4.7 from FIREBALL and Fig. 4.8 calculated with another semi-empirical theory [21], one notices a lot of similarities for both low and high energies. Both methods yield a low-energy triple peak, as well as similar peaks and peaks groups for the high energy range. This demonstrates that FIREBALL results agree with other computational works.

Note that application of full TDDFT, even with the block parameter, had an effect of collecting low energy peaks into a fewer peaks. If we had the ability to diagonalize the full transition matrix, we should likely have arrived at results similar to Fig. 4.9 [21], which shows the formation of a collective plasmon oscillation in the region of 20-30 eV.



**Figure 4.7** Optical absorption of  $C_{60}$ , double numeric with polarization data set, comparing approximations. Full TDDFT is limited to the range of 0 to 7.5 eV.



**Figure 4.8** Free response of  $C_{60}$  corresponding to Kohn-Sham levels, [21]

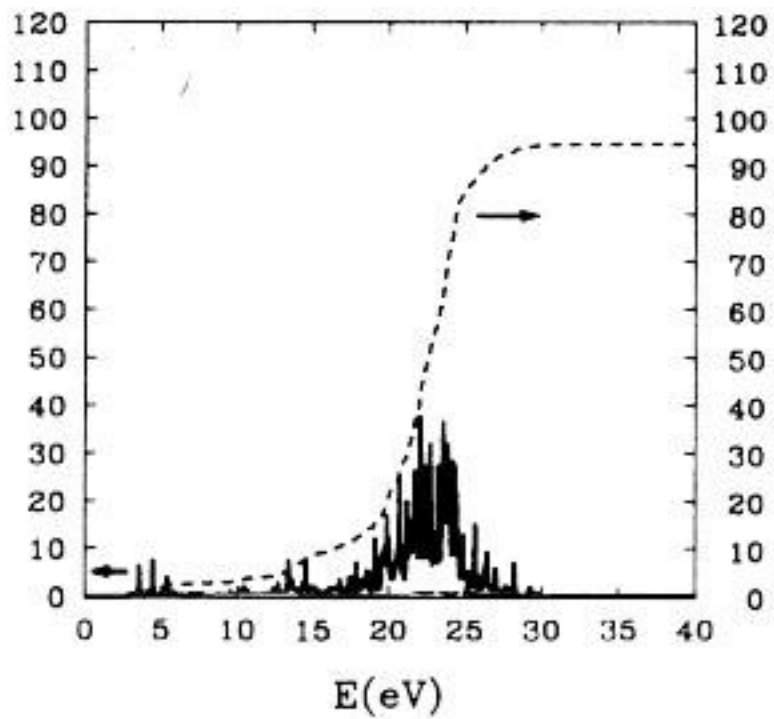


Figure 4.9 RPA response of C<sub>60</sub> [21]

## 5 Conclusion and future work

We have successfully implemented calculation of optical properties by using TDDFT into the FIREBALL suite. The approach implemented in FIREBALL suite is general enough to work with any structure. We have successfully used FIREBALL to calculate optical absorption of  $C_6H_6$  and  $C_{60}$ . Those results show that the approximations used to achieve faster calculations still produce good results and match quite well to the experimental data, at least for the low-energy transitions.

From the standpoint of software engineering, FIREBALL would greatly benefit from a systematic approach and careful review. Object-oriented programming would represent a positive improvement, although re-writing FIREBALL package would admittedly be a major undertaking.

A capability to more effectively extract eigenvalues and eigenvectors from huge matrices is clearly needed. Currently we are using the “dsyev” diagonalization procedure from a LAPACK fortran library to diagonalize the matrices and extract eigenvalues and eigenvectors needed for optical calculations. In the future, we hope to utilize more effective algorithms, like the Lanczos or Davidson-Liu methods [22, 23].

Another important avenue for progress in the future will be programming truly parallel computation of transition matrix routine. This portion of the calculation is by far the most time-consuming. Elements of this matrix are calculated by the same routine and are independent of each other, and therefore could benefit from parallel computing.

We did not calculate optical properties of nanoclusters or other large structures, as our focus was on the development of FIREBALL’s optical calculation branch. However,

it is completely feasible from a time standpoint to run a structure with a size on the order of 1000 atoms in the zero and first TDDFT orders. With future implementation of a better “eigensolver” it should be possible to run full TDDFT as well, at least for selected eigenvalues.

## 6 APPENDICES

### 6.1 APPENDIX A TABLE OF $Y_L^M$

$$L = 0 \quad Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

$$Y_1^{-1} = \sqrt{\frac{3}{8\pi}} \sin(\Theta) e^{-i\varphi}$$

$$L = 1 \quad Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos(\Theta)$$

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}} \sin(\Theta) e^{i\varphi}$$

$$Y_2^{-2} = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2(\Theta) e^{-2i\varphi}$$

$$Y_2^{-1} = \sqrt{\frac{15}{8\pi}} \sin(\Theta) \cos(\Theta) e^{-i\varphi}$$

$$L = 2 \quad Y_2^0 = \sqrt{\frac{5}{4\pi}} \left( \frac{3}{2} \cos^2(\Theta) - \frac{1}{2} \right)$$

$$Y_2^1 = -\sqrt{\frac{15}{8\pi}} \sin(\Theta) \cos(\Theta) e^{i\varphi}$$

$$Y_2^2 = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2(\Theta) e^{2i\varphi}$$

$$\begin{aligned}
Y_3^{-3} &= \frac{1}{4} \sqrt{\frac{35}{4\pi}} \sin^3(\Theta) e^{-3i\varphi} \\
Y_3^{-2} &= \frac{1}{4} \sqrt{\frac{105}{2\pi}} \sin^2(\Theta) \cos(\Theta) e^{-2i\varphi} \\
Y_3^{-1} &= \frac{1}{4} \sqrt{\frac{21}{4\pi}} \sin(\Theta) (5 \cos^2(\Theta) - 1) e^{-i\varphi} \\
L = 3 \quad Y_3^0 &= \sqrt{\frac{7}{4\pi}} \left( \frac{5}{2} \cos^2(\Theta) - \frac{3}{2} \cos(\Theta) \right) \\
Y_3^1 &= -\frac{1}{4} \sqrt{\frac{21}{4\pi}} \sin(\Theta) (5 \cos^2(\Theta) - 1) e^{i\varphi} \\
Y_3^2 &= \frac{1}{4} \sqrt{\frac{105}{2\pi}} \sin^2(\Theta) \cos(\Theta) e^{2i\varphi} \\
Y_3^3 &= -\frac{1}{4} \sqrt{\frac{35}{4\pi}} \sin^3(\Theta) e^{3i\varphi}
\end{aligned}$$

## 6.2 APPENDIX B FIREBALL Functions as $Y_L^M$

### 6.2.1 Definitions of FB orbitals

Below we identify all of our functions along with their exact mathematical meaning:

S-Orbital:

$$[1] = \sqrt{\frac{1}{4\pi}}$$

P-Orbitals:

$$[y] = y \frac{1}{r} \sqrt{\frac{3}{4\pi}}$$

$$[z] = z \frac{1}{r} \sqrt{\frac{3}{4\pi}}$$

$$[x] = x \frac{1}{r} \sqrt{\frac{3}{4\pi}}$$

D-Orbitals:

$$[xy] = xy \frac{1}{r^2} \sqrt{\frac{15}{4\pi}}$$

$$[zy] = zy \frac{1}{r^2} \sqrt{\frac{15}{4\pi}}$$

$$[zz] = \frac{3z^2 - r^2}{\sqrt{12}} \frac{1}{r^2} \sqrt{\frac{15}{4\pi}}$$

$$[zx] = zx \frac{1}{r^2} \sqrt{\frac{15}{4\pi}}$$

$$[x^2 - y^2] = \frac{x^2 - y^2}{2} \frac{1}{r^2} \sqrt{\frac{15}{4\pi}}$$

### 6.2.2 Derivations of relationships

We first represent each of the functions as a combination of  $Y_l^m$  's using

$$x = r \sin(\Theta) \cos(\varphi)$$

$$y = r \sin(\Theta) \sin(\varphi)$$

$$z = r \cos(\Theta)$$



$$[1] = \sqrt{\frac{1}{4\pi}} = Y_0^0$$

$$\begin{aligned} [y] &= y \frac{1}{r} \sqrt{\frac{3}{4\pi}} = \frac{1}{r} \sqrt{\frac{3}{4\pi}} r \sin(\Theta) \sin(\varphi) = \frac{1}{2i} \sqrt{\frac{3}{4\pi}} \sin(\Theta) (e^{i\varphi} - e^{-i\varphi}) \\ &= \frac{\sqrt{2}}{2i} \sqrt{\frac{3}{8\pi}} \sin(\Theta) (e^{i\varphi} - e^{-i\varphi}) = \frac{i}{\sqrt{2}} \sqrt{\frac{3}{8\pi}} \sin(\Theta) (-e^{i\varphi} + e^{-i\varphi}) \\ &= \frac{i}{\sqrt{2}} (Y_1^1 + Y_1^{-1}) = \frac{1}{\sqrt{2}} (iY_1^{-1} + iY_1^1) \end{aligned}$$

$$[z] = z \frac{1}{r} \sqrt{\frac{3}{4\pi}} = \frac{1}{r} \sqrt{\frac{3}{4\pi}} r \cos(\Theta) = Y_1^0 = \frac{1}{\sqrt{2}} (\sqrt{2}Y_1^0)$$

$$\begin{aligned} [x] &= x \frac{1}{r} \sqrt{\frac{3}{4\pi}} = \frac{1}{r} \sqrt{\frac{3}{4\pi}} r \sin(\Theta) \cos(\varphi) = \frac{1}{2} \sqrt{\frac{3}{4\pi}} \sin(\Theta) (e^{i\varphi} + e^{-i\varphi}) \\ &= \frac{\sqrt{2}}{2} \sqrt{\frac{3}{8\pi}} \sin(\Theta) (e^{i\varphi} + e^{-i\varphi}) = -\frac{1}{\sqrt{2}} \sqrt{\frac{3}{8\pi}} \sin(\Theta) (-e^{i\varphi} - e^{-i\varphi}) \\ &= -\frac{1}{\sqrt{2}} (Y_1^1 - Y_1^{-1}) = \frac{1}{\sqrt{2}} (Y_1^{-1} - Y_1^1) \end{aligned}$$

$$\begin{aligned} [zx] &= \frac{1}{r^2} \sqrt{\frac{15}{4\pi}} r^2 \cos(\Theta) \sin(\Theta) \cos(\varphi) = \frac{1}{2} \sqrt{\frac{15}{4\pi}} \cos(\Theta) \sin(\Theta) (e^{i\varphi} + e^{-i\varphi}) \\ &= -\frac{\sqrt{2}}{2} \left( -\sqrt{\frac{15}{8\pi}} \right) \sin(\Theta) \cos(\Theta) (e^{i\varphi} + e^{-i\varphi}) \\ &= -\frac{1}{\sqrt{2}} (Y_2^1 - Y_2^{-1}) \end{aligned}$$

$$\begin{aligned}
[x^2 - y^2] &= \frac{1}{2} \frac{1}{r^2} \sqrt{\frac{15}{4\pi}} \left\{ (r \sin(\Theta) \cos(\varphi))^2 - (r \sin(\Theta) \sin(\varphi))^2 \right\} \\
&= \frac{1}{2} \frac{1}{r^2} \sqrt{\frac{15}{4\pi}} r^2 \sin^2(\Theta) (\cos^2(\varphi) - \sin^2(\varphi)) \\
&= \frac{1}{2} \sqrt{\frac{15}{4\pi}} \sin^2(\Theta) \cos(2\varphi) = \frac{1}{4} \sqrt{\frac{15}{4\pi}} \sin^2(\Theta) (e^{2i\varphi} + e^{-2i\varphi}) \\
&= \frac{1}{\sqrt{2}} \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2(\Theta) (e^{2i\varphi} + e^{-2i\varphi}) \\
&= \frac{1}{\sqrt{2}} (Y_2^2 + Y_2^{-2})
\end{aligned}$$

$$\begin{aligned}
[xy] &= \frac{1}{r^2} \sqrt{\frac{15}{4\pi}} r^2 \sin^2(\Theta) \cos(\varphi) \sin(\varphi) = \frac{1}{2} \sqrt{\frac{15}{4\pi}} \sin^2(\Theta) \sin(2\varphi) \\
&= \frac{1}{4i} \sqrt{\frac{15}{4\pi}} \sin^2(\Theta) (e^{2i\varphi} - e^{-2i\varphi}) = \frac{1}{i\sqrt{2}} \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2(\Theta) (e^{2i\varphi} - e^{-2i\varphi}) \\
&= \frac{1}{i\sqrt{2}} (Y_2^2 - Y_2^{-2})
\end{aligned}$$

$$\begin{aligned}
[zy] &= \frac{1}{r^2} \sqrt{\frac{15}{4\pi}} r^2 \cos(\Theta) \sin(\Theta) \sin(\varphi) = \frac{1}{2i} \sqrt{\frac{15}{4\pi}} \cos(\Theta) \sin(\Theta) (e^{i\varphi} - e^{-i\varphi}) \\
&= -\frac{\sqrt{2}}{2i} \left\{ -\sqrt{\frac{15}{8\pi}} \cos(\Theta) \sin(\Theta) (e^{i\varphi} - e^{-i\varphi}) \right\} \\
&= -\frac{1}{i\sqrt{2}} (Y_2^1 + Y_2^{-1})
\end{aligned}$$

$$\begin{aligned}
[z^2] &= \frac{1}{\sqrt{12}} \frac{1}{r^2} \sqrt{\frac{15}{4\pi}} (3(r \cos(\Theta))^2 - r^2) = \frac{1}{\sqrt{12}} \sqrt{\frac{15}{4\pi}} (3 \cos^2(\Theta) - 1) \\
&= \frac{2\sqrt{3}}{\sqrt{12}} \sqrt{\frac{5}{4\pi}} \left( \frac{3}{2} \cos^2(\Theta) - \frac{1}{2} \right) \\
&= \frac{2}{\sqrt{4}} Y_2^0 = Y_2^0
\end{aligned}$$

