QUANTUM MONTE CARLO STUDY OF ELECTROSTATIC POLARIZABILITIES OF H AND HE ATOMS

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Abstract

The infinitesimal differential quantum Monte Carlo (QMC) technique is used to estimate electrostatic polarizabilities of the H and He atoms up to the sixth order in the electric field perturbation. All 542 different QMC estimators of the non-zero atomic polarizabilities are derived and used in order to decrease the statistical error and to obtain the maximum efficiency of the simulations. We are confident that the estimates are "exact" (free of systematic error): the two atoms are nodeless systems, hence no fixed-node error is introduced. Furthermore, we develope and use techniques which eliminate systematic error inherent when extrapolating our results to zero time-step and large stack-size.

The QMC results are consistent with published accurate values obtained using perturbation methods. The precision is found to be related to the number of perturbations, varying from 2 to 4 significant digits.

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Chapter 1

Introduction

Non-linear optical properties describe the response of a system to an external electro-magnetic field. These properties depend generally on the frequency of the field, and they are called the dynamic electric polarizabilities (or non-linear susceptibilities) of various degrees [1]. In the case of an electrostatic external field, the polarizabilities are referred to as the *electrostatic* polarizabilities [2, 3]. Essentially, they are dynamic polarizabilities evaluated at the zero frequency.

Both static and dynamic polarizabilities are of a great importance not only in non-linear optics [4–8], but also in the description of molecular interactions [2, 9–13] for simulations of gases and liquids and for understanding the chemical structure of large molecules.

Although low-order polarizabilities (up to 4th degree) have been successfully measured for several systems, the higher order ones remain a rather daring challenge for experimentalists [14–17]. On the other hand, there are many *ab initio* theoretical approaches dealing with high order polarizabilities within the framework of perturbation theories; see [18–30] (static) and [31–45] (dynamic). For relatively small systems, this approach can be used to converge to results with high precision. However, it becomes quite an impossible task for larger systems, because of the necessity to reconstruct excited states of the system.

Quantum Monte Carlo (QMC) methods of solving the Schrödinger equation for atoms and molecules have essentially the same level of complexity for systems of any size [46–50]. They have been used to estimate molecular dipoles [51, 52, 53],

dynamic polarizabilities [54], and other derivatives of the ground-state energy with respect to perturbations [55, 56, 57].

The objective of this work is to develop the QMC technique to estimate all atomic *electrostatic* polarizabilities up to the sixth degrees. We are interested in the static properties, because it allows us to test the technique without complications with the frequency dependence. Moreover, it seems that the extension of this work for the dynamic polarizabilities rests on a simple modification of the obtained theoretical formulation in this work.

The key idea of our approach is that by using the QMC algorithm without physical branching [58], we can estimate the polarizabilities directly *at zero* perturbation. In other words, no finite perturbation approximation is applied. To explore this technique, polarizabilities of H and He atoms are estimated. The fixed-node QMC algorithm provides unbiased estimates of the exact ground-state properties of these atoms, because they are node-less systems. This, and the fact that very accurate results of perturbation methods for static polarizabilities up to the sixth order of H and He have been published [26], makes them very suitable benchmark cases.

The advantage of these systems in particular is that we can investigate the statistical error of our results to gauge the feasibility of applying QMC to large systems. Towards this end, it is very important to design the simulations efficiently, so that the QMC estimates have the highest precision possible. In this work, in a sense *all* information contained in the simulation is used and the effectiveness of the method for various polarizabilities is compared.

The thesis is intended to provide all necessary background of the quantum Monte Carlo simulations (Chapter 2), such as equivalency of the diffusion and Schrödinger equation and procedures for simulating diffusion and for estimating the ground-state energy.

Selected topics from the theory of electrostatics, namely the concept of multipole moments, their traceless form, polarizabilities and atomic polarizabilities and relations between them due to the spherical symmetry are discussed in Chapter 3. Chapter 4 explains the so-called "infinitesimal differential diffusion Monte Carlo" technique [55] for estimating the polarizabilities and contains the main theoretical results of the thesis: formulas for QMC estimators for all non-zero atomic electrostatic polarizabilities up to the sixth degree. Technical details concerning the simulations are discussed in the Chapter 5, such as the basic structure of the programs, the trial functions used, and the procedure of extracting the maximum possible amount of information about the polarizabilities from the simulated data. Finally, Chapter 6 contains the simulation results, discussion, and conclusions.

Chapter 2

Diffusion and Quantum Mechanics

2.1 Simple Diffusion

Diffusion of particles is a stochastic process driven by differences in their density. In the case of isotropic diffusion in 3-dimensions with no external potential and a constant number of particles we can write for the density of particles $\rho(t, x, y, z)$ the diffusion equation in the form

$$\frac{\partial \rho}{\partial t} = D\nabla^2 \rho \tag{2.1}$$

where $D > 0$ is the diffusion constant. The solutions of this equation for any initial distribution $\rho(t_0, x, y, z)$ correspond to random motion of the particles from regions in space with larger density to regions with smaller density. Clearly, the equilibrium or steady state would be achieved after infinite time, when the particles would be spread all over the space. However, since all space is truly infinite, this ideal situation can not be reached, because the norm of the distribution which corresponds to the number of particles is constant. [1]

It is easy to generalize the described 3-dimensional diffusion to diffusion in a space with a general dimension N. The generalized diffusion equation remains in the form (2.1). The only change is that instead of a 3-dimensional spatial coordinate we have now a N-dimensional vector $\mathbf{R} = [x_1, \ldots, x_N]$ and $\nabla = [\frac{\partial}{\partial x_1}, \ldots, \frac{\partial}{\partial x_N}]$. From this point on we will assume that the dimension of space is general.

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[1] Equation (2.1) is nothing else than the equation of continuity for ρ with the flux of particles $J = -D\nabla\rho$ and no sources.

There are several ways to numerically solve equation (2.1) for a given initial state ρ_0 [59]. The Monte Carlo method uses explicitly the diffusion process described by the equation to simulate estimates of the distribution ρ at any $t > t_0$. Before we describe the method, it is essential to understand the basics of Green's functions formalism.

The diffusion equation in its integral form

$$\rho(t, \mathbf{R}) = \int G(\mathbf{R}, t, \mathbf{R}', t_0)\rho_0(\mathbf{R}')\, d^N\mathbf{R}' \tag{2.2}$$

defines a symmetric function $G(\mathbf{R}, t, \mathbf{R}', t_0)$, the so-called "Green's function" of the equation. Important properties of Green's functions are

1. $G(\mathbf{R}', t, \mathbf{R}, t_0) = G(\mathbf{R}, t, \mathbf{R}', t_0)$
2. $G(\mathbf{R}, t_0, \mathbf{R}', t_0) = \delta^N(\mathbf{R} - \mathbf{R}')$

Once we know the form of Green's function of a equation, we can calculate the solution $\rho(t, \mathbf{R})$ through the relation (2.2).

The Green's function of the diffusion equation (2.1) is known analytically and is equal to

$$G(\mathbf{R}, t, \mathbf{R}', t_0) = \frac{1}{(4\pi D(t - t_0))^{3N/2}} \exp\left[-\frac{(\mathbf{R} - \mathbf{R}')^2}{4D(t - t_0)}\right], \quad t > t_0 \tag{2.3}$$

It is easy to verify that the solution (2.2) with this Green's function plugged-in satisfies the original equation (2.1).

The fact that the Green's function (2.3) is simply a multidimensional Gaussian spreading in time allows us to simulate the diffusion process by the following procedure:

1. Choose a finite number of particles
2. Distribute them according to the initial distribution ρ_0

3. To obtain an estimate of ρ at any time $t > t_0$, move each particle according to

$$\mathbf{R} \mapsto \mathbf{R} + \sqrt{2D(t - t_0)}\ \bar{\eta} \tag{2.4}$$

where $\bar{\eta}$ is N-dimensional vector of random standard-normal deviates (for each particle a new one)

2.2 Diffusion in an External Potential

To generalize from the simple diffusion described in the previous section, let us consider an external potential generating an external force acting on the particles. In this case we still have a constant population, but together with the random diffusion motion there is a global systematic motion of the particles caused by the external force. This systematic motion is called the *drift* of the particles.

The diffusion equation for the density of the particles is now (in N dimensions)

$$\frac{\partial \rho}{\partial t} = D\nabla^2 \rho - \nabla \cdot (\rho \mathbf{F}) \tag{2.5}$$

where $\mathbf{F}(\mathbf{R})$ is the time-independent external N-dimensional drift field. The norm of ρ is conserved in time. [2] The steady state of the distribution is a solution of the equation (2.5) with zero partial time derivative on the left hand side. Generally an infinite time is required to reached this equilibrium.

Monte Carlo simulation of the diffusion process in the external potential is based on modification of Green's function (2.3). This modification rests on the idea that during a small time interval δt (the so-called "time-step"), we can assume the drift field to be constant on the corresponding path of a particle. Therefore we can view its motion as two independent motions: the diffusion and the drift displacement, which under these assumptions is simply $\delta t \mathbf{F}(\mathbf{R})$. Thus,

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[2] Again, this equation is the equation of continuity for the flux $J = -D\nabla\rho + \rho\mathbf{F}$.

the modified Green's function is a multidimensional Gaussian centered at the shifted position $\mathbf{R} + \delta t \mathbf{F}(\mathbf{R})$ of the particle

$$G(\mathbf{R}, t, \mathbf{R}', t_0) = \frac{1}{(4\pi D\delta t)^{3N/2}} \exp\left[-\frac{(\mathbf{R} - \mathbf{R}' - \delta t \mathbf{F}(\mathbf{R}'))^2}{4D\delta t}\right] \tag{2.6}$$

This Green's function is surely not the exact one, it violates the condition of symmetry mentioned earlier. It is just a (short-time) approximation to the unknown exact Green's function of the equation (2.5), but it converges to the exact Green's function as $\delta t \to 0$ [60].

Therefore Monte Carlo simulation of the diffusion in an external potential by using this Green's function is only an approximation to the process defined by (2.5). The simulation is strongly dependent on dividing any finite time difference into n small time intervals and performing n successive short-time diffusions. The last step (3.) of the procedure from the previous section now changes to

3. To obtain an estimate of ρ at a time $t > t_0$, move each particle $n = (t - t_0)/\delta t$ times according to

$$\mathbf{R} \mapsto \mathbf{R} + \delta t \mathbf{F}(\mathbf{R}) + \sqrt{2D\delta t}\ \bar{\eta} \tag{2.7}$$

   where δt is a small time-step chosen to meet some requirements of accuracy

Any information extracted from the simulated diffusion process is dependent on the chosen time step δt. The simulation described above should be repeated for different reasonable time steps and a proper $\delta t \to 0$ extrapolation of the information performed.

2.3 Diffusion in an External Potential with Sources

In the two previous sections we described diffusion processes, where the number of particles was a time-independent constant. It is very natural to generalize the

diffusion process further by assuming that new particles can be created or the existing particles can be removed locally. This situation corresponds to some source function $S(\mathbf{R})$ defined in the space with the meaning of a density of new particles created at position $\mathbf{R}$ during a unit time interval. If it is a hole, the density of new particles would be negative. The equation of such diffusion is

$$\frac{\partial \rho}{\partial t} = D\nabla^2\rho - \nabla \cdot (\rho\mathbf{F}) + S(t, \mathbf{R}) \tag{2.8}$$

The complex process described by this equation can be viewed as a combination of three separate processes: diffusion characterized by D, drift characterized by $\mathbf{F}$, and branching given by the source function S. It is important to note that this separation is again an approximation which allows us to simulate the diffusion, drift and the branching processes separately.

Before we show how to deal with the branching of the particles, we will first constrain ourselves to a special case of the source function describing a first-order rate process

$$S(t, \mathbf{R}) = k(\mathbf{R})\rho(t, \mathbf{R}) \tag{2.9}$$

The rate function $k(\mathbf{R})$ is a time-independent function of spatial coordinates. In regions where $k > 0$ new particles are created at a rate k, and where $k < 0$, the existing particles vanish at that rate.

The generalized diffusion equation (2.8) now has the following form

$$\frac{\partial \rho}{\partial t} = D\nabla^2\rho - \nabla \cdot (\rho\mathbf{F}) + k(\mathbf{R})\rho \tag{2.10}$$

If we look at the branching part of the equation (2.10) only, we will get the familiar first order rate equation

$$\frac{\partial \rho}{\partial t} = k(\mathbf{R})\rho \tag{2.11}$$

The solution of this partial differential equation with a initial condition ρ_0 is easily obtained

$$\rho(t, \mathbf{R}) = \rho_0(\mathbf{R}) \exp\left[k(\mathbf{R})(t - t_0)\right] \tag{2.12}$$

The simulation of branching is therefore based on replacing the initial number of particles at some point by $\exp(k(\mathbf{R})(t-t_0))$ new particles. Because this number is not generally an integer, the proper scheme is to replace the particle by the integer part of $(\exp(k(\mathbf{R})(t-t_0)) + \xi)$ new particles, where ξ is an uniformly distributed random number from 0 to 1.

To summarize the whole procedure of simulating diffusion, drift and branching, the following step is added to the description from the previous sections

4. Replace each particle by $int[\exp(k(\mathbf{R})(t-t_0))+\xi]$ new particles at the same position. If this number is zero, the particle is deleted. Random number ξ is uniformly generated from interval $0 \ldots 1$

Again, a proper extrapolation of any information obtained from simulations with various time step values is necessary to obtain unbiased information about the true diffusion-branching process. In this case it is even more critical than without sources, because we are using the approximate Green's function (2.6) as well as the assumption of the separability of diffusion, drift and branching processes. The limit $\delta t \to 0$ is fully legitimate in the sense that in this limit the combined diffusion and branching Green's functions approach the exact Green's function of equation (2.10) [60].

2.4 Quantum Monte Carlo Evaluation of Expectation Values

In this section we connect quantum and statistical mechanics, which is the basic idea behind quantum Monte Carlo simulations, see for example [46].

Let us suppose we want to calculate the ground-state energy of an atom or a molecule. Within the Bohr-Oppenheimer approximation, the Hamiltonian can be written as (atomic units, $m_e = e = \hbar = 1$)

$$\mathrm{H} = -\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2 + V(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{2.13}$$

where N is the number of electrons. The first term is the total electronic kinetic energy, and the second term is the potential energy consisting of three parts: electron-electron repulsion, electron-nucleus attraction, and nucleus-nucleus repulsion (for molecules).

Each electron has three spatial coordinates. Therefore each configuration of N electrons is represented by $3N$ coordinates. By utilizing the notation from previous sections, we define a $3N$-dimensional configuration vector $\mathbf{R}$ of the system and the corresponding Laplacian ∇ as

$$\mathbf{R} \equiv [\mathbf{r}_1, \ldots, \mathbf{r}_N] \tag{2.14}$$

$$\nabla \equiv [\nabla_1, \ldots, \nabla_N] \tag{2.15}$$

The Hamiltonian (2.13) has now the following compact form

$$\mathrm{H} = -\frac{1}{2}\nabla^2 + V(\mathbf{R}) \tag{2.16}$$

Any possible state $\phi(\mathbf{R}, t)$ of the system is a solution of the time-dependent Schrödinger equation

$$i\frac{\partial \phi(\mathbf{R}, t)}{\partial t} = (\mathrm{H} - E_T)\phi(\mathbf{R}, t) \tag{2.17}$$

where E_T is an arbitrary energy shift. According to the theory of partial differential equations, this is a parabolic wave equation with an initial condition

$$\phi(\mathbf{R}, t_0) = \phi_0(\mathbf{R}) \tag{2.18}$$

Its solution can be written as (spectral theorem)

$$\phi(\mathbf{R},t)=\sum_i C_i\Phi_i(\mathbf{R})\exp\left(-i(t-t_0)(E_i-E_T)\right) \tag{2.19}$$

where Φ_i and E_i are the eigenstates and eigenvalues of the Hamiltonian

$$\mathrm{H}\Phi_i(\mathbf{R})=E_i\Phi_i(\mathbf{R}) \tag{2.20}$$

The coefficients C_i are defined as

$$C_i=\int\phi_0(\mathbf{R})\Phi_i^*(\mathbf{R})\; d^{3N}\mathbf{R} \tag{2.21}$$

The index i denotes the eigenstates and eigenvalues Φ_i, E_i in such order that Φ_0 and E_0 are the ground-state eigenfunction and the ground-state energy of the system, respectively. Bound electronic eigenstates Φ_i of the Hamiltonian (2.16) can be assumed to be real functions.

Quantum Monte Carlo technique is based on the fact that the time-dependent Schröginger equation (2.17) transformed to an imaginary time is equivalent to the generalized diffusion equation (2.10). The proof of this theorem is as follows.

By defining the imaginary time

$$\tau=it \tag{2.22}$$

we can write the Schrödinger equation (2.17) and its solution (2.19) in the following forms

$$-\tfrac{\partial\phi(\mathbf{R},\tau)}{\partial\tau}=(-\tfrac{1}{2}\nabla^2+V(\mathbf{R})-E_T)\phi(\mathbf{R},\tau) \tag{2.23}$$

$$\phi(\mathbf{R},\tau)=\sum_i C_i\Phi_i(\mathbf{R})\exp\left(-(\tau-\tau_0)(E_i-E_T)\right) \tag{2.24}$$

where we used the definition of the Hamiltonian (2.16).

Let a $\Psi(\mathbf{R})$ to be a two-times differentiable real function which has everywhere in $3N$-dimensional space the same sign as the time-independent ground-state Φ_0

and satisfies [3]

$$\int \Psi(\mathbf{R})^2 \, d^{3N}\mathbf{R} < +\infty \tag{2.25}$$

Multiplying the equation (2.23) by $-\Psi$ and using a formula

$$\Psi\nabla^2\phi = \nabla^2(\Psi\phi) + \phi\nabla^2\Psi - 2\nabla\cdot(\phi\nabla\Psi) \tag{2.26}$$

yields to the following equivalent equation

$$\frac{\partial(\phi\Psi)}{\partial\tau} = \frac{1}{2}\nabla^2(\phi\Psi) - \nabla\cdot(\phi\nabla\Psi) - \left(-\frac{1}{2}\frac{\nabla^2\Psi}{\Psi} + V(\mathbf{R}) - E_T\right)\phi\Psi \tag{2.27}$$

By introducing a distribution function

$$\rho(\mathbf{R},\tau) = \phi(\mathbf{R},\tau)\Psi(\mathbf{R}) \tag{2.28}$$

a *drift* vetor field

$$\mathbf{F} = \frac{\nabla\Psi}{\Psi} \tag{2.29}$$

and the *local energy* function

$$E^{loc} = \frac{\mathrm{H}\Psi}{\Psi} \tag{2.30}$$

we can rewrite (2.27) into the following form

$$\frac{\partial\rho}{\partial\tau} = \frac{1}{2}\nabla^2\rho - \nabla\cdot(\mathbf{F}\rho) - \left(E^{loc}(\mathbf{R}) - E_T\right)\rho \tag{2.31}$$

This equation is equivalent to the time-dependent Schrödinger equation (2.17) describing an atom or a molecule, and its form is identical to that of the generalized diffusion equation (2.10). Thus, it describes a diffusion of particles with a density ρ (2.28), external drift $\mathbf{F}$ (2.29) and branching rate function $k = -(E^{loc} - E_T)$. The diffusion coefficient is $D = \frac{1}{2}$, and the particles are moving in $3N$-dimensional space.

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[3] These conditions ensure that Ψ can be an approximation of the ground-state Φ_0.

Now we will show that the diffusion process described by (2.31) converges after a sufficently long time to its steady state. For large imaginary times only the first term in (2.24) will dominate

$$\phi(\mathbf{R},\tau) \rightarrow C_0\Phi_0(\mathbf{R})\exp\left(-(\tau-\tau_0)(E_0-E_T)\right), \ \tau\rightarrow\infty \tag{2.32}$$

and the distribution function ρ will reach in this limit the so-called "mixed distribution"

$$\rho(\mathbf{R},\tau) \rightarrow C_0\Phi_0(\mathbf{R})\exp\left(-(\tau-\tau_0)(E_0-E_T)\right)\Psi(\mathbf{R}) \propto \Phi_0\Psi \equiv \rho_m(\mathbf{R}) \tag{2.33}$$

The existence of the steady state of the diffusion process allows us to estimate the ground-state energy of an atom or a molecule. Even though we don't know the exact ground-state solution Φ_0, by simulating the diffusion and branching process we will obtain, after a sufficiently large number of iterations of the procedure described in the previous section (equilibration), an estimate of the mixed distribution, which contains information about the unknown exact solution via (2.33).

This information can be extracted by using the hermiticity of the Hamiltonian and the following expression for the ground-state energy

$$E_0 = \frac{\langle\Phi_0|\mathrm{H}|\Psi\rangle}{\langle\Phi_0|\Psi\rangle} = \frac{\int \Phi_0\Psi\left(\frac{\mathrm{H}\Psi}{\Psi}\right)\, d^{3N}\mathbf{R}}{\int \Phi_0\Psi\ d^{3N}\mathbf{R}} = \frac{\int \rho_m E^{loc}\ d^{3N}\mathbf{R}}{\int \rho_m\ d^{3N}\mathbf{R}} \tag{2.34}$$

After equilibration, the last integral in (2.34) can be approximated by averaging the local energy over the ensemble of simulated particles. The time-step biased quantum Monte Carlo estimator of the exact ground-state energy is given by

$$E_0(\delta\tau) \approx \frac{1}{N_p}\sum_{i=1}^{N_p} E^{loc}(\mathbf{R}_i) \tag{2.35}$$

where N_p is the current number of particles and $\mathbf{R}_i$ is the position vector of the i-th particle in the $3N$-dimensional space.