Now, put all of that together:

$$[xy]_2^{-2} = \frac{1}{i\sqrt{2}}(Y_2^2 - Y_2^{-2}) = \frac{1}{\sqrt{2}}(iY_2^{-2} - iY_2^2)$$

$$[zy]_2^{-1} = -\frac{1}{i\sqrt{2}}(Y_2^1 + Y_2^{-1}) = \frac{1}{\sqrt{2}}(iY_2^{-1} + iY_2^1)$$

$$[z^2]_2^0 = Y_2^0 = \frac{1}{\sqrt{2}}(\sqrt{2}Y_2^0)$$

$$[zx]_2^1 = -\frac{1}{\sqrt{2}}(Y_2^1 - Y_2^{-1}) = \frac{1}{\sqrt{2}}(Y_2^{-1} - Y_2^1)$$

$$[x^2 - y^2]_2^2 = \frac{1}{\sqrt{2}}(Y_2^{-2} + Y_2^2)$$

In fact, we can make a matrix representation of transformation between  $Y_L^M$ 's and the FIREBALL's functions.

### 6.2.3 Matrix form of FB and $Y_L^M$ 's relationship

$$[1]_0^0 = Y_0^0$$

$$\begin{vmatrix} [y]_1^{-1} \\ [z]_1^0 \\ [x]_1^{+1} \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} i & 0 & i \\ 0 & \sqrt{2} & 0 \\ 1 & 0 & -1 \end{vmatrix} * \begin{vmatrix} Y_1^{-1} \\ Y_1^0 \\ Y_1^{+1} \end{vmatrix}$$

$$\begin{vmatrix} [xy]_2^{-2} \\ [zy]_2^{-1} \\ [z^2]_2^0 \\ [zx]_2^{+1} \\ [x^2 - y^2]_2^{+2} \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} i & 0 & 0 & 0 & -i \\ 0 & i & 0 & i & 0 \\ 0 & 0 & \sqrt{2} & 0 & 0 \\ 0 & 1 & 0 & -1 & 0 \\ 1 & 0 & 0 & 0 & 1 \end{vmatrix} * \begin{vmatrix} Y_2^{-2} \\ Y_2^{-1} \\ Y_2^0 \\ Y_2^1 \\ Y_2^2 \end{vmatrix}$$

The indexes for FIREBALL functions are as follows: the lower represents L and the upper represents M according to FIREBALL notation.

### 6.3 APPENDIX C *XYZ Dipole selection Rules*

#### 6.3.1 *Derivations of the dipole selection rules.*

One way to derive those rules is to note that in order for integral to be non-zero, all coordinates  $x$ ,  $y$  and  $z$  should come as even powers before integration. Otherwise, if even one of the coordinates is odd, an even power will be produced after integration, and then considering symmetric limits, the integral will be zero. Remember that the  $z$  coordinate is a direction between two atoms (cylindrical coordinates), so it has a constant -  $z \pm d/2$ .

One of the examples is selection rules between p and d-orbitals:

$$\left\langle \begin{array}{c|c} y & x \\ z + d/2 & y \\ x & z \end{array} \middle| \begin{array}{c} xy \\ y(z - d/2) \\ 2(z - d/2)^2 - x^2 - y^2 \\ (z - d/2)x \\ x^2 - y^2 \end{array} \right\rangle$$

If we, for example, take  $(z + d/2)$ -(whatever)- $(xy)$ , then all of the elements are entering as odd powers of at least one coordinate, so this element is zero. On the other hand,  $(z + d/2)$ -( $y$ )- $(y(z - d/2))$  has  $zyyz$  and  $d/2 yyd/2$  terms which render this term as a non-zero.

### 6.3.2 Dipole selection rules for two identical atoms

	<b>1</b>	<b>y</b>	<b>z</b>	<b>x</b>	<b>xy</b>	<b>zy</b>	$(3z^2-r^2)/\sqrt{12}$	<b>zx</b>	$(x^2-y^2)/2$
L,M	0, 0	1,-1	1, 0	1, 1	2,-2	2,-1	2, 0	2, 1	2, 2
0,0		Y	Z	X		Y	Z	X	
1,-1	Y		Y		X	Z	Y		Y
1, 0	Z	Y		X		Y	Z	X	
1, 1	X		X		Y		X	Z	X
2,-2		X		Y		X		Y	
2,-1	Y	Z	Y		X		Y		Y
2, 0	Z	Y	Z	X		Y		X	
2, 1	X		X	Z	Y		X		X
2, 2		Y		X		Y		X	

This table represents non-zero combinations of FB functions with indicated dipole operator.

Number of non-zero dipoles for given combinations of L values:

<b>X/Y</b>	<b>0</b>	<b>1</b>	<b>2</b>
<b>0</b>	0	1	1
<b>1</b>	1	2	4
<b>2</b>	1	4	6

<b>Z</b>	<b>0</b>	<b>1</b>	<b>2</b>
<b>0</b>	0	1	1
<b>1</b>	1	0	3
<b>2</b>	1	3	0

Remember that these are NOT usual wavefunctions, but rather combinations of them (so they are real), and thus we are not dealing with a simple  $m_1 = m_2 \pm 1$ .

### 6.3.3 Dipole selection rules for two different atoms

The integration performed in cylindrical coordinates. Z-direction might need some more insight.

When two atoms are the same, the selection rules presented would be true. Although, when those atoms are not the same type, and thus symmetry along z axis is broken, we are only left with selection rules based solely on a phi-angle. This results in a situation when some of dipole elements are non-zero in places not typical for dipoles, e.g.  $m_1 = m_2$ . In those places, some dipoles will be zero (same atom types) and some will be not (different atoms).

To achieve a uniformity of the FIREBALL code we have included those Z-selections in a non-zero form.

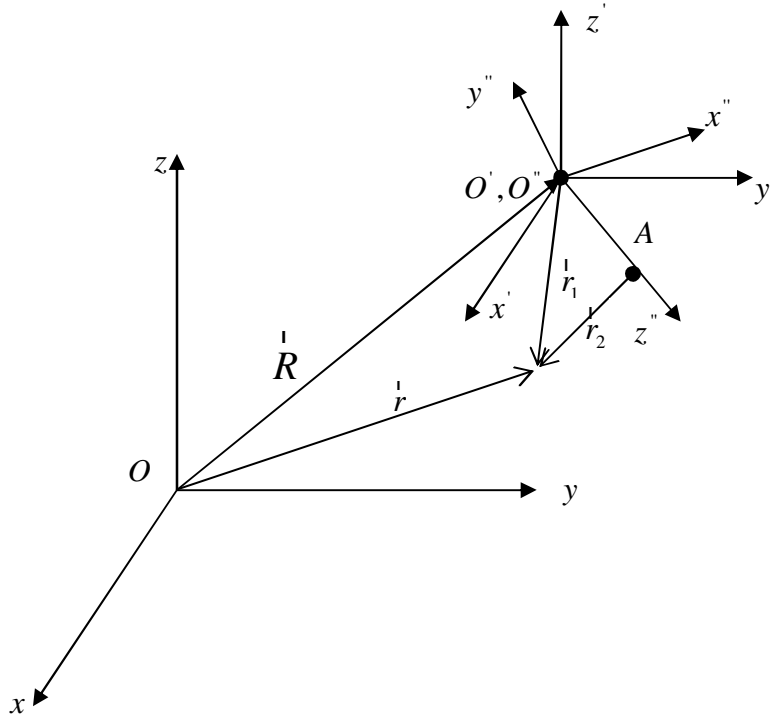
	<b>1</b>	<b>y</b>	<b>z</b>	<b>x</b>	<b>xy</b>	<b>zy</b>	$(3z^2-r^2)/\text{sqrt}(12)$	<b>zx</b>	$(x^2-y^2)/2$
L,M	0, 0	1,-1	1, 0	1, 1	2,-2	2,-1	2, 0	2, 1	2, 2
0,0	Z	Y	Z	X		Y	Z	X	
1,-1	Y	Z	Y	Z	X	Z	Y	Z	Y
1, 0	Z	Y	Z	X		Y	Z	X	
1, 1	X	Z	X	Z	Y	Z	X	Z	X
2,-2		X		Y	Z	X		Y	Z
2,-1	Y	Z	Y	Z	X	Z	Y	Z	Y
2, 0	Z	Y	Z	X		Y	Z	X	
2, 1	X	Z	X	Z	Y	Z	X	Z	X
2, 2		Y		X	Z	Y		X	Z

This table represents non-zero combinations of FB functions with indicated dipole operator.

Number of non-zero Z-dipoles for given combinations of L values:

Z	0	1	2
0	1	1	1
1	1	5	5
2	1	5	9

## 6.4 APPENDIX D Dipole rotations from CREATE to FIREBALL



Here we have the following:

$Oxyz$  - Crystal coordinate system

$O'x'y'z'$  - System of coordinates parallel to crystal and centered on atom #1

$O''x''y''z''$  - Atomic coordinate system – Atom #1 is at the center, atom #2 is on  $O''z''$  at point A

$\vec{r}$  - Point of integration in crystal coordinates

$\vec{r}_1, \vec{r}_2$  - Vectors to the same integration point from atoms #1 and #2

$\vec{d}$  (not shown on the picture) – Vector from atom #1 to atom #2

We are looking to calculate dipole  $\langle \varphi_L(\vec{r} - \vec{R}) | x | \varphi_R(\vec{r} - [\vec{R} + \vec{d}]) \rangle = \langle \varphi_L(\vec{r}_1) | x | \varphi_R(\vec{r}_2) \rangle$  in crystal coordinates out of pre-made dipoles in molecular coordinates.

The first step to consider is rotation of the dipole from  $O''x''y''z''$  into  $O'x'y'z'$ .

We have matrices  $\alpha_L$  and  $\alpha_R$  rotating  $\varphi_L''$  and  $\varphi_R''$  which already exist in FIREBALL and  $\alpha_C$ , which rotates  $x''$  into  $x'$ . Here we have a usual convention when repeating indices are being summed over and capitals meaning the “super-matrices” of the FIREBALL.

$$\begin{aligned}
\langle \varphi_L^i | x^i | \varphi_R^j \rangle &= \langle (\alpha_L)_f^i (\varphi_L)_k^f (\alpha_C)_g (x^g) (\varphi_R)_h^j (\alpha_R)_k^h \rangle \\
&= A_L \Phi_L^i (\alpha_C)_g (x^g) \Phi_R^j A_R = A_L \{ (\alpha_C)_g [\Phi_L^i (x^g) \Phi_R^j] \} A_R \\
&= A_L \{ (\alpha_C)_g (d^g) \} A_R
\end{aligned}$$

Note that  $(\alpha_C)_g (d^g)$  is nothing more than a linear combination of the dipoles in molecular coordinates, where coefficients  $\alpha_C$  are coefficients which transform  $x^g$  into  $x^i$ .

So the recipe is to feed the center matrix for the rotation procedure in FIREBALL with the correct linear combination of the dipoles.

The next step is transformation between  $O^i x^i y^i z^i$  and  $Oxyz$ .

This is quite simple, because both  $\varphi_L^i$  and  $\varphi_R^i$  depend only on  $r_1^i$  and  $r_2^i$ . It does not matter where the center of the coordinate system is. The center piece is the only part of our dipole which depends on the coordinate system origin.

$$\begin{aligned}
&\langle \varphi_L^i(r_1^i) | x^i | \varphi_R^i(r_2^i) \rangle \\
&= \langle \varphi_L^i(r_1^i) | x^i + X | \varphi_R^i(r_2^i) \rangle \\
&= \langle \varphi_L^i(r_1^i) | x^i | \varphi_R^i(r_2^i) \rangle + X \langle \varphi_L^i(r_1^i) | \varphi_R^i(r_2^i) \rangle
\end{aligned}$$

Where  $X$  is appropriate coordinate of shift vector  $\hat{R}$

Thus we need to add an integral already existing in the FIREBALL.