The quantum Monte Carlo simulation as described can be performed only for finite values of time-steps $\delta\tau$. As it was discussed in the previous sections, the simulation resembles the true diffusion process only in the limit $\delta\tau \to 0$. Thus, it is neccessary to extrapolate several ground-state energy estimates obtained by (2.35) for different time-steps of the diffusion simulation to get an estimate of the exact ground-state energy of the system, given by the $\delta\tau = 0$ intercept.

The value of the energy shift E_T does not affect estimated values of the ground-state energy. It only controls the total growth (or decay) of the population of particles. The best control is achieved by choosing E_T to be close to the unknown E_0, which is the reason why E_T is called the *trial energy*. By monitoring the particle populations in successive runs we can estimate the ground-state energy as well (see, for example, Section 3.2.3 in [46]).

In quantum Monte Carlo simulations the function Ψ is taken as a reasonably good approximation of the exact ground-state Φ_0, and it is referred to as the *trial function*. It is usually a result of sophisticated optimization procedures, and its quality has a direct bearing on the standard deviation of the ground-state energy estimators.

The condition implied that the trial function has the same sign as the unknown exact solution Φ_0 obviously can not be satisfied for systems with nodes, because we generally don't know the exact solution. Thus, for a given approximate Ψ, the described algorithm converges to a mixed distribution (2.33), which is not neccessarily positive everywhere in the configurational space, and the interpretation of the diffusion process is problematic. However, it was shown that the algorithm under these circumstances gives *variational* (upper-bound) estimates of the exact ground-state energy [61]. The difference of the fixed-node energy and the true E_0 is called the *fixed-node error*.

Equation (2.35) is a time-step biased estimator of the exact energy given

the mixed distribution of the particles, but there is no estimator of the exact expectation value of properties represented by operators which do not commute with the Hamiltonian. An example is the operator of the position of an electron $\mathbf{r}_i$. One could use an *approximate* formula [62]

$$\langle \mathbf{r}_i \rangle_e \approx 2\frac{\langle \Phi_0 | \mathbf{r}_i | \Psi \rangle}{\langle \Phi_0 | \Psi \rangle} - \frac{\langle \Psi | \mathbf{r}_i | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{2.36}$$

but this requires two separate simulations: one with branching (to obtain the mean over the mixed distribution) and another without branching at all (to obtain the variational distribution). This point will be discussed in the next section.

2.5 Algorithm with Constant Population

The algorithm with physical branching does not provide estimators of exact ground-state expectation values of operators which do not commute with the Hamiltonian. Also, the procedure of creating and deleting the particles due to the branching term can be expensive and time-consuming. Therefore, other QMC algorithms were developed which do not change the population of the particles [63, 58, 64].

By excluding the branching term from the equation (2.31) we get the following diffusion equation

$$\frac{\partial \rho}{\partial \tau} = \frac{1}{2}\nabla^2 \rho - \nabla \cdot (\mathbf{F}\rho) \tag{2.37}$$

which has the same form as (2.5) and describes the diffusion and drift of a constant number of particles.

The steady long-time limit solution of this equation is the *variational distribution*

$$\rho(\mathbf{R}, \tau) \to \Psi^2(\mathbf{R}) \equiv \rho_v(\mathbf{R}), \;\; \tau \to \infty \tag{2.38}$$

This is can be verified by evaluating the right-hand side of (2.37) for $\rho = \rho_v$

$$\frac{\partial(\Psi^2)}{\partial\tau} = \frac{1}{2}\nabla^2(\Psi^2) - \nabla\cdot(\frac{\nabla\Psi}{\Psi}\Psi^2) = 0 \tag{2.39}$$

which shows us that once reached, the variational distribution will no longer change in time.

The quantum Monte Carlo algorithm with constant population (or without branching) is based on simulating the diffusion process described by (2.37) (Section 2.2) and replacing the branching of particles by their relative weights. The weight for an individual particle reflects the effective importance of that particle. It estimates the number of particles we *would* have instead of that one particle, if we used the algorithm with branching.

Defining the *branching factor* of the i-th particle at j-th iteration

$$b_{i,j} = \exp\left(-\delta\tau(E^{loc}(\mathbf{R}_{i,j}) - E_T)\right) \tag{2.40}$$

where $\delta\tau$ is the time-step of the simulation and $\mathbf{R}_{i,j}$ is the configuration of the particle, we can write for its *past weight*

$$w_{i,j}^{(p)} = \prod_{k=j-L+1}^{j} b_{i,k} \tag{2.41}$$

Given by accummulating the L last branching factors of a particle, the past weight is a tool for replacing the actual branching process. The "length of memory" L may not be arbitrarily large, as that would yield to an excessively large variance of the weights and estimates [65, 66].

The time-step biased ground-state energy estimator differs from (2.35) by weighting the average over the particles

$$E_0(\delta\tau) \approx \frac{\sum_{i=1}^{N_p}\sum_{j=1}^{N_i} E^{loc}(\mathbf{R}_{i,j})w_{i,j}^{(p)}}{\sum_{i=1}^{N_p}\sum_{j=1}^{N_i} w_{i,j}^{(p)}} \tag{2.42}$$

where N_p is the fixed number of particles and N_i is the number of successive iterations.

Because the particles are after *equilibration* of the ensemble distributed according to the variational distribution (2.38), from the following equation

$$E_0 = \frac{\langle\Phi_0|\mathrm{H}|\Psi\rangle}{\langle\Phi_0|\Psi\rangle} = \frac{\int \Psi^2 \left(\frac{\mathrm{H}\Psi}{\Psi}\right)\left(\frac{\Phi_0}{\Psi}\right)\, d^{3N}\mathbf{R}}{\int \Psi^2 \left(\frac{\Phi_0}{\Psi}\right)\, d^{3N}\mathbf{R}} = \frac{\int \rho_v E^{loc}\left(\frac{\Phi_0}{\Psi}\right)\, d^{3N}\mathbf{R}}{\int \rho_v \left(\frac{\Phi_0}{\Psi}\right)\, d^{3N}\mathbf{R}} \tag{2.43}$$

compared to (2.42), we can conclude that the past weight of a particle at $\mathbf{R}_{i,j}$ position in the configurational space is an estimate of the ratio of Φ_0 and Ψ evaluated at that position, multiplied by a constant

$$w_{i,j}^{(p)} \propto \frac{\Phi_0(\mathbf{R}_{i,j})}{\Psi(\mathbf{R}_{i,j})} \tag{2.44}$$

The distribution of weights can be used to sample the exact distribution Φ_0^2 and to estimate expectation values of non-differential operators, shown as follows.

The exact expectation value of a non-differential operator A in the ground-state can be written as

$$\langle A\rangle_e \equiv \langle\Phi_0|\mathrm{A}|\Phi_0\rangle = \frac{\int \Psi^2 A(\mathbf{R})\left(\frac{\Phi_0}{\Psi}\right)^2\, d^{3N}\mathbf{R}}{\int \Psi^2 \left(\frac{\Phi_0}{\Psi}\right)^2\, d^{3N}\mathbf{R}} = \frac{\int \rho_v A(\mathbf{R})\left(\frac{\Phi_0}{\Psi}\right)^2\, d^{3N}\mathbf{R}}{\int \rho_v \left(\frac{\Phi_0}{\Psi}\right)^2\, d^{3N}\mathbf{R}} \tag{2.45}$$

Assuming that we can simulate the variational distribution appearing in the last expression, we would be able to estimate the expectation value if we were able to estimate square of the ratio $\frac{\Phi_0}{\Psi}$. The obvious solution to use the square of the past weights is incorrect, because generally a squared estimator is not an estimator of a square [67, 68].

We need one more estimator of the ratio *at the same* position $\mathbf{R}_{i,j}$, and then by multiplying this new weight by the past weight (2.44) we would obtain the estimator of the squared ratio.

This can be done by using a so-called "future walking algorithm" [58], in which the last L iterations on a particle are viewed as the future positions of

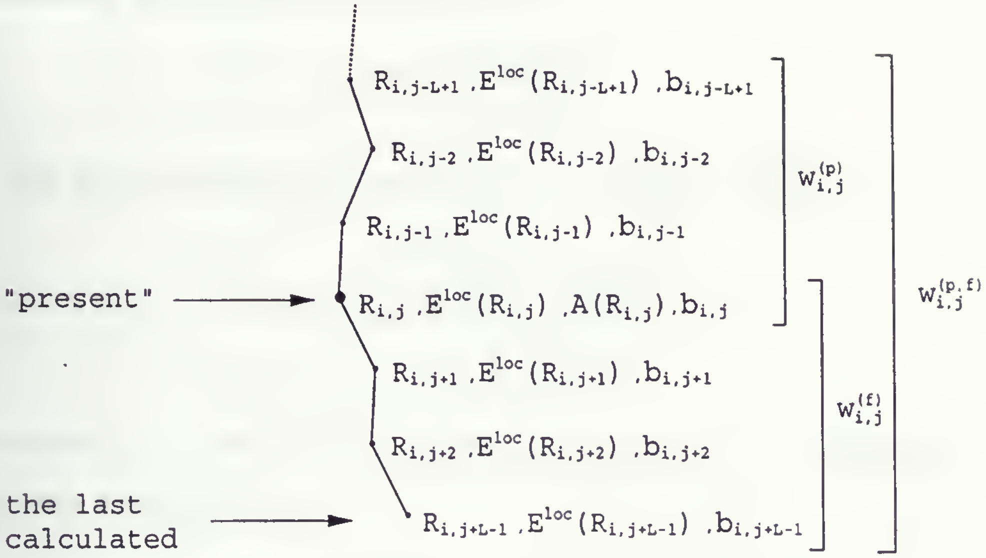

Figure 2.1: An illustrative picture of a QMC simulation with constant population ($L = 4$)

the particle located at a position in the present (Figure 2.1). As the diffusion simulation can be reversed in time[4], the *future* weights, given by the product of L "future" branching factors,

$$w^{(f)}_{i,j} = \prod_{k=j}^{j+L-1} b_{i,k} \tag{2.46}$$

have to be also an estimator of the ratio equivalent to (2.44)

$$w^{(f)}_{i,j} \propto \frac{\Phi_0(\mathbf{R}_{i,j})}{\Psi(\mathbf{R}_{i,j})} \tag{2.47}$$

By defining the *past-future* weight as a product of the past and the future weights

$$w^{(p,f)}_{i,j} = w^{(p)}_{i,j} w^{(f)}_{i,j} \tag{2.48}$$

---

[4] In the limit $\delta\tau \to 0$

we obtain a weight which is distributed as

$$w_{i,j}^{(p,f)} \propto \left(\frac{\Phi_0(\mathbf{R}_{i,j})}{\Psi(\mathbf{R}_{i,j})} \right)^2 \tag{2.49}$$