## 6.5 APPENDIX E Rotations of p and d functions

### 6.5.1 Rotations summary

Let us assume that we have an  $\epsilon$  matrix describing the rotations from primed to unprimed coordinates:

$$\hat{\epsilon} = \begin{vmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{21} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{31} & \epsilon_{32} & \epsilon_{33} \end{vmatrix}$$

Each element of  $\hat{\epsilon}$  is an appropriate dot product of unit vectors of primed and unprimed systems. The transformation for p-functions is quite easy:

$$\overset{\uparrow}{p} = \hat{\epsilon} \overset{\uparrow}{p}, \text{ i.e.}$$

$$p_x = \epsilon_{11} p'_x + \epsilon_{12} p'_y + \epsilon_{13} p'_z$$

$$p_y = \epsilon_{21} p'_x + \epsilon_{22} p'_y + \epsilon_{23} p'_z$$

$$p_z = \epsilon_{31} p'_x + \epsilon_{32} p'_y + \epsilon_{33} p'_z$$

Some math is required for the d-functions, but we will show the final result up in front:

$$\begin{vmatrix} [xy]_2^{-2} \\ [zy]_2^{-1} \\ [z^2]_2^0 \\ [zx]_2^{+1} \\ [x^2 - y^2]_2^{+2} \end{vmatrix} = \hat{D} \times \begin{vmatrix} [xy]_2^{-2} \\ [zy]_2^{-1} \\ [z^2]_2^0 \\ [zx]_2^{+1} \\ [x^2 - y^2]_2^{+2} \end{vmatrix},$$

where

$$\hat{D} = \begin{vmatrix} \begin{pmatrix} \varepsilon_1 \varepsilon_{22}^+ \\ +\varepsilon_1 \varepsilon_{21} \end{pmatrix} & \begin{pmatrix} \varepsilon_1 \varepsilon_{23}^+ \\ +\varepsilon_1 \varepsilon_{22} \end{pmatrix} & \frac{1}{2} \begin{pmatrix} 2\varepsilon_1 \varepsilon_{23} - \varepsilon_1 \varepsilon_{21}^- \\ -\varepsilon_1 \varepsilon_{22} \end{pmatrix} & \begin{pmatrix} \varepsilon_1 \varepsilon_{23}^+ \\ +\varepsilon_1 \varepsilon_{21} \end{pmatrix} & \frac{1}{2} \begin{pmatrix} \varepsilon_1 \varepsilon_{21}^- \\ -\varepsilon_1 \varepsilon_{22} \end{pmatrix} \\ \begin{pmatrix} \varepsilon_2 \varepsilon_{32}^+ \\ +\varepsilon_2 \varepsilon_{22} \end{pmatrix} & \begin{pmatrix} \varepsilon_2 \varepsilon_{33}^+ \\ +\varepsilon_2 \varepsilon_{23} \end{pmatrix} & \frac{1}{2} \begin{pmatrix} 2\varepsilon_2 \varepsilon_{33} - \varepsilon_2 \varepsilon_{31}^- \\ -\varepsilon_2 \varepsilon_{32} \end{pmatrix} & \begin{pmatrix} \varepsilon_2 \varepsilon_{23}^+ \\ +\varepsilon_2 \varepsilon_{33} \end{pmatrix} & \frac{1}{2} \begin{pmatrix} \varepsilon_2 \varepsilon_{31}^- \\ -\varepsilon_2 \varepsilon_{32} \end{pmatrix} \\ \frac{1}{2} \begin{pmatrix} 2\varepsilon_3 \varepsilon_{32} - \varepsilon_1 \varepsilon_{12}^- \\ -\varepsilon_2 \varepsilon_{22} \end{pmatrix} & \frac{1}{2} \begin{pmatrix} 2\varepsilon_3 \varepsilon_{33} - \varepsilon_1 \varepsilon_{13}^- \\ -\varepsilon_2 \varepsilon_{23} \end{pmatrix} & \frac{1}{2} \begin{pmatrix} 4\varepsilon_{33}^2 - 2\varepsilon_{13}^2 - 2\varepsilon_{23}^2 - 2\varepsilon_{31}^2 + \varepsilon_{11}^2 \\ +\varepsilon_{21}^2 - 2\varepsilon_{32}^2 + \varepsilon_{12}^2 + \varepsilon_{22}^2 \end{pmatrix} & \frac{1}{2} \begin{pmatrix} 2\varepsilon_3 \varepsilon_{33} - \varepsilon_1 \varepsilon_{13}^- \\ -\varepsilon_2 \varepsilon_{23} \end{pmatrix} & \frac{1}{2} \begin{pmatrix} 2\varepsilon_{31}^2 - \varepsilon_{11}^2 - \varepsilon_{21}^2 \\ -2\varepsilon_{32}^2 + \varepsilon_{12}^2 + \varepsilon_{22}^2 \end{pmatrix} \\ \begin{pmatrix} \varepsilon_1 \varepsilon_{32}^+ \\ +\varepsilon_1 \varepsilon_{12} \end{pmatrix} & \begin{pmatrix} \varepsilon_1 \varepsilon_{32}^+ \\ +\varepsilon_1 \varepsilon_{33} \end{pmatrix} & \frac{1}{2} \begin{pmatrix} 2\varepsilon_1 \varepsilon_{33} - \varepsilon_1 \varepsilon_{31}^- \\ -\varepsilon_1 \varepsilon_{32} \end{pmatrix} & \begin{pmatrix} \varepsilon_1 \varepsilon_{33}^+ \\ +\varepsilon_1 \varepsilon_{31} \end{pmatrix} & \frac{1}{2} \begin{pmatrix} \varepsilon_1 \varepsilon_{31}^- \\ -\varepsilon_1 \varepsilon_{32} \end{pmatrix} \\ \begin{pmatrix} \varepsilon_1 \varepsilon_{12}^- \\ -\varepsilon_2 \varepsilon_{22} \end{pmatrix} & \begin{pmatrix} \varepsilon_1 \varepsilon_{13}^- \\ -\varepsilon_2 \varepsilon_{23} \end{pmatrix} & \frac{1}{2} \begin{pmatrix} 2\varepsilon_{13}^2 - \varepsilon_{11}^2 - \varepsilon_{12}^2 \\ -2\varepsilon_{23}^2 + \varepsilon_{21}^2 + \varepsilon_{22}^2 \end{pmatrix} & \begin{pmatrix} \varepsilon_1 \varepsilon_{13}^- \\ -\varepsilon_2 \varepsilon_{23} \end{pmatrix} & \frac{1}{2} \begin{pmatrix} \varepsilon_{11}^2 - \varepsilon_{21}^2 \\ -\varepsilon_{12}^2 + \varepsilon_{22}^2 \end{pmatrix} \end{vmatrix}$$

### 6.5.2 Derivation of rotational formulas

The method here is to take the function  $f$ , apply rotation to it, then find the projection of the result onto all non-primed functions thus obtaining the desired coefficients.

It is worth remembering that all odd terms vanish, and

$$\langle x^4 \rangle = \langle y^4 \rangle = \langle z^4 \rangle$$

$$\langle x^2 y^2 \rangle = \langle y^2 z^2 \rangle = \langle z^2 x^2 \rangle$$

etc

Let  $R$  denote the appropriate rotation.

$$6.5.2.1 \quad [x^2 - y^2]$$

$$\begin{aligned} R[x^2 - y^2] &= (\varepsilon_{11}x + \varepsilon_{12}y + \varepsilon_{13}z)^2 - (\varepsilon_{21}x + \varepsilon_{22}y + \varepsilon_{23}z)^2 = \\ &= \varepsilon_{11}^2 x^2 + \varepsilon_{12}^2 y^2 + \varepsilon_{13}^2 z^2 + 2\varepsilon_{11}\varepsilon_{12}xy + 2\varepsilon_{11}\varepsilon_{13}xz + 2\varepsilon_{12}\varepsilon_{13}yz - \\ &- \varepsilon_{21}^2 x^2 + \varepsilon_{22}^2 y^2 + \varepsilon_{23}^2 z^2 + 2\varepsilon_{21}\varepsilon_{22}xy + 2\varepsilon_{21}\varepsilon_{23}xz + 2\varepsilon_{22}\varepsilon_{23}yz = \\ &= (\varepsilon_{11}^2 - \varepsilon_{21}^2)x^2 + (\varepsilon_{12}^2 - \varepsilon_{22}^2)y^2 + (\varepsilon_{13}^2 - \varepsilon_{23}^2)z^2 + \\ &2(\varepsilon_{11}\varepsilon_{12} - \varepsilon_{21}\varepsilon_{22})xy + 2(\varepsilon_{11}\varepsilon_{13} - \varepsilon_{21}\varepsilon_{23})xz + 2(\varepsilon_{12}\varepsilon_{13} - \varepsilon_{22}\varepsilon_{23})yz \end{aligned}$$

$$\begin{aligned}
& \langle [x^2 - y^2] R[x^2 - y^2] \rangle = \{\text{Keeping only non - vanishing terms}\} = \\
& = \langle (x^2 - y^2) [(\epsilon_{11}^2 - \epsilon_{21}^2)x^2 + (\epsilon_{12}^2 - \epsilon_{22}^2)y^2 + (\epsilon_{13}^2 - \epsilon_{23}^2)z^2] \rangle = \\
& = \left\langle x^2(\epsilon_{11}^2 - \epsilon_{21}^2)x^2 + x^2(\epsilon_{12}^2 - \epsilon_{22}^2)y^2 + x^2(\epsilon_{13}^2 - \epsilon_{23}^2)z^2 - \right. \\
& \quad \left. - y^2(\epsilon_{11}^2 - \epsilon_{21}^2)x^2 - y^2(\epsilon_{12}^2 - \epsilon_{22}^2)y^2 - y^2(\epsilon_{13}^2 - \epsilon_{23}^2)z^2 \right\rangle = \\
& = \langle x^4 \rangle (\epsilon_{11}^2 - \epsilon_{21}^2 - \epsilon_{12}^2 + \epsilon_{22}^2) + \langle x^2 y^2 \rangle (\epsilon_{12}^2 - \epsilon_{22}^2 + \epsilon_{13}^2 - \epsilon_{23}^2 - \epsilon_{11}^2 + \epsilon_{21}^2 - \epsilon_{13}^2 + \epsilon_{23}^2) = \\
& = \langle x^4 \rangle (\epsilon_{11}^2 - \epsilon_{21}^2 - \epsilon_{12}^2 + \epsilon_{22}^2) - \langle x^2 y^2 \rangle (\epsilon_{11}^2 - \epsilon_{21}^2 - \epsilon_{12}^2 + \epsilon_{22}^2) = \\
& = (\epsilon_{11}^2 - \epsilon_{21}^2 - \epsilon_{12}^2 + \epsilon_{22}^2) \langle x^4 - x^2 y^2 \rangle = \\
& = \frac{1}{2} (\epsilon_{11}^2 - \epsilon_{21}^2 - \epsilon_{12}^2 + \epsilon_{22}^2) \langle x^4 - 2x^2 y^2 + y^4 \rangle = \\
& = \frac{1}{2} (\epsilon_{11}^2 - \epsilon_{21}^2 - \epsilon_{12}^2 + \epsilon_{22}^2)
\end{aligned}$$

$$\begin{aligned}
& \langle [zx] R[x^2 - y^2] \rangle = \langle zx 2(\epsilon_{11}\epsilon_{13} - \epsilon_{21}\epsilon_{23})zx \rangle = \\
& = 2(\epsilon_{11}\epsilon_{13} - \epsilon_{21}\epsilon_{23}) \langle (zx)^2 \rangle = \\
& = 2(\epsilon_{11}\epsilon_{13} - \epsilon_{21}\epsilon_{23})
\end{aligned}$$

$$\begin{aligned}
& \langle [zy] R[x^2 - y^2] \rangle = \langle zy 2(\epsilon_{12}\epsilon_{13} - \epsilon_{22}\epsilon_{23})yz \rangle = \\
& = 2(\epsilon_{12}\epsilon_{13} - \epsilon_{22}\epsilon_{23}) \langle (zy)^2 \rangle = \\
& = 2(\epsilon_{12}\epsilon_{13} - \epsilon_{22}\epsilon_{23})
\end{aligned}$$

$$\begin{aligned}
& \langle [xy] R[x^2 - y^2] \rangle = \langle xy 2(\epsilon_{11}\epsilon_{12} - \epsilon_{21}\epsilon_{22})xy \rangle = \\
& = 2(\epsilon_{11}\epsilon_{12} - \epsilon_{21}\epsilon_{22}) \langle (xy)^2 \rangle = \\
& = 2(\epsilon_{11}\epsilon_{12} - \epsilon_{21}\epsilon_{22})
\end{aligned}$$