Now we can write energy estimator (2.42) using the future weights

$$E_0(\delta\tau) \approx \frac{\sum\limits_{i=1}^{N_p} \sum\limits_{j=1}^{N_i} E^{loc}(\mathbf{R}_{i,j}) w_{i,j}^{(f)}}{\sum\limits_{i=1}^{N_p} \sum\limits_{j=1}^{N_i} w_{i,j}^{(f)}} \tag{2.50}$$

or an energy estimator which combines both past and future weights (effectively using the average of them)

$$E_0(\delta\tau) \approx \frac{\sum\limits_{i=1}^{N_p} \sum\limits_{j=1}^{N_i} E^{loc}(\mathbf{R}_{i,j}) (w_{i,j}^{(p)} + w_{i,j}^{(f)})}{\sum\limits_{i=1}^{N_p} \sum\limits_{j=1}^{N_i} (w_{i,j}^{(p)} + w_{i,j}^{(f)})} \tag{2.51}$$

A very important difference between this algorithm and one with branching is that by using the future walking concept we can estimate the exact expectation value (2.45) of a non-differential operator A by taking the past-future-weighed average over the ensemble

$$\langle A \rangle_e \approx \frac{\sum\limits_{i=1}^{N_p} \sum\limits_{j=1}^{N_i} A(\mathbf{R}_{i,j}) w_{i,j}^{(p,f)}}{\sum\limits_{i=1}^{N_p} \sum\limits_{j=1}^{N_i} w_{i,j}^{(p,f)}} \tag{2.52}$$

We introduced the new parameter L, giving the number of branching factors entering past or future weights. Of course, theoretically, this number should be infinite. As it was said, large values of L yield to unstable behavior: one particle would end up with a tremendous weight after some number of iterations and all the other particles would have weights relatively close to zero. That is the reason why we keep L finite and constant during the simulation for a given time-step $\delta\tau$.

However, in order to obtain an unbiased limit of expectation values, it was shown that we have to increase L as a smaller time-step is chosen. The proper time-step dependence of L is given by this relation [58]

$$L = L_0 \left(\frac{\delta\tau_0}{\delta\tau} \right)^{1.5} \propto \frac{1}{\delta\tau^{1.5}} \tag{2.53}$$

where $\delta\tau_0$ is the maximum time-step used, and L_0 is the chosen value of L for the maximum time-step simulation.

The initial value L_0 can not be reasonably chosen before the complete simulation. Therefore we must use *several* (N_L) initial values of L. It is possible to calculate all N_L estimates at any time-step for all quantities in one quantum Monte Carlo run and to deal with the finite L-bias after the $\delta\tau \to 0$ extrapolation procedure.

Also, the proper ensemble size time-step dependence has to be satisfied. The smaller the time-step, the larger number of particles N_p, and the number of iterations N_i has to be chosen according to

$$N_p \propto \frac{1}{\delta\tau} \tag{2.54}$$

$$N_i \propto \frac{1}{\delta\tau} \tag{2.55}$$

The trial energy E_T now does not affect the simulation at all. Its only function is to control the magnitude of the exponent in the branching factors (2.40). In order to obtain the exponent evenly distributed around zero, E_T must be an estimate of the variational energy of the trial function Ψ.

For the sake of clarity, an outline of a quantum Monte Carlo simulation without branching follows:

Suppose we want to estimate the ground-state energy and an expectation value of a non-differential operator A of a system with Hamiltonian H. We have a given trial function Ψ (a result of an optimization procedure), therefore we can

calculate the drift vector (2.29) and the local energy (2.30) for any configuration $\mathbf{R}$ of the system. Also, a value of the variational energy E_T is provided.

1. The first step of the simulation is the initialization of all parameters. We have to choose several (N_T) time-steps we want to use. A safe choice is 5–7 evenly distributed values of time-steps, with a reasonable maximum time-step $\delta\tau_0$ [69]. Our simulation will perform separate diffusion simulations for each of these time-steps, in the order from the maximum to the minimum time-step. We also have to choose initial values of the number of particles N_{p0}, the number of iterations N_{i0}, and a set of N_L values of the L's.

2. For a given time-step (according to the mentioned descending order), update values of the number of particles N_p, the number of iterations N_i, and all N_L values of L according to the relations (2.53–2.55). Of course, in the case of the maximum time-step, all initial values are unchanged. Initialize the positions of all particles, for example by placing them randomly in a $3N$-dimensional unit cube around a meaningful location (usually the origin of the $3N$ dimensional coordinate system).

3. Perform a sufficient number of times more than the current N_i iterations the moving procedure described in Section 2.2. This will ensure that the ensemble has reached the long-time asymptotical solution, the variational distribution. This process is called the equilibration of the ensemble. There is no need to evaluate the local energy or the property A for the configurations during this phase.

4. Perform another $2L_{max} - 1$ iterations, where L_{max} is the maximum value among the chosen (and updated) L's. This time for each iteration calculate the local energy $E^{loc}(\mathbf{R}_{i,j})$ and the property $A(\mathbf{R}_{i,j})$ for each particle. Place

all $N_p(2L_{max} - 1)$ local energies and the same number of properties A in memory. This phase can be referred to as filling the memory (stacks).

5. From now on, for each new iteration we will update the memory, such that only the last $2L_{max} - 1$ values of local energies and properties A for each particle will be stored. That means for each iteration we can extract from the memory values of all N_L past, future and past-future weights as well as the "present" values of the local energy and the property A for each particle (Figure 2.1) By doing this, we perform N_i iterations, updating the N_L values for the sum of the past, future, past-future weights and the sums corresponding to the numerator of estimators (2.42), (2.50), (2.51) and (2.52).

6. After all N_i iterations are finished, use those sums and the estimators to calculate all N_L values of the ground-state energy and of the ground-state expectation value of A. Therefore, each time-step will result in N_L values for each estimated quantity.

7. Repeat steps 2–6 until all time-steps are used. We will end up with $N_L \times N_T$ values for the ground-state energy and for the non-differential property A. The last phase of the simulation is to perform a reasonable $\delta\tau \to 0$ extrapolation of those values for each initial L separately. This will result in N_L $\delta\tau = 0$ intercepts of the ground-state energy and the property A. To obtain the final exact ground-state estimate of each quantity, choose it to be the estimate for the smallest L for which the value of the quantity does not have any visible finite-L-bias. An idealized situation is depicted in Figure 2.2, which could be a result of a quantum Monte Carlo simulations with $N_L = 8$. The final estimate of the expectation value of A is the fourth initial L, because this result is within a one-sigma range of all results for

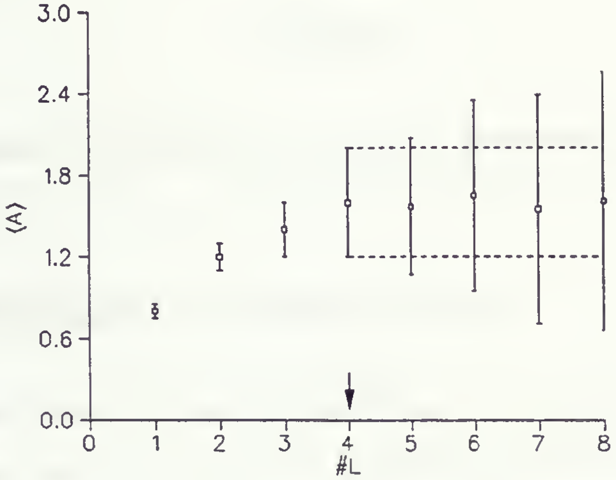

Figure 2.2: A typical result of a QMC simulation

larger L's, and the finite-L-bias is not visible after this value of L.

The quantum Monte Carlo algorithm with constant population (without physical branching) appears to be more useful than the branching algorithm. For example, we successfully applied it to estimate the overlap integral of the trial and the exact wavefunction $\langle\Psi|\Phi_0\rangle$ [70]. It will be shown in the next chapters how can it be used for estimating electrostatic polarizabilities of atoms and molecules as well.

Chapter 3

System of Charges in an External Electrostatic Field

3.1 Mutlipole Expansion of Classical Energy

Atoms, molecules or any systems of charged particles interact with an externally imposed electric field. This interaction causes the system to change its properties. One of the most important is the classical energy of the system E given by

$$E = E_0 + \sum_i q_i \phi(\mathbf{r}_i) \tag{3.1}$$

where E_0 is the energy of the system without the field imposed, index i labels charges q_i placed at positions $\mathbf{r}_i$, and $\phi(\mathbf{r})$ is the potential of the external electrostatic field. The theory of electrostatics defines the vector electric field generated by its potential ϕ by the following relation

$$\mathbf{E}(\mathbf{r}) = -\nabla\phi(\mathbf{r}) \tag{3.2}$$

We are interested in local characteristics of the external field in the vicinity of the system of charged particles. It is natural to expand the presumably smooth function of coordinates $\phi(\mathbf{r})$ into its Taylor series around the coordinate origin, where the system can be placed without any loss of generality

$$\phi(\mathbf{r}) = \phi(O) + r_\alpha \frac{\partial}{\partial r_\alpha}\phi(O) + \frac{1}{2!} r_\alpha r_\beta \frac{\partial^2}{\partial r_\alpha \partial r_\beta}\phi(O) + \frac{1}{3!} r_\alpha r_\beta r_\gamma \frac{\partial^3}{\partial r_\alpha \partial r_\beta \partial r_\gamma}\phi(O) + \ldots \tag{3.3}$$

Greek suffixes run through the Cartesian indices x, y, z, and summation over a repeated suffix is implied. After inserting this expansion into (3.1), the energy of

the system can be written as

$$E = E_0 + \phi(O)\sum_i q_i - E_\alpha \sum_i q_i r_{i\alpha} - \frac{1}{2!}E_{\alpha\beta}\sum_i q_i r_{i\alpha} r_{i\beta} - \frac{1}{3!}E_{\alpha\beta\gamma}\sum_i q_i r_{i\alpha} r_{i\beta} r_{i\gamma} - \dots \tag{3.4}$$

where $r_{i\alpha}$ stands for the α component of the position vector $\mathbf{r}_i$, and a set of new symbols for the electric field components and their derivatives calculated at the origin O has been introduced. Following the definition (3.2)

$$E_\alpha = -\frac{\partial}{\partial r_\alpha}\phi(O) \tag{3.5}$$

$$E_{\alpha\beta} = \frac{\partial E_\alpha}{\partial r_\beta} = -\frac{\partial^2}{\partial r_\alpha \partial r_\beta}\phi(O) \tag{3.6}$$

$$E_{\alpha\beta\gamma} = \frac{\partial^2 E_\alpha}{\partial r_\beta \partial r_\gamma} = -\frac{\partial^3}{\partial r_\alpha \partial r_\beta \partial r_\gamma}\phi(O) \tag{3.7}$$

the components of the electric field, the electric field gradient and the electric field hyper-gradient are defined, respectively. Note that the components of the field gradient, hyper-gradient and every other possible higher order derivative of $\mathbf{E}$ are invariant under interchange of any two suffixes, and therefore they form symmetric tensors.