$$\begin{aligned}
\langle [z^2]R[x^2 - y^2] \rangle &= \langle (3z^2 - r^2) \left[ (\epsilon_{11}^2 - \epsilon_{21}^2)x^2 + (\epsilon_{12}^2 - \epsilon_{22}^2)y^2 + (\epsilon_{13}^2 - \epsilon_{23}^2)z^2 \right] \rangle = \\
&= \langle (2z^2 - x^2 - x^2) \left[ (\epsilon_{11}^2 - \epsilon_{21}^2)x^2 + (\epsilon_{12}^2 - \epsilon_{22}^2)y^2 + (\epsilon_{13}^2 - \epsilon_{23}^2)z^2 \right] \rangle = \\
&= \left\langle \begin{aligned} &2z^2(\epsilon_{11}^2 - \epsilon_{21}^2)x^2 + 2z^2(\epsilon_{12}^2 - \epsilon_{22}^2)y^2 + 2z^2(\epsilon_{13}^2 - \epsilon_{23}^2)z^2 - \\ &-x^2(\epsilon_{11}^2 - \epsilon_{21}^2)x^2 - x^2(\epsilon_{12}^2 - \epsilon_{22}^2)y^2 - x^2(\epsilon_{13}^2 - \epsilon_{23}^2)z^2 - \\ &-y^2(\epsilon_{11}^2 - \epsilon_{21}^2)x^2 - y^2(\epsilon_{12}^2 - \epsilon_{22}^2)y^2 - y^2(\epsilon_{13}^2 - \epsilon_{23}^2)z^2 \end{aligned} \right\rangle = \\
&= \langle z^4 \rangle (2\epsilon_{13}^2 - 2\epsilon_{23}^2 - \epsilon_{11}^2 + \epsilon_{21}^2 - \epsilon_{12}^2 + \epsilon_{22}^2) - \\
&- \langle z^2 x^2 \rangle (-2\epsilon_{11}^2 + 2\epsilon_{21}^2 - 2\epsilon_{12}^2 + 2\epsilon_{22}^2 + \epsilon_{12}^2 - \epsilon_{22}^2 + \epsilon_{13}^2 - \epsilon_{23}^2 + \epsilon_{11}^2 - \epsilon_{21}^2 + \epsilon_{13}^2 - \epsilon_{23}^2) = \\
&= \langle z^4 \rangle (2\epsilon_{13}^2 - 2\epsilon_{23}^2 - \epsilon_{11}^2 + \epsilon_{21}^2 - \epsilon_{12}^2 + \epsilon_{22}^2) - \langle z^2 x^2 \rangle (2\epsilon_{13}^2 - 2\epsilon_{23}^2 - \epsilon_{11}^2 + \epsilon_{21}^2 - \epsilon_{12}^2 + \epsilon_{22}^2) = \\
&= (2\epsilon_{13}^2 - 2\epsilon_{23}^2 - \epsilon_{11}^2 + \epsilon_{21}^2 - \epsilon_{12}^2 + \epsilon_{22}^2) \langle z^4 - z^2 x^2 \rangle
\end{aligned}$$

For the future projections on  $[z^2]$  we will work out the  $\langle z^4 - z^2 x^2 \rangle$  term:

$$\begin{aligned}
\langle z^4 - z^2 x^2 \rangle &= \frac{1}{2} \langle z^4 - 2z^2 x^2 + x^4 \rangle = \frac{1}{2} \langle x^4 - 2x^2 y^2 + y^4 \rangle = \\
&= \frac{1}{2} \langle (x^2 - y^2)^2 \rangle = \frac{1}{2}
\end{aligned}$$

thus

$$\begin{aligned}
\langle [z^2]R[x^2 - y^2] \rangle &= \\
&= (2\epsilon_{13}^2 - 2\epsilon_{23}^2 - \epsilon_{11}^2 + \epsilon_{21}^2 - \epsilon_{12}^2 + \epsilon_{22}^2) \langle z^4 - z^2 x^2 \rangle = \\
&= \frac{1}{2} (2\epsilon_{13}^2 - 2\epsilon_{23}^2 - \epsilon_{11}^2 + \epsilon_{21}^2 - \epsilon_{12}^2 + \epsilon_{22}^2)
\end{aligned}$$

### 6.5.2.2 $[zx]$

$$\begin{aligned}
R|zx\rangle &= (\epsilon_{31}x + \epsilon_{32}y + \epsilon_{33}z)(\epsilon_{11}x + \epsilon_{12}y + \epsilon_{13}z) = \\
&= \epsilon_{11}\epsilon_{31}xx + \epsilon_{12}\epsilon_{31}xy + \epsilon_{13}\epsilon_{31}xz + \\
&+ \epsilon_{11}\epsilon_{32}yx + \epsilon_{12}\epsilon_{32}yy + \epsilon_{13}\epsilon_{32}yz + \\
&+ \epsilon_{11}\epsilon_{33}zx + \epsilon_{12}\epsilon_{33}zy + \epsilon_{13}\epsilon_{33}zz = \\
&= \epsilon_{11}\epsilon_{31}x^2 + \epsilon_{12}\epsilon_{32}y^2 + \epsilon_{13}\epsilon_{33}z^2 + \\
&+ (\epsilon_{12}\epsilon_{31} + \epsilon_{11}\epsilon_{32})xy + (\epsilon_{13}\epsilon_{32} + \epsilon_{12}\epsilon_{33})zy + (\epsilon_{13}\epsilon_{31} + \epsilon_{11}\epsilon_{33})zx
\end{aligned}$$

$$\begin{aligned}
\langle [x^2 - y^2] | R[zx] \rangle &= \langle (x^2 - y^2) [\epsilon_{11}\epsilon_{31}x^2 + \epsilon_{12}\epsilon_{32}y^2 + \epsilon_{13}\epsilon_{33}z^2] \rangle = \\
&= \left\langle \begin{aligned} &x^2\epsilon_{11}\epsilon_{31}x^2 + x^2\epsilon_{12}\epsilon_{32}y^2 + x^2\epsilon_{13}\epsilon_{33}z^2 - \\ &-y^2\epsilon_{11}\epsilon_{31}x^2 - y^2\epsilon_{12}\epsilon_{32}y^2 - y^2\epsilon_{13}\epsilon_{33}z^2 \end{aligned} \right\rangle = \\
&= \langle x^4 \rangle (\epsilon_{11}\epsilon_{31} - \epsilon_{12}\epsilon_{32}) + \langle x^2y^2 \rangle (\epsilon_{12}\epsilon_{32} + \epsilon_{13}\epsilon_{33} - \epsilon_{11}\epsilon_{31} - \epsilon_{13}\epsilon_{33}) = \\
&= \langle x^4 \rangle (\epsilon_{11}\epsilon_{31} - \epsilon_{12}\epsilon_{32}) - \langle x^2y^2 \rangle (\epsilon_{11}\epsilon_{31} - \epsilon_{12}\epsilon_{32}) = \\
&= \frac{1}{2} (\epsilon_{11}\epsilon_{31} - \epsilon_{12}\epsilon_{32}) \langle x^4 - 2x^2y^2 + y^4 \rangle = \\
&= \frac{1}{2} (\epsilon_{11}\epsilon_{31} - \epsilon_{12}\epsilon_{32})
\end{aligned}$$

$$\begin{aligned}
\langle [zx] | R[zx] \rangle &= \langle zx(\epsilon_{13}\epsilon_{31} + \epsilon_{11}\epsilon_{33})zx \rangle = \\
&= (\epsilon_{13}\epsilon_{31} + \epsilon_{11}\epsilon_{33}) \langle (zx)^2 \rangle = \\
&= (\epsilon_{13}\epsilon_{31} + \epsilon_{11}\epsilon_{33})
\end{aligned}$$

$$\begin{aligned}
\langle [z^2] | R[zx] \rangle &= \langle (2z^2 - x^2 - y^2) (\epsilon_{11}\epsilon_{31}x^2 + \epsilon_{12}\epsilon_{32}y^2 + \epsilon_{13}\epsilon_{33}z^2) \rangle = \\
&= \left\langle \begin{aligned} &2z^2\epsilon_{11}\epsilon_{31}x^2 + 2z^2\epsilon_{12}\epsilon_{32}y^2 + 2z^2\epsilon_{13}\epsilon_{33}z^2 - \\ &-x^2\epsilon_{11}\epsilon_{31}x^2 - x^2\epsilon_{12}\epsilon_{32}y^2 - x^2\epsilon_{13}\epsilon_{33}z^2 - \\ &-y^2\epsilon_{11}\epsilon_{31}x^2 - y^2\epsilon_{12}\epsilon_{32}y^2 - y^2\epsilon_{13}\epsilon_{33}z^2 \end{aligned} \right\rangle = \\
&= \langle z^4 \rangle (2\epsilon_{13}\epsilon_{33} - \epsilon_{11}\epsilon_{31} - \epsilon_{12}\epsilon_{32}) - \\
&- \langle z^2x^2 \rangle (-2\epsilon_{11}\epsilon_{31} - 2\epsilon_{12}\epsilon_{32} + \epsilon_{12}\epsilon_{32} + \epsilon_{13}\epsilon_{33} + \epsilon_{11}\epsilon_{31} + \epsilon_{13}\epsilon_{33}) = \\
&= \langle z^4 \rangle (2\epsilon_{13}\epsilon_{33} - \epsilon_{11}\epsilon_{31} - \epsilon_{12}\epsilon_{32}) - \langle z^2x^2 \rangle (2\epsilon_{13}\epsilon_{33} - \epsilon_{11}\epsilon_{31} - \epsilon_{12}\epsilon_{32}) = \\
&= (2\epsilon_{13}\epsilon_{33} - \epsilon_{11}\epsilon_{31} - \epsilon_{12}\epsilon_{32}) \langle z^4 - z^2x^2 \rangle = \\
&= \frac{1}{2} (2\epsilon_{13}\epsilon_{33} - \epsilon_{11}\epsilon_{31} - \epsilon_{12}\epsilon_{32})
\end{aligned}$$

$$\begin{aligned}
\langle [zy] | R[zx] \rangle &= \langle zy(\epsilon_{13}\epsilon_{32} + \epsilon_{12}\epsilon_{33})zy \rangle = \\
&= (\epsilon_{13}\epsilon_{32} + \epsilon_{12}\epsilon_{33}) \langle (zy)^2 \rangle = \\
&= (\epsilon_{13}\epsilon_{32} + \epsilon_{12}\epsilon_{33})
\end{aligned}$$

$$\begin{aligned}
\langle [xy] | R[zx] \rangle &= \langle xy(\epsilon_{12}\epsilon_{31} + \epsilon_{11}\epsilon_{32})xy \rangle = \\
&= (\epsilon_{12}\epsilon_{31} + \epsilon_{11}\epsilon_{32}) \langle (xy)^2 \rangle = \\
&= (\epsilon_{12}\epsilon_{31} + \epsilon_{11}\epsilon_{32})
\end{aligned}$$

### 6.5.2.3 $[zy]$

$$\begin{aligned} R|[zy] &= (\varepsilon_{31}x + \varepsilon_{32}y + \varepsilon_{33}z)(\varepsilon_{21}x + \varepsilon_{22}y + \varepsilon_{23}z) = \\ &= \varepsilon_{31}\varepsilon_{21}xx + \varepsilon_{31}\varepsilon_{22}xy + \varepsilon_{31}\varepsilon_{23}xz + \\ &+ \varepsilon_{32}\varepsilon_{21}yx + \varepsilon_{32}\varepsilon_{22}yy + \varepsilon_{32}\varepsilon_{23}yz + \\ &+ \varepsilon_{33}\varepsilon_{21}zx + \varepsilon_{33}\varepsilon_{22}zy + \varepsilon_{33}\varepsilon_{23}zz = \end{aligned}$$

$$\begin{aligned} &= \varepsilon_{31}\varepsilon_{21}x^2 + \varepsilon_{32}\varepsilon_{22}y^2 + \varepsilon_{33}\varepsilon_{23}z^2 + \\ &+ (\varepsilon_{31}\varepsilon_{22} + \varepsilon_{32}\varepsilon_{21})xy + (\varepsilon_{32}\varepsilon_{23} + \varepsilon_{33}\varepsilon_{22})yz + (\varepsilon_{31}\varepsilon_{23} + \varepsilon_{33}\varepsilon_{21})zx \end{aligned}$$

$$\begin{aligned} \langle [x^2 - y^2] | R|[zy] \rangle &= \langle (x^2 - y^2)(\varepsilon_{31}\varepsilon_{21}x^2 + \varepsilon_{32}\varepsilon_{22}y^2 + \varepsilon_{33}\varepsilon_{23}z^2) \rangle = \\ &= \left\langle \begin{aligned} &x^2\varepsilon_{31}\varepsilon_{21}x^2 + x^2\varepsilon_{32}\varepsilon_{22}y^2 + x^2\varepsilon_{33}\varepsilon_{23}z^2 - \\ &- y^2\varepsilon_{31}\varepsilon_{21}x^2 - y^2\varepsilon_{32}\varepsilon_{22}y^2 - y^2\varepsilon_{33}\varepsilon_{23}z^2 \end{aligned} \right\rangle = \\ &= \langle x^4 \rangle (\varepsilon_{31}\varepsilon_{21} - \varepsilon_{32}\varepsilon_{22}) + \langle x^2y^2 \rangle (\varepsilon_{32}\varepsilon_{22} + \varepsilon_{33}\varepsilon_{23} - \varepsilon_{31}\varepsilon_{21} - \varepsilon_{33}\varepsilon_{23}) = \\ &= \langle x^4 \rangle (\varepsilon_{31}\varepsilon_{21} - \varepsilon_{32}\varepsilon_{22}) - \langle x^2y^2 \rangle (\varepsilon_{31}\varepsilon_{21} - \varepsilon_{32}\varepsilon_{22}) = \\ &= (\varepsilon_{31}\varepsilon_{21} - \varepsilon_{32}\varepsilon_{22}) \langle x^4 - x^2y^2 \rangle = \\ &= \frac{1}{2} (\varepsilon_{31}\varepsilon_{21} - \varepsilon_{32}\varepsilon_{22}) \langle x^4 - 2x^2y^2 + y^4 \rangle = \\ &= \frac{1}{2} (\varepsilon_{31}\varepsilon_{21} - \varepsilon_{32}\varepsilon_{22}) \end{aligned}$$

$$\begin{aligned} \langle [zx] | R|[zy] \rangle &= \langle zx(\varepsilon_{31}\varepsilon_{23} + \varepsilon_{33}\varepsilon_{21})zx \rangle = \\ &= (\varepsilon_{31}\varepsilon_{23} + \varepsilon_{33}\varepsilon_{21}) \langle (zx)^2 \rangle = \\ &= (\varepsilon_{31}\varepsilon_{23} + \varepsilon_{33}\varepsilon_{21}) \end{aligned}$$

$$\begin{aligned} \langle [zy] | R|[zy] \rangle &= \langle zy(\varepsilon_{32}\varepsilon_{23} + \varepsilon_{33}\varepsilon_{22})yz \rangle = \\ &= (\varepsilon_{32}\varepsilon_{23} + \varepsilon_{33}\varepsilon_{22}) \langle (zy)^2 \rangle = \\ &= (\varepsilon_{32}\varepsilon_{23} + \varepsilon_{33}\varepsilon_{22}) \end{aligned}$$

$$\begin{aligned} \langle [xy] | R|[zy] \rangle &= \langle xy(\varepsilon_{31}\varepsilon_{22} + \varepsilon_{32}\varepsilon_{21})xy \rangle = \\ &= (\varepsilon_{31}\varepsilon_{22} + \varepsilon_{32}\varepsilon_{21}) \langle (xy)^2 \rangle = \\ &= (\varepsilon_{31}\varepsilon_{22} + \varepsilon_{32}\varepsilon_{21}) \end{aligned}$$

$$\begin{aligned}
\langle [z^2] | R | [zy] \rangle &= \langle (2z^2 - x^2 - y^2) (\epsilon_{31} \epsilon_{21} x^2 + \epsilon_{32} \epsilon_{22} y^2 + \epsilon_{33} \epsilon_{23} z^2) \rangle = \\
&= \left\langle \begin{aligned} &2z^2 \epsilon_{31} \epsilon_{21} x^2 + 2z^2 \epsilon_{32} \epsilon_{22} y^2 + 2z^2 \epsilon_{33} \epsilon_{23} z^2 - \\ &- x^2 \epsilon_{31} \epsilon_{21} x^2 - x^2 \epsilon_{32} \epsilon_{22} y^2 - x^2 \epsilon_{33} \epsilon_{23} z^2 - \\ &- y^2 \epsilon_{31} \epsilon_{21} x^2 - y^2 \epsilon_{32} \epsilon_{22} y^2 - y^2 \epsilon_{33} \epsilon_{23} z^2 \end{aligned} \right\rangle = \\
&= \langle z^4 \rangle (2\epsilon_{33} \epsilon_{23} - \epsilon_{31} \epsilon_{21} - \epsilon_{32} \epsilon_{22}) - \\
&- \langle z^2 x^2 \rangle (-2\epsilon_{31} \epsilon_{21} - 2\epsilon_{32} \epsilon_{22} + \epsilon_{32} \epsilon_{22} + \epsilon_{33} \epsilon_{23} + \epsilon_{31} \epsilon_{21} + \epsilon_{33} \epsilon_{23}) = \\
&= \langle z^4 \rangle (2\epsilon_{33} \epsilon_{23} - \epsilon_{31} \epsilon_{21} - \epsilon_{32} \epsilon_{22}) - \langle z^2 x^2 \rangle (2\epsilon_{33} \epsilon_{23} - \epsilon_{31} \epsilon_{21} - \epsilon_{32} \epsilon_{22}) = \\
&= (2\epsilon_{33} \epsilon_{23} - \epsilon_{31} \epsilon_{21} - \epsilon_{32} \epsilon_{22}) \langle z^4 - z^2 x^2 \rangle = \\
&= \frac{1}{2} (2\epsilon_{33} \epsilon_{23} - \epsilon_{31} \epsilon_{21} - \epsilon_{32} \epsilon_{22})
\end{aligned}$$

#### 6.5.2.4 [xy]

$$\begin{aligned}
R | [xy] \rangle &= (\epsilon_{11} x + \epsilon_{12} y + \epsilon_{13} z) (\epsilon_{21} x + \epsilon_{22} y + \epsilon_{23} z) = \\
&= \epsilon_{11} \epsilon_{21} xx + \epsilon_{11} \epsilon_{22} xy + \epsilon_{11} \epsilon_{23} xz + \\
&+ \epsilon_{12} \epsilon_{21} yx + \epsilon_{12} \epsilon_{22} yy + \epsilon_{12} \epsilon_{23} yz + \\
&+ \epsilon_{13} \epsilon_{21} zx + \epsilon_{13} \epsilon_{22} zy + \epsilon_{13} \epsilon_{23} zz = \\
&= \epsilon_{11} \epsilon_{21} x^2 + \epsilon_{12} \epsilon_{22} y^2 + \epsilon_{13} \epsilon_{23} z^2 + \\
&+ (\epsilon_{11} \epsilon_{22} + \epsilon_{12} \epsilon_{21}) xy + (\epsilon_{12} \epsilon_{23} + \epsilon_{13} \epsilon_{22}) yz + (\epsilon_{11} \epsilon_{23} + \epsilon_{13} \epsilon_{21}) zx \\
\langle [x^2 - y^2] | R | [xy] \rangle &= \langle (x^2 - y^2) (\epsilon_{11} \epsilon_{21} x^2 + \epsilon_{12} \epsilon_{22} y^2 + \epsilon_{13} \epsilon_{23} z^2) \rangle = \\
&= \left\langle \begin{aligned} &x^2 \epsilon_{11} \epsilon_{21} x^2 + x^2 \epsilon_{12} \epsilon_{22} y^2 + x^2 \epsilon_{13} \epsilon_{23} z^2 - \\ &- y^2 \epsilon_{11} \epsilon_{21} x^2 - y^2 \epsilon_{12} \epsilon_{22} y^2 - y^2 \epsilon_{13} \epsilon_{23} z^2 \end{aligned} \right\rangle = \\
&= \langle x^4 \rangle (\epsilon_{11} \epsilon_{21} - \epsilon_{12} \epsilon_{22}) + \langle x^2 y^2 \rangle (\epsilon_{12} \epsilon_{22} + \epsilon_{13} \epsilon_{23} - \epsilon_{11} \epsilon_{21} - \epsilon_{13} \epsilon_{23}) = \\
&= \langle x^4 \rangle (\epsilon_{11} \epsilon_{21} - \epsilon_{12} \epsilon_{22}) - \langle x^2 y^2 \rangle (\epsilon_{11} \epsilon_{21} - \epsilon_{12} \epsilon_{22}) = \\
&= (\epsilon_{11} \epsilon_{21} - \epsilon_{12} \epsilon_{22}) \langle x^4 - x^2 y^2 \rangle = \\
&= \frac{1}{2} (\epsilon_{11} \epsilon_{21} - \epsilon_{12} \epsilon_{22}) \langle x^4 - 2x^2 y^2 + y^4 \rangle = \\
&= \frac{1}{2} (\epsilon_{11} \epsilon_{21} - \epsilon_{12} \epsilon_{22})
\end{aligned}$$

$$\begin{aligned}
\langle [zx] | R | [xy] \rangle &= \langle zx(\varepsilon_{11}\varepsilon_{23} + \varepsilon_{13}\varepsilon_{21})zx \rangle = \\
&= (\varepsilon_{11}\varepsilon_{23} + \varepsilon_{13}\varepsilon_{21}) \langle (zx)^2 \rangle = \\
&= (\varepsilon_{11}\varepsilon_{23} + \varepsilon_{13}\varepsilon_{21})
\end{aligned}$$

$$\begin{aligned}
\langle [z^2] | R | [xy] \rangle &= \langle (2z^2 - x^2 - y^2)(\varepsilon_{11}\varepsilon_{21}x^2 + \varepsilon_{12}\varepsilon_{22}y^2 + \varepsilon_{13}\varepsilon_{23}z^2) \rangle = \\
&= \left\langle \begin{aligned} &2z^2\varepsilon_{11}\varepsilon_{21}x^2 + 2z^2\varepsilon_{12}\varepsilon_{22}y^2 + 2z^2\varepsilon_{13}\varepsilon_{23}z^2 - \\ &-x^2\varepsilon_{11}\varepsilon_{21}x^2 - x^2\varepsilon_{12}\varepsilon_{22}y^2 - x^2\varepsilon_{13}\varepsilon_{23}z^2 - \\ &-y^2\varepsilon_{11}\varepsilon_{21}x^2 - y^2\varepsilon_{12}\varepsilon_{22}y^2 - y^2\varepsilon_{13}\varepsilon_{23}z^2 \end{aligned} \right\rangle = \\
&= \langle z^4 \rangle (2\varepsilon_{13}\varepsilon_{23} - \varepsilon_{11}\varepsilon_{21} - \varepsilon_{12}\varepsilon_{22}) - \\
&- \langle z^2x^2 \rangle (-2\varepsilon_{11}\varepsilon_{21} - 2\varepsilon_{12}\varepsilon_{22} + \varepsilon_{12}\varepsilon_{22} + \varepsilon_{13}\varepsilon_{23} + \varepsilon_{11}\varepsilon_{21} + \varepsilon_{13}\varepsilon_{23}) = \\
&= \langle z^4 \rangle (2\varepsilon_{13}\varepsilon_{23} - \varepsilon_{11}\varepsilon_{21} - \varepsilon_{12}\varepsilon_{22}) - \langle z^2x^2 \rangle (2\varepsilon_{13}\varepsilon_{23} - \varepsilon_{11}\varepsilon_{21} - \varepsilon_{12}\varepsilon_{22}) = \\
&= (2\varepsilon_{13}\varepsilon_{23} - \varepsilon_{11}\varepsilon_{21} - \varepsilon_{12}\varepsilon_{22}) \langle z^4 - z^2x^2 \rangle = \\
&= \frac{1}{2} (2\varepsilon_{13}\varepsilon_{23} - \varepsilon_{11}\varepsilon_{21} - \varepsilon_{12}\varepsilon_{22})
\end{aligned}$$

$$\begin{aligned}
\langle [zy] | R | [xy] \rangle &= \langle zy(\varepsilon_{12}\varepsilon_{23} + \varepsilon_{13}\varepsilon_{22})yz \rangle = \\
&= (\varepsilon_{12}\varepsilon_{23} + \varepsilon_{13}\varepsilon_{22}) \langle (zy)^2 \rangle = \\
&= (\varepsilon_{12}\varepsilon_{23} + \varepsilon_{13}\varepsilon_{22})
\end{aligned}$$

$$\begin{aligned}
\langle [xy] | R | [xy] \rangle &= \langle xy(\varepsilon_{11}\varepsilon_{22} + \varepsilon_{12}\varepsilon_{21})xy \rangle = \\
&= (\varepsilon_{11}\varepsilon_{22} + \varepsilon_{12}\varepsilon_{21}) \langle (xy)^2 \rangle = \\
&= (\varepsilon_{11}\varepsilon_{22} + \varepsilon_{12}\varepsilon_{21})
\end{aligned}$$