The expansion (3.4) is called the *multipole expansion* of classical energy of the system, and its coefficients define components of *multipole moments tensors* in their so-called traced Cartesian form [71]. The first of them is the *total charge* of the system

$$q \equiv \sum_i q_i \tag{3.8}$$

which is equal to zero for neutral systems such as neutral atoms and molecules in their ground state. Even for non-neutral systems ($q \neq 0$) the term in the multipole expansion (3.4) containing the total charge is redundant. The reason is the gauge invariance of the electrostatic potential ϕ, which gives us the possibility to adjust it in such a way that $\phi(O) = 0$. Therefore, we will not write this term in the next formulas.

The next terms of (3.4) are more interesting. They define components of the *dipole moment vector* of the system

$$\mu_\alpha \equiv \sum_i q_i r_{i\alpha} \tag{3.9}$$

the *quadrupole moment tensor*

$$Q_{\alpha\beta} \equiv \sum_i q_i r_{i\alpha} r_{i\beta} \tag{3.10}$$

and components of the *octupole moment tensor*

$$R_{\alpha\beta\gamma} \equiv \sum_i q_i r_{i\alpha} r_{i\beta} r_{i\gamma} \tag{3.11}$$

in the traced Cartesian form. Multipole tensors of higher ranks can be similarly defined, and all of them are symmetric with respect to interchange of any two suffixes. Now, the multipole expansion of the energy has the following compact form

$$E = E_0 - \mu_\alpha E_\alpha - \frac{1}{2!} Q_{\alpha\beta} E_{\alpha\beta} - \frac{1}{3!} R_{\alpha\beta\gamma} E_{\alpha\beta\gamma} - \ldots \tag{3.12}$$

Although the above approach sufficiently describes energy dependence of any system of charged particles in an external electric field, a different, but equivalent definition of the multipole moments is often used.

3.2 Traceless Form of Multipole Moments

There is a similarity between the gauge invariance of the electrostatic potential and the possibility to define multipole moments in different ways. For example, by adding a constant to a given electrostatic potential ϕ we will not change Maxwell's equations.[1] In other words, for the same problem there are many equivalent possible choices of actual description of the physics of the problem, in this case it is the function ϕ.

---

[1] This is just a special case of gauge transformation.

A very similar situation is with the definition of the multipole moments. We have many ways of expressing the multipole moments in the energy expansion (3.12) without changing the physics of the interaction. In this case this means *without changing the overall summation* on the right hand side of (3.12), which corresponds to the energy of the system.

Fortunately, there is a condition which mutlipole moments must satisfy only in their unique form. The condition is based on the following fact: exposed to an external electrostatic field, a system of charged particles does not encounter any space filled with charges causing this external field. In other words, at the position of the system Laplace's theorem is satisfied

$$\nabla.(\nabla\phi) = 0 \tag{3.13}$$

In the terms of the components of the electrostatic field $\mathbf{E}$ this property of the external potential ϕ means that for every electric field tensor $E_{\alpha\beta}, E_{\alpha\beta\gamma}, \ldots$ contraction of any pair of indices gives zero

$$E_{\alpha\alpha} = 0 \tag{3.14}$$

$$E_{\alpha\alpha\gamma} = E_{\alpha\gamma\alpha} = E_{\gamma\alpha\alpha} = 0 \tag{3.15}$$

and so forth for high-rank tensors.

These equations are the reasons why we can add to any multipole moment tensor with rank larger than one any multiple of the unit Kronecker δ tensor. The Kronecker deltas simply contract the corresponding indices of the electric field tensor, and therefore they do not contribute to the total energy expansion. This kind of transformation of the multipole tensors is the one which is used to construct the unique *traceless form* of multipole moments.

The traceless form requires multipole moments to have contraction of any pair of indices equal to zero. Because this can not be satisfied for the dipole moment

as a tensor of rank one, its definition remains the same as in the traced Cartesian form (3.9). The quadrupole moment in the traceless form is designated $\Theta_{\alpha\beta}$, and the octupole moment $\Omega_{\alpha\beta\gamma}$. Their components are given by

$$\Theta_{\alpha\beta} = \frac{1}{2}\sum_i q_i(3r_{i\alpha}r_{i\beta} - r_i^2\delta_{\alpha\beta}) \tag{3.16}$$

$$\Omega_{\alpha\beta\gamma} = \frac{1}{2}\sum_i q_i\left(5r_{i\alpha}r_{i\beta}r_{i\gamma} - r_i^2(r_{i\alpha}\delta_{\beta\gamma} + r_{i\beta}\delta_{\alpha\gamma} + r_{i\gamma}\delta_{\alpha\beta})\right) \tag{3.17}$$

or, in general case

$$M_{\alpha\beta\ldots\mu} = \frac{(-1)^m}{m!}\sum_i q_i r_i^{2m+1}\frac{\partial^m}{\partial r_{i\alpha}\partial r_{i\beta}\ldots\partial r_{i\mu}}\left(\frac{1}{r_i}\right) \tag{3.18}$$

where m is the rank of the multipole tensor $M_{\alpha\beta\ldots\mu}$ [72]. It is easy to see that the condition of contraction to be zero is satisfied; for example,

$$\Theta_{\alpha\alpha} = \frac{1}{2}\sum_i q_i\left(3r_i^2 - r_i^2\delta_{\alpha\alpha}\right) = 0 \tag{3.19}$$

Properties of multipole moments and field tensors can be summarized as follows:

1. $\Theta_{\alpha\beta}, \Omega_{\alpha\beta\gamma}, E_{\alpha\beta}, E_{\alpha\beta\gamma}, \ldots$ are symmetric in all their indices
2. $\nabla\cdot(\nabla\phi) = 0 \Rightarrow E_{\alpha\alpha} = 0, E_{\alpha\alpha\ldots} = 0$
3. $\Theta_{\alpha\alpha} = 0, \Omega_{\alpha\alpha\gamma} = 0, \ldots$

It is important to note that the traceless form of quadrupole and octupole moments differs from their traced Cartesian forms not only by the added δ tensors, but also by multiplicative constants. Therefore, the multipole expansion in terms of the traceless multipole moments slightly differs from its traced Cartesian counterpart (3.12), and it is given by [26]

$$E = E_0 - \mu_\alpha E_\alpha - \frac{1}{3}\Theta_{\alpha\beta}E_{\alpha\beta} - \frac{1}{15}\Omega_{\alpha\beta\gamma}E_{\alpha\beta\gamma} - \ldots \tag{3.20}$$

There is another important form of the multipole moments called the *spherical form* [73, 74]. It is obtained by expanding the electrostatic potential into spherical harmonics. We will not use the sperical form in this work.

3.3 Perturbed Hamiltonian and Polarizabilities

Static polarizabilities of a system describe its response to an external electrostatic perturbation. Microscopic systems such as atoms and molecules have to be treated in the framework of quantum mechanics. The first step towards a quantum mechanical picture is constructing the energy operator. This is done by replacing the classical Hamiltonian by its operator version.

Following the previous section and its main result (3.20), the Hamiltonian operator for an atom or a molecule in an external electrostatic field can be written in the form of the multipole expansion (extended up to the sixth order following (3.18))

$$\begin{aligned}\mathrm{H} = \mathrm{H}_0 - \mu_\alpha E_\alpha - \frac{1}{3}\Theta_{\alpha\beta}E_{\alpha\beta} - \frac{1}{15}\Omega_{\alpha\beta\gamma}E_{\alpha\beta\gamma} \\ -\frac{1}{105}\Phi_{\alpha\beta\gamma\delta}E_{\alpha\beta\gamma\delta} - \frac{1}{945}M_{\alpha\beta\gamma\delta\varepsilon}E_{\alpha\beta\gamma\delta\varepsilon} \\ -\frac{1}{10395}M_{\alpha\beta\gamma\delta\varepsilon\zeta}E_{\alpha\beta\gamma\delta\varepsilon\zeta} - \ldots\end{aligned} \tag{3.21}$$

where μ_α, $\Theta_{\alpha\beta}$, $\Omega_{\alpha\beta\gamma}$, $\Phi_{\alpha\beta\gamma\delta}$, $M_{\alpha\beta\gamma\delta\varepsilon}$, $M_{\alpha\beta\gamma\delta\varepsilon\zeta}$ are operators of the dipole, quadrupole, octupole, hexadecapole, dotriacontapole and tetrahexadecapole moment, respectively.

To obtain the perturbed ground-state energy E of the system one has to solve the time-independent Schrödinger equation

$$\mathrm{H}\Phi = E\Phi \tag{3.22}$$

to find the perturbed ground-state wavefunction Φ.

Because the Hamiltonian (3.21) is a function of field tensors components $E_\alpha, E_{\alpha\beta}, E_{\alpha\beta\gamma}, \ldots$, its eigenstate Φ and eigenvalue E also have to be functions of the field tensors components. We can expand both functions $\Phi(E_\alpha, E_{\alpha\beta}, E_{\alpha\beta\gamma}, \ldots)$ and $E(E_\alpha, E_{\alpha\beta}, E_{\alpha\beta\gamma}, \ldots)$ into their multivariate Taylor expansion and build the

perturbation theory, but we are interested only in the expansion of the ground-state energy of the system, because that is the one which defines polarizabilities of the system.

The perturbed ground-state energy of a general system with no symmetry can be Taylor-expanded in the electric field tensors components, where the components of polarizability tensors are the Taylor coefficients. There are different notations for this in the literature.