6.5.2.5  $[z^2]$

$$\begin{aligned}
R|[z^2]\rangle &= R|2z^2 - x^2 - y^2\rangle = \\
&= 2(\varepsilon_{31}x + \varepsilon_{32}y + \varepsilon_{33}z)^2 - (\varepsilon_{11}x + \varepsilon_{12}y + \varepsilon_{13}z)^2 - (\varepsilon_{21}x + \varepsilon_{22}y + \varepsilon_{23}z)^2 = \\
&= 2\varepsilon_{31}^2x^2 + 2\varepsilon_{32}^2y^2 + 2\varepsilon_{33}^2z^2 + 4\varepsilon_{31}\varepsilon_{32}xy + 4\varepsilon_{32}\varepsilon_{33}yz + 4\varepsilon_{33}\varepsilon_{31}zx - \\
&\quad - \varepsilon_{11}^2x^2 - \varepsilon_{12}^2y^2 - \varepsilon_{13}^2z^2 - 2\varepsilon_{11}\varepsilon_{12}xy - 2\varepsilon_{12}\varepsilon_{13}yz - 2\varepsilon_{13}\varepsilon_{11}zx - \\
&\quad - \varepsilon_{21}^2x^2 - \varepsilon_{22}^2y^2 - \varepsilon_{23}^2z^2 - 2\varepsilon_{21}\varepsilon_{22}xy - 2\varepsilon_{22}\varepsilon_{23}yz - 2\varepsilon_{23}\varepsilon_{21}zx = \\
&= (2\varepsilon_{31}^2 - \varepsilon_{11}^2 - \varepsilon_{21}^2)x^2 + (2\varepsilon_{32}^2 - \varepsilon_{12}^2 - \varepsilon_{22}^2)y^2 + (2\varepsilon_{33}^2 - \varepsilon_{13}^2 - \varepsilon_{23}^2)z^2 + \\
&\quad + 2(2\varepsilon_{31}\varepsilon_{32} - \varepsilon_{11}\varepsilon_{12} - \varepsilon_{21}\varepsilon_{22})xy + \\
&\quad + 2(2\varepsilon_{32}\varepsilon_{33} - \varepsilon_{12}\varepsilon_{13} - \varepsilon_{22}\varepsilon_{23})yz + \\
&\quad + 2(2\varepsilon_{33}\varepsilon_{31} - \varepsilon_{13}\varepsilon_{11} - \varepsilon_{23}\varepsilon_{21})zx \\
\langle [x^2 - y^2] | R|[z^2]\rangle &= \langle (x^2 - y^2) | (2\varepsilon_{31}^2 - \varepsilon_{11}^2 - \varepsilon_{21}^2)x^2 + (2\varepsilon_{32}^2 - \varepsilon_{12}^2 - \varepsilon_{22}^2)y^2 + (2\varepsilon_{33}^2 - \varepsilon_{13}^2 - \varepsilon_{23}^2)z^2 \rangle = \\
&= \left\langle x^2(2\varepsilon_{31}^2 - \varepsilon_{11}^2 - \varepsilon_{21}^2)x^2 + x^2(2\varepsilon_{32}^2 - \varepsilon_{12}^2 - \varepsilon_{22}^2)y^2 + x^2(2\varepsilon_{33}^2 - \varepsilon_{13}^2 - \varepsilon_{23}^2)z^2 - \right. \\
&\quad \left. - y^2(2\varepsilon_{31}^2 - \varepsilon_{11}^2 - \varepsilon_{21}^2)x^2 - y^2(2\varepsilon_{32}^2 - \varepsilon_{12}^2 - \varepsilon_{22}^2)y^2 - y^2(2\varepsilon_{33}^2 - \varepsilon_{13}^2 - \varepsilon_{23}^2)z^2 \right\rangle = \\
&= \langle x^4 \rangle (2\varepsilon_{31}^2 - \varepsilon_{11}^2 - \varepsilon_{21}^2 - 2\varepsilon_{32}^2 + \varepsilon_{12}^2 + \varepsilon_{22}^2) - \\
&\quad - \langle x^2y^2 \rangle (-2\varepsilon_{32}^2 + \varepsilon_{12}^2 + \varepsilon_{22}^2 - 2\varepsilon_{33}^2 + \varepsilon_{13}^2 + \varepsilon_{23}^2 + 2\varepsilon_{31}^2 - \varepsilon_{11}^2 - \varepsilon_{21}^2 + 2\varepsilon_{33}^2 - \varepsilon_{13}^2 - \varepsilon_{23}^2) = \\
&= \langle x^4 \rangle (2\varepsilon_{31}^2 - \varepsilon_{11}^2 - \varepsilon_{21}^2 - 2\varepsilon_{32}^2 + \varepsilon_{12}^2 + \varepsilon_{22}^2) - \langle x^2y^2 \rangle (2\varepsilon_{31}^2 - \varepsilon_{11}^2 - \varepsilon_{21}^2 - 2\varepsilon_{32}^2 + \varepsilon_{12}^2 + \varepsilon_{22}^2) = \\
&= (2\varepsilon_{31}^2 - \varepsilon_{11}^2 - \varepsilon_{21}^2 - 2\varepsilon_{32}^2 + \varepsilon_{12}^2 + \varepsilon_{22}^2) \langle x^4 - x^2y^2 \rangle = \\
&= \frac{1}{2} (2\varepsilon_{31}^2 - \varepsilon_{11}^2 - \varepsilon_{21}^2 - 2\varepsilon_{32}^2 + \varepsilon_{12}^2 + \varepsilon_{22}^2) \\
\langle [zx] | R|[z^2]\rangle &= \langle zx | 2(2\varepsilon_{33}\varepsilon_{31} - \varepsilon_{13}\varepsilon_{11} - \varepsilon_{23}\varepsilon_{21})zx \rangle = \\
&= 2(2\varepsilon_{33}\varepsilon_{31} - \varepsilon_{13}\varepsilon_{11} - \varepsilon_{23}\varepsilon_{21}) \langle (zx)^2 \rangle = \\
&= 2(2\varepsilon_{33}\varepsilon_{31} - \varepsilon_{13}\varepsilon_{11} - \varepsilon_{23}\varepsilon_{21})
\end{aligned}$$

$$\begin{aligned}
\langle [z^2] | R | [z^2] \rangle &= \langle (2z^2 - x^2 - y^2) \left( (2\epsilon_{31}^2 - \epsilon_{11}^2 - \epsilon_{21}^2)x^2 + (2\epsilon_{32}^2 - \epsilon_{12}^2 - \epsilon_{22}^2)y^2 + (2\epsilon_{33}^2 - \epsilon_{13}^2 - \epsilon_{23}^2)z^2 \right) \rangle = \\
&= \left\langle \begin{aligned} &2z^2(2\epsilon_{31}^2 - \epsilon_{11}^2 - \epsilon_{21}^2)x^2 + 2z^2(2\epsilon_{32}^2 - \epsilon_{12}^2 - \epsilon_{22}^2)y^2 + 2z^2(2\epsilon_{33}^2 - \epsilon_{13}^2 - \epsilon_{23}^2)z^2 - \\ &-x^2(2\epsilon_{31}^2 - \epsilon_{11}^2 - \epsilon_{21}^2)x^2 - x^2(2\epsilon_{32}^2 - \epsilon_{12}^2 - \epsilon_{22}^2)y^2 - x^2(2\epsilon_{33}^2 - \epsilon_{13}^2 - \epsilon_{23}^2)z^2 - \\ &-y^2(2\epsilon_{31}^2 - \epsilon_{11}^2 - \epsilon_{21}^2)x^2 - y^2(2\epsilon_{32}^2 - \epsilon_{12}^2 - \epsilon_{22}^2)y^2 - y^2(2\epsilon_{33}^2 - \epsilon_{13}^2 - \epsilon_{23}^2)z^2 \end{aligned} \right\rangle = \\
&= \langle z^4 \rangle (4\epsilon_{33}^2 - 2\epsilon_{13}^2 - 2\epsilon_{23}^2 - 2\epsilon_{31}^2 + \epsilon_{11}^2 + \epsilon_{21}^2 - 2\epsilon_{32}^2 + \epsilon_{12}^2 + \epsilon_{22}^2) - \\
&- \langle z^2 x^2 \rangle \left( \begin{aligned} &-4\epsilon_{31}^2 + 2\epsilon_{11}^2 + 2\epsilon_{21}^2 - 4\epsilon_{32}^2 + 2\epsilon_{12}^2 + 2\epsilon_{22}^2 + 2\epsilon_{33}^2 - \epsilon_{12}^2 - \epsilon_{22}^2 + 2\epsilon_{33}^2 - \epsilon_{13}^2 - \epsilon_{23}^2 + \\ &+ 2\epsilon_{31}^2 - \epsilon_{11}^2 - \epsilon_{21}^2 + 2\epsilon_{33}^2 - \epsilon_{13}^2 - \epsilon_{23}^2 \end{aligned} \right) = \\
&= \langle z^4 \rangle (4\epsilon_{33}^2 - 2\epsilon_{13}^2 - 2\epsilon_{23}^2 - 2\epsilon_{31}^2 + \epsilon_{11}^2 + \epsilon_{21}^2 - 2\epsilon_{32}^2 + \epsilon_{12}^2 + \epsilon_{22}^2) - \\
&- \langle z^2 x^2 \rangle (4\epsilon_{33}^2 - 2\epsilon_{13}^2 - 2\epsilon_{23}^2 - 2\epsilon_{31}^2 + \epsilon_{11}^2 + \epsilon_{21}^2 - 2\epsilon_{32}^2 + \epsilon_{12}^2 + \epsilon_{22}^2) = \\
&= (4\epsilon_{33}^2 - 2\epsilon_{13}^2 - 2\epsilon_{23}^2 - 2\epsilon_{31}^2 + \epsilon_{11}^2 + \epsilon_{21}^2 - 2\epsilon_{32}^2 + \epsilon_{12}^2 + \epsilon_{22}^2) \langle z^4 - z^2 x^2 \rangle = \\
&= \frac{1}{2} (4\epsilon_{33}^2 - 2\epsilon_{13}^2 - 2\epsilon_{23}^2 - 2\epsilon_{31}^2 + \epsilon_{11}^2 + \epsilon_{21}^2 - 2\epsilon_{32}^2 + \epsilon_{12}^2 + \epsilon_{22}^2)
\end{aligned}$$

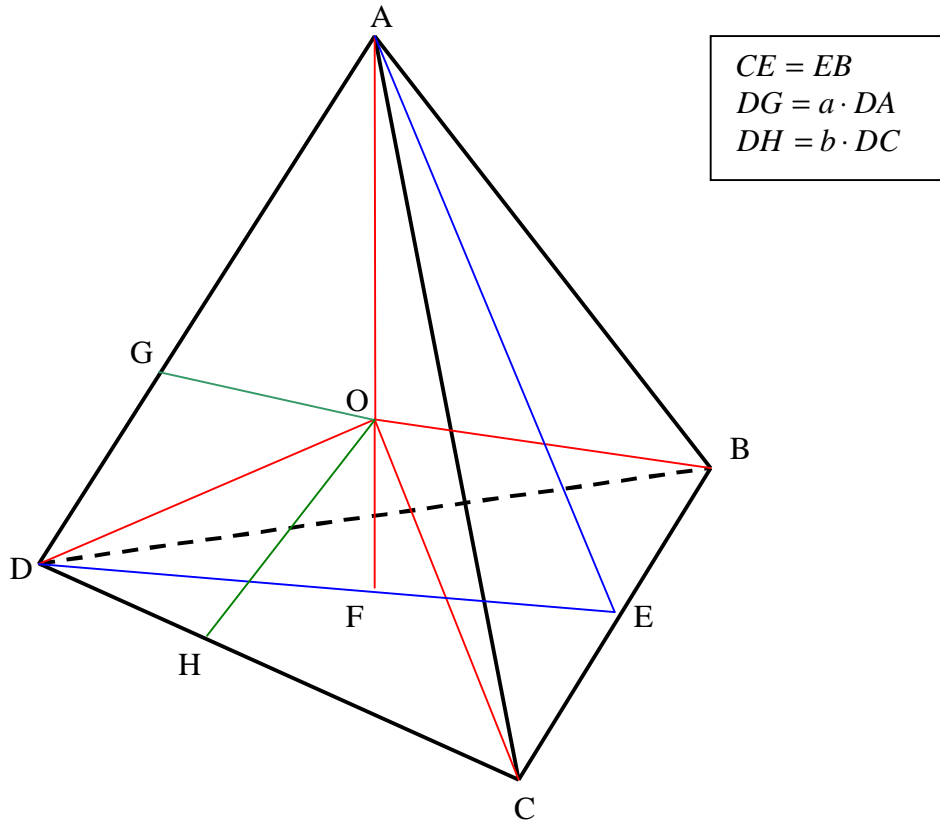
$$\begin{aligned}
\langle [zy] | R | [z^2] \rangle &= \langle zy 2(2\epsilon_{32}\epsilon_{33} - \epsilon_{12}\epsilon_{13} - \epsilon_{22}\epsilon_{23})yz \rangle = \\
&= 2(2\epsilon_{32}\epsilon_{33} - \epsilon_{12}\epsilon_{13} - \epsilon_{22}\epsilon_{23}) \langle (zy)^2 \rangle = \\
&= 2(2\epsilon_{32}\epsilon_{33} - \epsilon_{12}\epsilon_{13} - \epsilon_{22}\epsilon_{23})
\end{aligned}$$

$$\begin{aligned}
\langle [xy] | R | [z^2] \rangle &= \langle xy 2(2\epsilon_{31}\epsilon_{32} - \epsilon_{11}\epsilon_{12} - \epsilon_{21}\epsilon_{22})xy \rangle = \\
&= 2(2\epsilon_{31}\epsilon_{32} - \epsilon_{11}\epsilon_{12} - \epsilon_{21}\epsilon_{22}) \langle (xy)^2 \rangle = \\
&= 2(2\epsilon_{31}\epsilon_{32} - \epsilon_{11}\epsilon_{12} - \epsilon_{21}\epsilon_{22})
\end{aligned}$$

## 6.6 APPENDIX F Geometry of a perfect tetrahedron

On many occasions while constructing atomic positions of nanoclusters, it was necessary to refer to the information summarized below.

Point O is the center of the tetrahedron.



$$1. \cos(\angle AED) = \frac{1}{3}$$

$$2. \quad \text{If side of FCC cube} = 1: AF = \frac{\sqrt{3}}{3}, AO = \frac{\sqrt{3}}{4}, OF = \frac{\sqrt{3}}{12}$$

$$\text{If } AB = 1: AF = \frac{\sqrt{6}}{3}, AO = \frac{\sqrt{6}}{4}, OF = \frac{\sqrt{6}}{12}$$

$$3. \angle FAD = \frac{1}{2} \angle AED$$

$$4. \cos(\angle FAD) = \frac{2}{\sqrt{6}}$$

$$5. \cos(\angle AOD) = -\frac{1}{3}$$

$$6. \cos(\angle AOG) = \frac{-\frac{1}{3}[1-4a]}{\sqrt{\frac{1}{3}(3-8a+8a^2)}}$$

$$\text{For } a = \frac{1}{3}, \cos(\angle AOG) = \frac{1}{\sqrt{33}}$$

$$\text{For } a = \frac{1}{2}, \cos(\angle AOG) = \frac{1}{\sqrt{3}}$$

$$\text{For } a = \frac{2}{3}, \cos(\angle AOG) = \frac{5}{\sqrt{33}}$$

$$7. \cos(\angle AOH) = -\frac{1}{3\sqrt{1-\frac{8}{3}b+\frac{8}{3}b^2}}$$

$$\text{For } b = \frac{1}{3} \Rightarrow \cos(\angle AOH) = -\sqrt{\frac{3}{11}}$$

$$8. \cos(\angle ADE) = \frac{1}{\sqrt{3}}$$

### 6.6.1 Proofs of the identities mentioned

$$1. \cos(\angle AED) = \frac{1}{3}$$

$\triangle AEC$  :

$$\angle AEC = \frac{\pi}{2}$$

$$AE = \sqrt{1^2 - \left(\frac{1}{2}\right)^2} = \frac{\sqrt{3}}{2}$$

$\triangle AED$  :

$$AD^2 = AE^2 + ED^2 - 2 \cdot AE \cdot ED \cdot \cos(\angle AED)$$

$$AE = ED$$

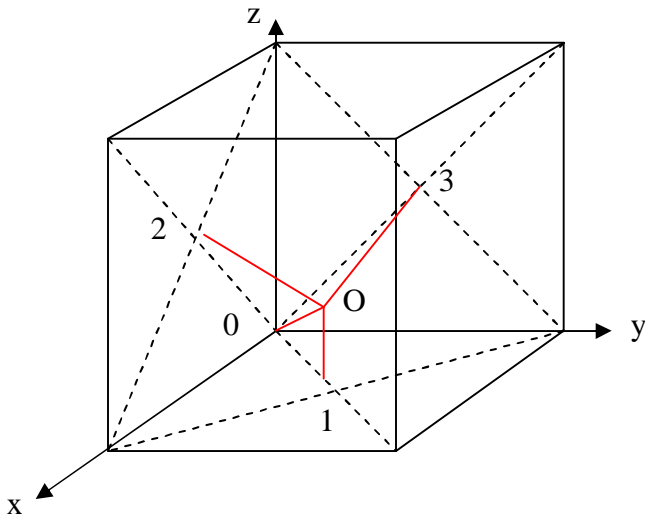
$$AD^2 = 2 \cdot AE^2(1 - \cos(\angle AED))$$

$$1 = \frac{3}{2}(1 - \cos(\angle AED))$$

$$\cos(\angle AED) = \frac{1}{3}$$

2. If side of FCC cube = 1:  $AF = \frac{\sqrt{3}}{3}, AO = \frac{\sqrt{3}}{4}, OF = \frac{\sqrt{3}}{12}$   
 If AB = 1:  $AF = \frac{\sqrt{6}}{3}, AO = \frac{\sqrt{6}}{4}, OF = \frac{\sqrt{6}}{12}$

To prove this, it is most convenient to assign some coordinates.  
 Imagine our tetrahedron is inside the usual FCC cube (cube side = 1)  
 Then the coordinates:



$$O: \frac{1}{4}(1,1,1)$$

$$1: \frac{1}{2}(1,1,0)$$

$$13: \frac{1}{2}(-1,0,1)$$

$$2: \frac{1}{2}(1,0,1)$$

$$12: \frac{1}{2}(0,-1,1)$$

$$3: \frac{1}{2}(0,1,1)$$

, So vectors

The plane is defined by vectors 12 and 13:

$$\vec{r} = \begin{pmatrix} -1 \\ 0 \\ 1 \end{pmatrix} t_1 + \begin{pmatrix} 0 \\ -1 \\ 1 \end{pmatrix} t_2 + \begin{pmatrix} 1/2 \\ 1/2 \\ 0 \end{pmatrix} = \begin{pmatrix} 1/2 - t_1 \\ 1/2 - t_2 \\ t_1 + t_2 \end{pmatrix}$$

0-O line is defined by

$$r_x = \frac{\begin{vmatrix} 1 \\ 1 \\ 1 \end{vmatrix}}{\begin{vmatrix} 1 \\ 1 \\ 1 \end{vmatrix}} t_3$$

Solving the system of three simple equations to find  $t_3$  at which OA intersects plane 123, we can find that  $t_3 = \frac{1}{3}$

So the intersect point coordinate is  $r_x = \frac{1}{3} \begin{vmatrix} 1 \\ 1 \\ 1 \end{vmatrix}$ , and its distance is  $\frac{\sqrt{3}}{3}$ .

Since the distance to point O is  $\frac{\sqrt{3}}{4}$ , subtraction will reveal the last value.

Making the cube side = 1 had made our edge length =  $\frac{\sqrt{2}}{2}$ .

So rescaling to edge length = 1 will yield the last results.

$$3. \angle FAD = \frac{1}{2} \angle AED$$

$\Delta AED$  :

$$\angle AED + \angle EAD + \angle ADE = \pi$$

$$\angle EAD = \angle ADE$$

$$2\angle ADE + \angle AED = \pi$$

$$\angle ADE = \frac{\pi}{2} - \frac{\angle AED}{2}$$

$\Delta FAD$  :

$$\angle FAD = \frac{\pi}{2} - \angle ADE = \frac{\angle AED}{2}$$

$$4. \cos(\angle FAD) = \frac{2}{\sqrt{6}}$$

Using the result of 2, where we choose AB = 1 and cosine theorem on the  $\Delta OAB$  :

$$OB^2 = OA^2 + AB^2 - 2 * OA * AB * \cos(\angle OAB)$$

Substituting and solving for  $\cos(\angle OAB)$  gives the result immediately.

$$5. \cos(\angle AOD) = -\frac{1}{3}$$

$\Delta AOD$ :

$$AD^2 = AO^2 + OD^2 - 2 \cdot AO \cdot OD \cdot \cos(\angle AOD)$$

$$AO = OD$$

$$AD^2 = 2 \cdot AO^2(1 - \cos(\angle AOD))$$

$$1^2 = 2 \cdot \left(\frac{\sqrt{6}}{4}\right)^2 (1 - \cos(\angle AOD))$$

$$\cos(\angle AOD) = -\frac{1}{3}$$

$$6. \quad \cos(\angle AOG) = \frac{-\frac{1}{3}[1-4a]}{\sqrt{\frac{1}{3}(3-8a+8a^2)}}$$

$$\text{For } a = \frac{1}{3}, \cos(\angle AOG) = \frac{1}{\sqrt{33}}$$

$$\text{For } a = \frac{2}{3}, \cos(\angle AOG) = \frac{5}{\sqrt{33}}$$

Let us now set coordinates in the following way:

OZ is along OA,

OY is in the AOD plane,

Point O is zero.

Since we are looking for angles, linear sizes do not matter, so we will make  $OA = 1$ .

Using our previous knowledge on angles:

$$OA = (0,0,1)$$

$$OD = \left(0, \sqrt{\frac{8}{9}}, -\frac{1}{3}\right)$$

$$DA = OA - OD = \left(0, -\sqrt{\frac{8}{9}}, \frac{4}{3}\right)$$

$$OG = OD + a \cdot DA = \left(0, \sqrt{\frac{8}{9}}[1-a], -\frac{1}{3}[1-4a]\right)$$

$$|OG| = \sqrt{\frac{8}{9}(1-a)^2 + \frac{1}{9}(1-4a)^2} = \sqrt{\frac{1}{3}(3-8a+8a^2)}$$

$$|OA| = 1$$

$$OG \bullet OA = -\frac{1}{3}[1-4a] = \sqrt{\frac{1}{3}(3-8a+8a^2)} \cos(\angle AOG)$$

$$\cos(\angle AOG) = \frac{-\frac{1}{3}[1-4a]}{\sqrt{\frac{1}{3}(3-8a+8a^2)}}$$

Finally, substitution of  $a = \frac{1}{3}$  and  $a = \frac{2}{3}$  will give the particular cases.

$$7. \quad \cos(\angle AOH) = -\frac{1}{3\sqrt{1-\frac{8}{3}b+\frac{8}{3}b^2}}$$

$$b = \frac{1}{3} \Rightarrow \cos(\angle AOH) = -\sqrt{\frac{3}{11}}$$

For coordinates like in the previous section, add Ox pointing towards you. (We found ourselves in a left-handed system, but that did not pose a problem)

$$OA = (0,0,1)$$

$$OD = \left(0, \sqrt{\frac{8}{9}}, -\frac{1}{3}\right)$$

$$OC = \left(\sqrt{\frac{2}{3}}, -\frac{\sqrt{2}}{3}, -\frac{1}{3}\right)$$

$$DC = OC - OD = \left(\sqrt{\frac{2}{3}}, -\sqrt{2}, 0\right)$$

$$OH = OD + DH = OD + b \cdot DC = \left(b\sqrt{\frac{2}{3}}, \sqrt{2}\left[\frac{2}{3}-b\right], -\frac{1}{3}\right)$$

$$|OA| = 1$$

$$|OH| = \sqrt{\frac{2}{3}b^2 + 2\left(\frac{2}{3}-b\right)^2 + \frac{1}{9}} = \sqrt{1-\frac{8}{3}b+\frac{8}{3}b^2}$$

$$OA \cdot OH = -\frac{1}{3} = \sqrt{1-\frac{8}{3}b+\frac{8}{3}b^2} \cos(\angle AOH)$$

$$\cos(\angle AOH) = -\frac{1}{3\sqrt{1-\frac{8}{3}b+\frac{8}{3}b^2}}$$

$$b = \frac{1}{3} \Rightarrow \cos(\angle AOH) = -\sqrt{\frac{3}{11}}$$



$$8. \quad \cos(\angle ADE) = \frac{1}{\sqrt{3}}$$

$$AE = DE = \sqrt{\frac{3}{4}}$$

$$AE^2 = DA^2 + DE^2 - 2 \cdot DA \cdot DE \cdot \cos(\angle ADE)$$

$$\frac{3}{4} = 1^2 + \frac{3}{4} - 2 \cdot 1 \cdot \frac{\sqrt{3}}{2} \cos(\angle ADE)$$

$$\cos(\angle ADE) = \frac{1}{\sqrt{3}}$$

## 6.7 APPENDIX G *Various Programs*

### 6.7.1 *Calculator*

This program is a simple utility which allows one to calculate some numbers recorded in reverse polish notation. The other utilities described below are using same calculator format notation in their respective configuration files.

To execute:

**> ./Calculator <name of config file>**

config file – file containing an algebraic expression enclosed between the opening and closing tokens. One can change opening and closing tokens by changing the macros in the code and recompiling the program. Currently the tokens are square brackets: [ ]

The rules of calculator are in the **calc.rules.txt** file shown below

```
=====  
Calculator rules file.  
=====
```

This calculator will calculate a result of expression between OPEN and CLOSE tokens which you can define in the calling program. Those tokens should be something unique, for example [ and ].

Any other token inbetween OPEN and CLOSE will be processed by calculator.

Tokens processed should be valid tokens.

Tokens should be separated by at least one SPACE

Invalid tokens will result in calc\_error and abort.

Calculator is polish (stack) notation,  
i.e. you need to fill stack and then say what operations to do.  
For example to calculate  $\sqrt{3}/2$  you will need to enter  
[3 sqrt 2 div]

Or to get  $\sin(\pi/3)$  you will need to enter  
[PI 3 div sin]

It behaves exactly like the HP calculators

Valid tokens include NUMBERS, CONSTANTS and OPERANDS  
NOTE: ALL constants and operands are CASE SENSITIVE !  
so if you will put Sqrt, it will NOT recognize it.