In the notation introduced by Buckingham [14, 2, 10]

$$
\begin{aligned}
E(E_\alpha, E_{\alpha\beta}, E_{\alpha\beta\gamma}, \ldots) = E_0 - \mu^{(0)}_\alpha E_\alpha - \frac{1}{3}\Theta^{(0)}_{\alpha\beta} E_{\alpha\beta} - \frac{1}{15}\Omega^{(0)}_{\alpha\beta\gamma} E_{\alpha\beta\gamma} \\
-\frac{1}{2}\alpha_{\alpha\beta} E_\alpha E_\beta - \frac{1}{3!}\beta_{\alpha\beta\gamma} E_\alpha E_\beta E_\gamma - \frac{1}{4!}\gamma_{\alpha\beta\gamma\delta} E_\alpha E_\beta E_\gamma E_\delta \\
-\frac{1}{5!}\delta_{\alpha\beta\gamma\delta\varepsilon} E_\alpha E_\beta E_\gamma E_\delta E_\varepsilon - \frac{1}{6!}\epsilon_{\alpha\beta\gamma\delta\varepsilon\zeta} E_\alpha E_\beta E_\gamma E_\delta E_\varepsilon E_\zeta \\
-\frac{1}{3} A_{\alpha,\beta\gamma} E_\alpha E_{\beta\gamma} - \frac{1}{6} B_{\alpha\beta,\gamma\delta} E_\alpha E_\beta E_{\gamma\delta} - \frac{1}{6} C_{\alpha\beta,\gamma\delta} E_{\alpha\beta} E_{\gamma\delta} \\
-\frac{1}{15} E_{\alpha,\beta\gamma\delta} E_\alpha E_{\beta\gamma\delta} - \frac{1}{3!3} D_{\alpha\beta,\gamma\delta,\varepsilon\zeta} E_{\alpha\beta} E_{\gamma\delta} E_{\varepsilon\zeta} \\
-\frac{1}{2!2!3} P_{\alpha,\beta,\gamma\delta,\varepsilon\zeta} E_\alpha E_\beta E_{\gamma\delta} E_{\varepsilon\zeta} - \frac{1}{4!3} X_{\alpha,\beta,\gamma,\delta,\varepsilon\zeta} E_\alpha E_\beta E_\gamma E_\delta E_{\varepsilon\zeta} \\
-\frac{1}{2!15} R_{\alpha\beta\gamma,\delta\varepsilon\zeta} E_{\alpha\beta\gamma} E_{\delta\varepsilon\zeta} - \frac{1}{45} S_{\alpha,\beta\gamma,\delta\varepsilon\zeta} E_\alpha E_{\beta\gamma} E_{\delta\varepsilon\zeta} \\
-\frac{1}{3!15} Q_{\alpha,\beta,\gamma,\delta\varepsilon\zeta} E_\alpha E_\beta E_\gamma E_{\delta\varepsilon\zeta} - \frac{1}{210} U_{\alpha,\beta,\gamma\delta\varepsilon\zeta} E_\alpha E_\beta E_{\gamma\delta\varepsilon\zeta} - \ldots \qquad (3.23)
\end{aligned}
$$

where E_0 is the unperturbed ground-state energy, and $\mu^{(0)}_\alpha$, $\Theta^{(0)}_{\alpha\beta}$, $\Omega^{(0)}_{\alpha\beta\gamma}$ are the components of *permanent* dipole, quadrupole and octupole of the system, respectively. Symbols $\alpha_{\alpha\beta}, \beta_{\alpha\beta\gamma}, A_{\alpha,\beta\gamma}, B_{\alpha\beta,\gamma\delta}, \ldots$ denote components of various polarizability tensors (dipole polarizability, dipole hyper-polarizability, dipole-quadrupole polarizability, dipole-dipole-quadrupole hyper-polarizability, etc).

A more recent and systematic notation was suggested by Bishop and Pipin in terms of X symbols [26]

$$
E(E_\alpha, E_{\alpha\beta}, E_{\alpha\beta\gamma}, \ldots) = E_0 - X^{\cdot 0}_\alpha E_\alpha - \frac{1}{2!} X^{\cdot 1}_{\alpha,\beta} E_\alpha E_\beta - \frac{1}{3} X^{0}_{\alpha\beta} E_{\alpha\beta}
$$

$$
\begin{aligned}
&-\frac{1}{3!}X^{2}_{\alpha,\beta,\gamma}E_{\alpha}E_{\beta}E_{\gamma}-\frac{1}{3}X^{1}_{\alpha\beta,\gamma}E_{\alpha\beta}E_{\gamma}-\frac{1}{15}X^{0}_{\alpha\beta\gamma}E_{\alpha\beta\gamma}\\
&-\frac{1}{4!}X^{3}_{\alpha,\beta,\gamma,\delta}E_{\alpha}E_{\beta}E_{\gamma}E_{\delta}-\frac{1}{2!3}X^{2}_{\alpha\beta,\gamma,\delta}E_{\alpha\beta}E_{\gamma}E_{\delta}\\
&-\frac{1}{2!3^{2}}X^{1}_{\alpha\beta,\gamma\delta}E_{\alpha\beta}E_{\gamma\delta}-\frac{1}{15}X^{1}_{\alpha\beta\gamma,\delta}E_{\alpha\beta\gamma}E_{\delta}-\frac{1}{105}X^{0}_{\alpha\beta\gamma\delta}E_{\alpha\beta\gamma\delta}\\
&-\frac{1}{5!}X^{4}_{\alpha,\beta,\gamma,\delta,\varepsilon}E_{\alpha}E_{\beta}E_{\gamma}E_{\delta}E_{\varepsilon}-\frac{1}{3!3}X^{3}_{\alpha\beta,\gamma,\delta,\varepsilon}E_{\alpha\beta}E_{\gamma}E_{\delta}E_{\varepsilon}\\
&-\frac{1}{2!3^{2}}X^{2}_{\alpha\beta,\gamma\delta,\varepsilon}E_{\alpha\beta}E_{\gamma\delta}E_{\varepsilon}-\frac{1}{2!15}X^{2}_{\alpha\beta\gamma,\delta,\varepsilon}E_{\alpha\beta\gamma}E_{\delta}E_{\varepsilon}\\
&-\frac{1}{15\times 3}X^{1}_{\alpha\beta\gamma,\delta\varepsilon}E_{\alpha\beta\gamma}E_{\delta\varepsilon}-\frac{1}{105}X^{1}_{\alpha\beta\gamma\delta,\varepsilon}E_{\alpha\beta\gamma\delta}E_{\varepsilon}\\
&-\frac{1}{945}X^{0}_{\alpha\beta\gamma\delta\varepsilon}E_{\alpha\beta\gamma\delta\varepsilon}-\frac{1}{6!}X^{5}_{\alpha,\beta,\gamma,\delta,\varepsilon,\zeta}E_{\alpha}E_{\beta}E_{\gamma}E_{\delta}E_{\varepsilon}E_{\zeta}\\
&-\frac{1}{4!3}X^{4}_{\alpha\beta,\gamma,\delta,\varepsilon,\zeta}E_{\alpha\beta}E_{\gamma}E_{\delta}E_{\varepsilon}E_{\zeta}-\frac{1}{2!2!3^{2}}X^{3}_{\alpha\beta,\gamma\delta,\varepsilon,\zeta}E_{\alpha\beta}E_{\gamma\delta}E_{\varepsilon}E_{\zeta}\\
&-\frac{1}{3!3^{3}}X^{2}_{\alpha\beta,\gamma\delta,\varepsilon\zeta}E_{\alpha\beta}E_{\gamma\delta}E_{\varepsilon\zeta}-\frac{1}{3!15}X^{3}_{\alpha\beta\gamma,\delta,\varepsilon,\zeta}E_{\alpha\beta\gamma}E_{\delta}E_{\varepsilon}E_{\zeta}\\
&-\frac{1}{15\times 3}X^{2}_{\alpha\beta\gamma,\delta\varepsilon,\zeta}E_{\zeta\beta\gamma}E_{\delta\varepsilon}E_{\zeta}-\frac{1}{2!15^{2}}X^{1}_{\alpha\beta\gamma,\delta\varepsilon\zeta}E_{\alpha\beta\gamma}E_{\delta\varepsilon\zeta}\\
&-\frac{1}{2!105}X^{2}_{\alpha\beta\gamma\delta,\varepsilon,\zeta}E_{\alpha\beta\gamma\delta}E_{\varepsilon}E_{\zeta}-\frac{1}{105\times 3}X^{1}_{\alpha\beta\gamma\delta,\varepsilon\zeta}E_{\alpha\beta\gamma\delta}E_{\varepsilon\zeta}\\
&-\frac{1}{945}X^{1}_{\alpha\beta\gamma\delta\varepsilon,\zeta}E_{\alpha\beta\gamma\delta\varepsilon}E_{\zeta}-\frac{1}{10395}X^{0}_{\alpha\beta\gamma\delta\varepsilon\zeta}E_{\alpha\beta\gamma\delta\varepsilon\zeta}-\dots
\end{aligned}
\tag{3.24}
$$

where we explicitly write all polarizability tensors up to the sixth degree.[2] All X symbols are referred to simply as "polarizabilities" (no hyper-polarizabilities) of a certain degree.

From both expansions (3.23) and (3.24) it is clear that the polarizability tensors satisfy several trivial symmetries related to the fact that each electric field tensor of a rank larger that 2 is totally symmetric in its indices, and that a product of electric field tensors with the same rank is symmetric. Here is an example of these symmetries for $X^{3}_{\alpha\beta,\gamma\delta,\varepsilon,\zeta}$ tensor (P in Buckingham's notation)

$$
X^{3}_{\alpha\beta,\gamma\delta,\varepsilon,\zeta}=X^{3}_{\alpha\beta,\gamma\delta,\zeta,\varepsilon}=X^{3}_{\gamma\delta,\alpha\beta,\varepsilon,\zeta}=X^{3}_{\beta\alpha,\gamma\delta,\varepsilon,\zeta}=X^{3}_{\alpha\beta,\delta\gamma,\varepsilon,\zeta}
\tag{3.25}
$$

Every polarizability tensor has an unique set of these trivial symmetries, which in fact defines its position in the expansion (3.24).

---

[2] In the sense of Taylor series of electrostatic potential

Polarizability tensors of any system are required to be traceless in order to be defined in an unique way. The situation is the same as in the case of the traceless definition of multipole moments, because in the expansion (3.24) some of polarizabilities are contracted with electric field tensors of higher rank than two. Thus, we can require the trace of corresponding indices to be zero.

Continuing with the example, $X^3_{\alpha\beta,\gamma\delta,\varepsilon,\zeta}$ in addition to its trivial symmetries (3.25) satisfies the following conditions

$$X^3_{\alpha\alpha,\gamma\delta,\varepsilon,\zeta} = 0, \; X^3_{\alpha\beta,\gamma\gamma,\varepsilon,\zeta} = 0 \tag{3.26}$$

but, of course, $X^3_{\alpha\beta,\gamma\delta,\varepsilon,\varepsilon} \neq 0$. Similar equations hold for all the polarizabilities.

The two conditions (3.25) and (3.26) affect the maximum number of constants specifying the polarizability tensor of a system with no symmetry. For example, the $X^1_{\alpha,\beta}$ tensor is simply a symmetric matrix, which is generally specified by its 6 components. However, the maximum number of specifying constants for $X^0_{\alpha\beta}$ is one less, because its components are subject to the equation $X^0_{\alpha\alpha} = 0$.

The maximum numbers of specifying constants (m. n. c.), the conversion between notations (3.23) and (3.24), and the SI equivalent for one atomic unit of each polarizability up to the sixth degree are listed in Table 3.1. The units were calculated using the most recent values of fundamental physical constants (Appendix A). From this point only the systematic and logical X-symbol notation is used in this work. As it will be shown in the next chapter, this notation is very convenient for estimating the polarizabilities.

3.4 Atomic Polarizabilities

Spherical symmetry of atoms implies strong restrictions on atomic polarizability tensors: the number of specifying constants is drastically decreased (Table 3.1).