ALL tokens must be separated by spaces.

-NUMBERS

Can be any number in any format.

If you want negative, put minus sign in front.

There should be no spaces between neg.sign and number.  
Plus sign also available.

Examples:

1  
-1  
1.0  
-1.0E-5

-CONSTANTS

PI = 3.1415...  
EE = base of natural log

-OPERANDS

Stack ops:

sdv - remove and Discard top stack value  
scv - Copy top stack value into next stack cell  
( push top value once more )

Memory ops:

# = 0 ... MAX\_MEM - integer index  
mca - All mem = 0  
# mc - mem# is set to 0  
(X) # ms - mem# = X, X remains in stack unchanged  
(X) # m+ - mem# += X, X remains in stack unchanged  
(X) # m- - mem# -= X, X remains in stack unchanged  
# mg - Value from mem# being pushed into stack  
( # is removed from stack before all mem ops )

Math ops:

neg - negates number on the top of the stack  
mul - multiply 2 number on the top of the stack  
div - division  
add - addition  
sub - subtraction  
sqrt - square root  
sqr - x squared

sin - sin  
cos - cos  
tan - tan  
asin - arc sin  
acos - arc cos  
atan - arc tan

log - natural log  
log10 - log base 10  
exp - natural exponent (e to the power of x)  
exp10 - 10 to the power of x  
pow - x to the power of y (y is the last entered, on the top of

stack)

## 6.7.2 CrSlab

The purpose of this utility is to facilitate creation of nanostructures which are cut out of periodic structure.

The boundary is composed of a sphere and any number of planes.

To execute:

```
> ./CrSlab <name of config file>
```

where <config file> is filename of your file containing information about your structure. The example config file is shown below (some comments and explanations are following the file)

```
# This is example config file for CrSlab
# Feel free to change helps/numbers,
# but not the order of arguments in this file.
#
# Whenever you can see [], you can use calculator expressions.
# For rules and available commands see file calc.rules.txt
# Limitations of calc due to CrSlab:
# MAX length of control string = 1020 symbols
# MAX stack is 64 numbers
# OPEN and CLOSE tokens = [ and ] respectively
#
# This example creates a one FCC cube

# Output filename, should never exceed 1024 - 1 symbol
fcc.xyz

# Number of "sublattices"
# plain number, no calc
1

# Here we have one type of species for one sub-lattice.
# Tell me Z of every sub-lattice
# Plain number, no calc
48.0

# Now tell the origins of every sub-lattice
# first sub-lattice
[0.00] [0.00] [0.00]

# And basis vectors for every sub-lattice
# first sub-lattice
[0.5] [0.5] [0.0]
[0.5] [0.0] [0.5]
[0.0] [0.5] [0.5]

# The sphere information:
# Sphere origin
[0.0] [0.0] [0.0]

# Sphere radius - should be either boundary
```

```

# or a maximum sphere including all your structure
[2.0]

# Now the planes.
# Tell the number of planes:
[6]

# Tell me vector defining each plane:
# Format is [<scale factor>] [<x>] [<y>] [<z>]
# You dont need to put + or - in front of number,
# I put it just to align numbers nicely
[1.0] [+1.1] [+0.0] [+0.0]
[1.0] [-0.1] [+0.0] [+0.0]

[1.0] [+0.0] [+1.1] [+0.0]
[1.0] [+0.0] [-0.1] [+0.0]

[1.0] [+0.0] [+0.0] [+1.1]
[1.0] [+0.0] [+0.0] [-0.1]

```

**sublattice** – a simple structure defined by three basis vectors and an origin. You can have any number of those. For example CdSe structure could be described as two FCC sublattices.

**sphere** and **planes** – are boundaries of the structure.

**Sphere** is defined by origin coordinates and radius; it is also used in calculation of maximum indices for your structure. So even if you not using it, do not make it smaller than your structure, but at the same time don't make it too big.

**Planes** are defined by vectors from the coordinate origin. Those vectors are perpendicular to the planes and they are defining the distances from origin to the planes. Scale factors are introduced for the convenience – one has an option to use unit vectors and put the length into scale factor.

### 6.7.3 *MicroCluster*

Sometimes you need to create a simple or small structure for FIREBALL, but also need to use a calculator for the coordinates. The **MicroCluster** is a tool you might consider using in such a situation.

To execute:

```
> ./MicroCluster <in-file> <out-file>
```

**in-file** – file containing FIREBALL-like format, but with **Calculator** expressions.

The format is:

```
<number-of-atoms>
```

```
Z [X] [Y] [Z]
```

```
...
```

**Microcluster** will read only <number-of-atoms> non-empty lines from top to bottom.

**out-file** – file with resulting coordinates.

As an example, the ideal benzene file is included below.

Notice the usage of calculator memory to avoid repetition of the same calculations.

12

```
6.0 [3 sqrt 8 div 0 ms] [0 mg 1.4 div 0 mg add 1 ms sdv 0] [0]
6.0 [0 mg 2 div 2 ms] [0 mg 3 sqrt 2 div mul 3 ms] [0]
6.0 [2 mg neg] [3 mg] [0]
6.0 [0 mg neg] [0] [0]
6.0 [2 mg neg] [3 mg neg] [0]
6.0 [2 mg] [3 mg neg] [0]

1.0 [1 mg 2 div 4 ms] [1 mg 3 sqrt 2 div mul 5 ms] [0]
1.0 [4 mg neg] [5 mg] [0]
1.0 [1 mg neg] [0] [0]
1.0 [4 mg neg] [5 mg neg] [0]
1.0 [4 mg] [5 mg neg] [0]
1.0 [1 mg] [0] [0]
```

#### 6.7.4 Cluster

This program will create a structure out of **sub-clusters**. One can create a number of “Lego building blocks” and then use **Cluster** to put them together. There is no need to create a number of ligands if you can use same one rotated and positioned appropriately! This program can rotate, shift, scale and insert a comment for correct VMD file format. To execute:

```
> ./Cluster <config file>
```

The simplest example of config file is in **cfg.example.Cluster.txt** file shown below

```
# Example config file for Cluster program

# Put comment for VMD?
# The comment will be ONLY in the LAST fragment,
# Fragments are like separate runs of program bundled together.
# I.e. All files after fragment is done are closed and written,
# so in the next fragment you can use result of previous one.
# Comment or NO (NO is Case sensitive)
A comment

# Total number of fragments
1

# For each fragment:
# Output filename, max length is 1024-1 = 1023
out.xyz

# Number of sub-clusters
1
```

```

# For each sub-cluster,
# tell some data in the following format:
#
#
# <filename>          - filename of sub-cluster
#                      max length = 1024-1 = 1023
#
# <coord.option>      - x, y, z coords below is:
#                      -1 - do not shift, leave Rotational Center (RC)
#                          where it was
#                      0 - cartesian          [x] [y] [z]
#                      1 - polar spherical   [rho] [theta] [phi]
#                          (in radians)
#                      in the case of polar, only rho is being scaled
#
# [scale vector] [x] [y] [z]
#                      - where to put RC of this sub-cluster
#                      ( depend on the above option)
#
# [scale cluster] - With respect to RC, scale coordinats
#                      by multiplying by this number
#
# <rc.option>         0 - rotate WR to center of the cluster
#                      (xyz of RC will be replaced by center)
#                      1 - rotate about coordinates given
#
# [x] [y] [z]         - RC coordiantes (cartesian only!)
# [a] [b] [c]         - Turn angles as explained below.
#
# Turn angles explained:
# This is most common Euler angles.
# Rotation is performed around RC of the sub-cluster
# a - phi - rotation about Z
# b - theta - rotation about new X
# c - psi - rotation about new Z
# all angles is in radians!
#
# Note:
# First it finds vector of a point with respect to RC
# Next it scales it (WR to RC!)
# Then rotates (about RC!)
# And finally shifts RC into given coordinates X

fcc.xyz
0
[1.0] [0.0] [0.0] [0.0]
[3.5]
0
[0] [0] [0]
[PI 4 div] [0.0] [0.0]

```

The better explanation of configuration file for the **Cluster** program is presented in a block diagram below.

```
# A comment for VMD? Put NO (case sensitive) for none
# It will be on the last fragment
A comment
```

```
# Total number of fragments
N
```

```
# Output filename of fragment
fragment_1_out.txt

# Number of sub-clusters
M
```

Fragment  
header

```
sub_cluster_input_1.xyz
0
[1.0] [0.0] [0.0] [0.0]
[3.5]
0
[0] [0] [0]
[PI 4 div] [0.0] [0.0]
```

...

```
sub_cluster_input_M.xyz
0
[1.0] [0.0] [0.0] [0.0]
[3.5]
0
[0] [0] [0]
[PI 4 div] [0.0] [0.0]
```

M of those blocks  
describing the  
positioning of each  
sub-cluster  
**NO** comments  
**inside** each block!

repeat for  
each of the  
N  
fragments

```
<sub-cluster input filename>
<coord.option>
    -1 - do not shift, leave Rotational Center where it was
    0 - cartesian          [x] [y] [z]
    1 - polar spherical    [rho] [theta] [phi]
[scale vector] [x] [y] [z]
    Shift Vector of this sub-cluster
    (depend on above coord.option)
    Describes where Rotational Center (RC) will be put
[scale cluster]
    With respect to RC, scale coordinates by multiplying by
    this number
<rc.option>
    0 - RC is geometrical center of the cluster
    1 - RC coordinates are given below
[X] [Y] [Z]
    RC coordinates - Cartesian. Ignored if rc.option = 0
[phi] [theta] [psi]
    Rotational angles with respect to RC
```



## 7 REFERENCES

- 1 Likharev K. K., 1999 Proc. IEEE 87 606
- 2 L. Y. Gorelik, A. Isacson, M. V. Voinova, B. Kasemo, R. I. Shekhter, M. Jonson, Phys. Rev. Letters, Vol. 80, No. 20, 8 May 1998, 4526-4529
- 3 S. P. Gubin, Yu. V. Gulayev, G. B. Khomutov, V. V. Kislov, V. V. Kolesov, E. S. Soldatov, K. S. Sulaimankulov, A. S. Trifonov, Nanotechnology 13 (2002) 185-194
- 4 E. S. Soldatov, V. V. Khanin, A. S. Trifonov, D. E. Presnov, S. A. Yakovenko, G. B. Khomutov, JETP Lett., Vol. 64, No. 7, 10 Oct 1996 556-560
- 5 S. E. Kubatkin, A. V. Danilov, A. L. Bogdanov, H. Olin, T. Claeson, Appl. Phys. Lett., Vol. 73, No. 24, 14 Dec 1998 3604-3606
- 6 A. V. Danilov, D. S. Golubev, S. E. Kubatkin, Phys. Rev. B, Vol. 65, 125312
- 7 Freitas, Robert A., Jr., Nanotech. Biol. Med. 1(March 2005):2-9
- 8 Bullis, Kevin (Mar/Apr 2006), Technology Review 109 (1): 58-59
- 9 Langar, Robert, David A. LaVan, Terry McGuire., Nature Biotechnology Oct. 2006: 1184-1191
- 10 Allen, Theresa M, and Peter R. Cullis., Science 303 (2004): 1818-1822
- 11 Otto F. Sankey, David J. Niklewski, Physical Review B, Vol. 40 (Num. 6), 3979 (15 Aug 1989-II)
- 12 James P. Lewis, Kurt R. Glaesemann, Gregory A. Voth, Jürgen Fritsch, Alexander A. Demkov, José Ortega, Otto F. Sankey, Physical review B, Vol. 64, 195103
- 13 Adrian P. Sutton, *Electronic structure of materials*, ISBN 0-19-851754-8
- 14 Marder, Michael P., 1960, *Condensed matter physics*, ISBN 0-471-17779-2
- 15 E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).
- 16 Mark E. Casida, in *Recent Developments and Applications of Modern Density Functional Theory*, (ed. J.M. Seminario, Elsevier Science B.V., 1996)
- 17 Christine Jamorski, Mark E. Casida, and Dennis R. Salahub, J. Chem. Phys. 104 (13), 1 April 1996, 5134-5147
- 18 R.S. Mulliken, J. Chem. Phys., 1955, Vol. 23, 1833-1840
- 19 E. E. Koch, A. Otto, Chem. Phys. Letters, Vol. 12, No. 3, 1 Jan 1972, 476-480
- 20 Rudiger Bauernschmitt, Reinhart Ahlrichs, Frank H. Hennrich, and Manfred M. Kappes, J. Am. Chem. Soc. 1998, 120, 5052-5059
- 21 George F. Bertsch, Aurel Bulgac, David Tomanek and Yang Wang, Phys. Rev. Lett., Vol. 67, No. 19, 4 Nov. 1991, 2690-2693

- 22 Brent Walker, A. Marco Saitta, Ralph Gebauer, and Stefano Baroni, PRL 96, 113001 (2006), 24 March 2006
- 23 Ernest R. Davidson, Computers in Physics, Vol. 7, No. 5, Sep/Oct 1993, 519-522