Polarizability	Alternate	1 au in SI	m. n. c.	n. c. (sphere)
X^0_{α}	$\mu^{(0)}_{\alpha}$	$8.4783527 \times 10^{-30}$ Cm	3	0
$X^1_{\alpha,\beta}$	$\alpha_{\alpha\beta}$	$1.6487772 \times 10^{-41}$ $\mathrm{C^2m^2J^{-1}}$	6	1
$X^0_{\alpha\beta}$	$\Theta^{(0)}_{\alpha\beta}$	$4.4865510 \times 10^{-40}$ $\mathrm{Cm^2}$	5	0
$X^2_{\alpha,\beta,\gamma}$	$\beta_{\alpha\beta\gamma}$	$3.2063616 \times 10^{-53}$ $\mathrm{C^3m^3J^{-2}}$	10	0
$X^1_{\alpha\beta,\gamma}$	$A_{\gamma,\alpha\beta}$	$8.7249534 \times 10^{-52}$ $\mathrm{C^2m^3J^{-1}}$	15	0
$X^0_{\alpha\beta\gamma}$	$\Omega^{(0)}_{\alpha\beta\gamma}$	$2.3741805 \times 10^{-50}$ $\mathrm{Cm^3}$	7	0
$X^3_{\alpha,\beta,\gamma,\delta}$	$\gamma_{\alpha\beta\gamma\delta}$	$6.2353811 \times 10^{-65}$ $\mathrm{C^4m^4J^{-3}}$	15	1
$X^2_{\alpha\beta,\gamma,\delta}$	$B_{\gamma\delta,\alpha\beta}$	$1.6967335 \times 10^{-63}$ $\mathrm{C^3m^4J^{-2}}$	30	1
$X^1_{\alpha\beta,\gamma\delta}$	$3C_{\alpha\beta,\gamma\delta}$	$4.6170465 \times 10^{-62}$ $\mathrm{C^2m^4J^{-1}}$	15	1
$X^1_{\alpha\beta\gamma,\delta}$	$E_{\delta,\alpha\beta\gamma}$	$4.6170465 \times 10^{-62}$ $\mathrm{C^2m^4J^{-1}}$	21	0
$X^0_{\alpha\beta\gamma\delta}$	$\Phi_{\alpha\beta\gamma\delta}$	$1.2563622 \times 10^{-60}$ $\mathrm{Cm^4}$	9	0
$X^4_{\alpha,\beta,\gamma,\delta,\varepsilon}$	$\delta_{\alpha\beta\gamma\delta\varepsilon}$	$1.2125887 \times 10^{-76}$ $\mathrm{C^5m^5J^{-4}}$	21	0
$X^3_{\alpha\beta,\gamma,\delta,\varepsilon}$		$3.2996216 \times 10^{-75}$ $\mathrm{C^4m^5J^{-3}}$	50	0
$X^2_{\alpha\beta,\gamma\delta,\varepsilon}$		$8.9787268 \times 10^{-74}$ $\mathrm{C^3m^5J^{-2}}$	45	0
$X^2_{\alpha\beta\gamma,\delta,\varepsilon}$		$8.9787268 \times 10^{-74}$ $\mathrm{C^3m^5J^{-2}}$	42	0
$X^1_{\alpha\beta\gamma,\delta\varepsilon}$		$2.4432358 \times 10^{-72}$ $\mathrm{C^2m^5J^{-1}}$	35	0
$X^1_{\alpha\beta\gamma\delta,\varepsilon}$		$2.4432358 \times 10^{-72}$ $\mathrm{C^2m^5J^{-1}}$	27	0
$X^0_{\alpha\beta\gamma\delta\varepsilon}$		$6.6483825 \times 10^{-71}$ $\mathrm{Cm^5}$	11	0
$X^5_{\alpha,\beta,\gamma,\delta,\varepsilon,\zeta}$	$\epsilon_{\alpha\beta\gamma\delta\varepsilon\zeta}$	$2.3581098 \times 10^{-88}$ $\mathrm{C^6m^6J^{-5}}$	28	1
$X^4_{\alpha\beta,\gamma,\delta,\varepsilon,\zeta}$	$X_{\gamma,\delta,\varepsilon,\zeta,\alpha\beta}$	$6.4167429 \times 10^{-87}$ $\mathrm{C^5m^6J^{-4}}$	75	1
$X^3_{\alpha\beta,\gamma\delta,\varepsilon,\zeta}$	$3P_{\varepsilon,\zeta,\alpha\beta,\gamma\delta}$	$1.7460845 \times 10^{-85}$ $\mathrm{C^4m^6J^{-3}}$	90	2
$X^2_{\alpha\beta,\gamma\delta,\varepsilon\zeta}$	$9D_{\alpha\beta,\gamma\delta,\varepsilon\zeta}$	$4.7513376 \times 10^{-84}$ $\mathrm{C^3m^6J^{-2}}$	35	1
$X^3_{\alpha\beta\gamma,\delta,\varepsilon,\zeta}$	$Q_{\delta,\varepsilon,\zeta,\alpha\beta\gamma}$	$1.7460845 \times 10^{-85}$ $\mathrm{C^4m^6J^{-3}}$	70	1
$X^2_{\alpha\beta\gamma,\delta\varepsilon,\zeta}$	$S_{\zeta,\delta\varepsilon,\alpha\beta\gamma}$	$4.7513376 \times 10^{-84}$ $\mathrm{C^3m^6J^{-2}}$	105	1
$X^1_{\alpha\beta\gamma,\delta\varepsilon\zeta}$	$15R_{\alpha\beta\gamma,\delta\varepsilon\zeta}$	$1.2929047 \times 10^{-82}$ $\mathrm{C^2m^6J^{-1}}$	28	1
$X^2_{\alpha\beta\gamma\delta,\varepsilon,\zeta}$	$U_{\varepsilon,\zeta,\alpha\beta\gamma\delta}$	$4.7513376 \times 10^{-84}$ $\mathrm{C^3m^6J^{-2}}$	54	0
$X^1_{\alpha\beta\gamma\delta,\varepsilon\zeta}$		$1.2929047 \times 10^{-82}$ $\mathrm{C^2m^6J^{-1}}$	45	0
$X^1_{\alpha\beta\gamma\delta\varepsilon,\zeta}$		$1.2929047 \times 10^{-82}$ $\mathrm{C^2m^6J^{-1}}$	33	0
$X^0_{\alpha\beta\gamma\delta\varepsilon\zeta}$		$3.5181725 \times 10^{-81}$ $\mathrm{Cm^6}$	13	0

Table 3.1: Unit conversions of polarizabilities and numbers of specifying constants

Several polarizabilities are identically zero, and nonzero components satisfy special conditions. The origin of these restrictions and the symmetry relations between nonzero components for each atomic polarizability up to the 6-th degree are discussed as follows.

Spherical symmetry in the context of quantum mechanics means that the Hamiltonian of the atom in an external electrostatic field (3.21) commutes with every operator of rotation of axes in 3-dimensions. Therefore, the perturbed ground-state energy (3.24) is the same in any two coordinate systems S, S' related to each other by linear transformation

$$r'_\alpha = R_{\alpha\beta} r_\beta \tag{3.27}$$

such that $R_{\alpha\beta}$ is a rotation matrix satisfying

$$R_{\alpha\beta} R_{\gamma\beta} = \delta_{\alpha\gamma} \tag{3.28}$$

$$\det R = +1 \tag{3.29}$$

From the definition of electric field tensors (3.5), (3.6) and (3.7), we can straightforwardly write the transformation rule for their components from system S to system S' as follows

$$E'_\alpha = \frac{\partial}{\partial r'_\alpha}\phi(O) = \frac{\partial \phi(O)}{\partial r_{\alpha'}}\frac{\partial r_{\alpha'}}{\partial r'_\alpha} = R^{-1}_{\alpha'\alpha} E_{\alpha'} = R_{\alpha\alpha'} E_{\alpha'} \tag{3.30}$$

$$E'_{\alpha\beta} = \frac{\partial^2}{\partial r'_\alpha \partial r'_\beta}\phi(O) = R_{\alpha\alpha'} R_{\beta\beta'} E_{\alpha'\beta'} \tag{3.31}$$

$$E'_{\alpha\beta\gamma} = \frac{\partial^3}{\partial r'_\alpha \partial r'_\beta \partial r'_\gamma}\phi(O) = R_{\alpha\alpha'} R_{\beta\beta'} R_{\gamma\gamma'} E_{\alpha'\beta'\gamma'} \tag{3.32}$$

or in general compact form

$$E'_{\alpha\beta\ldots} = R_{\alpha\alpha'} R_{\beta\beta'} \ldots E_{\alpha'\beta'\ldots} \tag{3.33}$$

In order to obtain the perturbed ground-state energy (3.24) in system S' we have to replace all electric field tensors by their transformed counterparts.

Because the energy has to remain the same after the transformation every transformed term in the expansion has to remain the same. By equating them to their original value in system S we will get the following conditions for the atomic polarizability tensors

$$X^0_{\alpha}R_{\alpha\alpha'} = X^0_{\alpha'} \tag{3.34}$$

$$X^1_{\alpha,\beta}R_{\alpha\alpha'}R_{\beta\beta'} = X^1_{\alpha',\beta'} \tag{3.35}$$

$$X^0_{\alpha\beta}R_{\alpha\alpha'}R_{\beta\beta'} = X^0_{\alpha'\beta'} \tag{3.36}$$

$$X^2_{\alpha,\beta,\gamma}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'} = X^2_{\alpha',\beta',\gamma'} \tag{3.37}$$

$$X^1_{\alpha\beta,\gamma}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'} = X^1_{\alpha'\beta',\gamma'} \tag{3.38}$$

$$X^0_{\alpha\beta\gamma}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'} = X^0_{\alpha'\beta'\gamma'} \tag{3.39}$$

$$X^3_{\alpha,\beta,\gamma,\delta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'} = X^3_{\alpha',\beta',\gamma',\delta'} \tag{3.40}$$

$$X^2_{\alpha\beta,\gamma,\delta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'} = X^2_{\alpha'\beta',\gamma',\delta'} \tag{3.41}$$

$$X^1_{\alpha\beta,\gamma\delta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'} = X^1_{\alpha'\beta',\gamma'\delta'} \tag{3.42}$$

$$X^1_{\alpha\beta\gamma,\delta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'} = X^1_{\alpha'\beta'\gamma',\delta'} \tag{3.43}$$

$$X^0_{\alpha\beta\gamma\delta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'} = X^0_{\alpha'\beta'\gamma'\delta'} \tag{3.44}$$

$$X^4_{\alpha,\beta,\gamma,\delta,\varepsilon}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'} = X^4_{\alpha',\beta',\gamma',\delta',\varepsilon'} \tag{3.45}$$

$$X^3_{\alpha\beta,\gamma,\delta,\varepsilon}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'} = X^3_{\alpha'\beta',\gamma',\delta',\varepsilon'} \tag{3.46}$$

$$X^2_{\alpha\beta,\gamma\delta,\varepsilon}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'} = X^2_{\alpha'\beta',\gamma'\delta',\varepsilon'} \tag{3.47}$$

$$X^2_{\alpha\beta\gamma,\delta,\varepsilon}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'} = X^2_{\alpha'\beta'\gamma',\delta',\varepsilon'} \tag{3.48}$$

$$X^1_{\alpha\beta\gamma,\delta\varepsilon}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'} = X^1_{\alpha'\beta'\gamma',\delta'\varepsilon'} \tag{3.49}$$

$$X^1_{\alpha\beta\gamma\delta,\varepsilon}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'} = X^1_{\alpha'\beta'\gamma'\delta',\varepsilon'} \tag{3.50}$$

$$X^0_{\alpha\beta\gamma\delta\varepsilon}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'} = X^0_{\alpha'\beta'\gamma'\delta'\varepsilon'} \tag{3.51}$$

$$X^5_{\alpha,\beta,\gamma,\delta,\varepsilon,\zeta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'}R_{\zeta\zeta'} = X^5_{\alpha',\beta',\gamma',\delta',\varepsilon',\zeta'} \tag{3.52}$$

$$X^4_{\alpha\beta,\gamma,\delta,\varepsilon,\zeta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'}R_{\zeta\zeta'} = X^4_{\alpha'\beta',\gamma',\delta',\varepsilon',\zeta'} \tag{3.53}$$

$$X^{3}_{\alpha\beta,\gamma\delta,\varepsilon,\zeta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'}R_{\zeta\zeta'} = X^{3}_{\alpha'\beta',\gamma'\delta',\varepsilon',\zeta'} \tag{3.54}$$

$$X^{2}_{\alpha\beta,\gamma\delta,\varepsilon\zeta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'}R_{\zeta\zeta'} = X^{2}_{\alpha'\beta',\gamma'\delta',\varepsilon'\zeta'} \tag{3.55}$$

$$X^{3}_{\alpha\beta\gamma,\delta,\varepsilon,\zeta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'}R_{\zeta\zeta'} = X^{3}_{\alpha'\beta'\gamma',\delta',\varepsilon',\zeta'} \tag{3.56}$$

$$X^{2}_{\alpha\beta\gamma,\delta\varepsilon,\zeta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'}R_{\zeta\zeta'} = X^{2}_{\alpha'\beta'\gamma',\delta'\varepsilon',\zeta'} \tag{3.57}$$

$$X^{1}_{\alpha\beta\gamma,\delta\varepsilon\zeta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'}R_{\zeta\zeta'} = X^{1}_{\alpha'\beta'\gamma',\delta'\varepsilon'\zeta'} \tag{3.58}$$

$$X^{2}_{\alpha\beta\gamma\delta,\varepsilon,\zeta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'}R_{\zeta\zeta'} = X^{2}_{\alpha'\beta'\gamma'\delta',\varepsilon',\zeta'} \tag{3.59}$$

$$X^{1}_{\alpha\beta\gamma\delta,\varepsilon\zeta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'}R_{\zeta\zeta'} = X^{1}_{\alpha'\beta'\gamma'\delta',\varepsilon'\zeta'} \tag{3.60}$$

$$X^{1}_{\alpha\beta\gamma\delta\varepsilon,\zeta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'}R_{\zeta\zeta'} = X^{1}_{\alpha'\beta'\gamma'\delta'\varepsilon',\zeta'} \tag{3.61}$$

$$X^{0}_{\alpha\beta\gamma\delta\varepsilon\zeta}R_{\alpha\alpha'}R_{\beta\beta'}R_{\gamma\gamma'}R_{\delta\delta'}R_{\varepsilon\varepsilon'}R_{\zeta\zeta'} = X^{0}_{\alpha'\beta'\gamma'\delta'\varepsilon'\zeta'} \tag{3.62}$$

These conditions are restrictions on polarizability tensors implied by the spherical symmetry of atoms, and they have to be satisfied for any rotation matrix R. Tensors which satisfy the conditions are called "isotropic tensors".

It is important to note that the conditions of isotropy are the same for polarizabilities with the same number of suffixes, no matter what the configuration of commas is. Therefore spherical symmetry does not distinguish between various polarizabilities of the same degree. As it was already said, it is the set of trivial symmetries together with conditions of vanishing traces which makes a polarizability tensor distinguishable from others.

The equation (3.34) means that the components X^{0}_{α} have to form a vector which is invariant under any rotation. Clearly, the only solution of the equation is the zero vector; therefore, the isotropic tensor of the first degree is identically zero

$$X^{0}_{\alpha} = 0 \tag{3.63}$$

and number of specifying constants is also zero as appears in Table 3.1. From the same table we see that polarizability X^{0}_{α} corresponds to the permanent dipole

moment of the system, which for atoms is indeed zero.

We can proceed to the next equation (3.35) and look for a matrix $X^1_{\alpha,\beta}$ which is invariant under any rotation. We would find that the solution is any multiple of the unit matrix

$$X^1_{\alpha,\beta} = c\delta_{\alpha\beta} \tag{3.64}$$

Inserting this solution to the equation (3.35) will show us how this works. The delta tensor contracts one rotation matrix with the other, which gives according to (3.28) again a delta tensor. The multiplicative real constant c is the only degree of freedom left, and it is the one specifying constant of the atomic $X^1_{\alpha,\beta}$.

Solving the equation for $X^0_{\alpha\beta}$ will help us to understand how the property of vanishing trace affects the solution. Because the equations (3.35) and (3.36) as it was noted are formally the same, we have again

$$X^0_{\alpha\beta} = c\delta_{\alpha\beta} \tag{3.65}$$

but requiring the traceless form of the polarizability tensor

$$X^0_{\alpha\alpha} = c\delta_{\alpha\alpha} = 3c = 0 \tag{3.66}$$

yields to a subsequent conclusion that $c = 0$ and

$$X^0_{\alpha\beta} = 0 \tag{3.67}$$

This polarizability tensor corresponds to the permanent quadrupole moment of an atom, which is known to be zero because of the symmetry.

Up to this point, we were able to find isotropic forms of tensor of rank one and two. To find the isotropic form of tensors of a higher rank is not a trivial exercise. The solution is based on results of Weyl's theory of invariant polynomials. The procedure how to generate an isotropic tensor in 3 dimensions of a general rank (number of indices) can be summarized as follows [3]

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[3] http://www.hydra.org.au/rks/docs/thesis/node48.html

- any even rank isotropic tensor must be expressed as a linear combination of products of the unit tensor (Kronecker delta)
- odd rank tensors must be expressed as a linear combination of products of the unit tensor and the Levi-Cevita (totally antisymmetric $\epsilon_{\alpha\beta\gamma}$, or the determinant tensor).

In practice, this means that we have to find every possible combination of indices of δ and ϵ. For example, an isotropic tensor of the third degree has to be a multiple of the determinant tensor. We can write for $X^0_{\alpha,\beta,\gamma}$

$$X^2_{\alpha,\beta,\gamma} = c\epsilon_{\alpha\beta\gamma} \tag{3.68}$$

But because at the same time the tensor has to be symmetric in all its indices, the only possibility for c is to be zero.

We can generalize this idea to any odd rank atomic polarizability tensor. According to Weyl's rules, each term of the linear combination of the products has to contain at least one determinant tensor. The trivial symmetries of polarizabilities tensors discussed in the previous section would result automatically to zero coefficient of that term. We can conclude that any atomic polarizability of odd rank is identically zero. Therefore, the number of specifying constants of those atomic polarizabilities is also zero.

Every polarizability tensor with a non-zero components must have even rank. We can write any fourth rank isotropic tensor $T_{\alpha\beta\gamma\delta}$ in the form of linear combination

$$T_{\alpha\beta\gamma\delta} = c_1\delta_{\alpha\beta}\delta_{\gamma\delta} + c_2\delta_{\alpha\gamma}\delta_{\beta\delta} + c_3\delta_{\alpha\delta}\delta_{\beta\gamma} \tag{3.69}$$

and any sixth order isotropic tensor $T_{\alpha\beta\gamma\delta\varepsilon\zeta}$ in the form

$$T_{\alpha\beta\gamma\delta\varepsilon\zeta} = c_1\delta_{\gamma\delta}\delta_{\beta\varepsilon}\delta_{\alpha\zeta} + c_2\delta_{\gamma\delta}\delta_{\beta\zeta}\delta_{\alpha\varepsilon} + c_3\delta_{\alpha\delta}\delta_{\gamma\beta}\delta_{\zeta\varepsilon}$$

$$\begin{aligned}&+c_4\delta_{\alpha\beta}\delta_{\delta\varepsilon}\delta_{\gamma\zeta}+c_5\delta_{\alpha\beta}\delta_{\delta\zeta}\delta_{\gamma\varepsilon}+c_6\delta_{\beta\delta}\delta_{\alpha\varepsilon}\delta_{\gamma\zeta}\\&+c_7\delta_{\beta\delta}\delta_{\alpha\zeta}\delta_{\gamma\varepsilon}+c_8\delta_{\beta\delta}\delta_{\gamma\alpha}\delta_{\zeta\varepsilon}+c_9\delta_{\alpha\delta}\delta_{\beta\zeta}\delta_{\gamma\varepsilon}\\&+c_{10}\delta_{\alpha\delta}\delta_{\beta\varepsilon}\delta_{\gamma\zeta}+c_{11}\delta_{\gamma\alpha}\delta_{\delta\zeta}\delta_{\beta\varepsilon}+c_{12}\delta_{\gamma\alpha}\delta_{\delta\varepsilon}\delta_{\beta\zeta}\\&+c_{13}\delta_{\gamma\beta}\delta_{\delta\zeta}\delta_{\alpha\varepsilon}+c_{14}\delta_{\gamma\beta}\delta_{\delta\varepsilon}\delta_{\alpha\zeta}+c_{15}\delta_{\gamma\delta}\delta_{\alpha\beta}\delta_{\zeta\varepsilon}\end{aligned}\tag{3.70}$$

where c_i are real numbers. We see that in general the fourth rank isotropic tensor has 3 specifying constants and the sixth rank isotropic tensor is specified by 15 constants.

It is straightforward to verify that all atomic polarizabilities of the fourth degree $X^3_{\alpha,\beta,\gamma,\delta}$, $X^2_{\alpha\beta,\gamma,\delta}$, $X^1_{\alpha\beta,\gamma\delta}$, $X^1_{\alpha\beta\gamma,\delta}$, $X^0_{\alpha\beta\gamma\delta}$ in the form (3.69) satisfy the conditions of spherical symmetry (3.40–3.44), and all eleven atomic polarizabilities of the sixth order $X^5_{\alpha,\beta,\gamma,\delta,\varepsilon,\zeta},\ldots,X^0_{\alpha\beta\gamma\delta\varepsilon\zeta}$ in the form (3.70) satisfy (3.52–3.62).

By requiring all trivial symmetries and conditions of vanishing traces for each fourth and sixth degree atomic polarizability we can obtain further relations between the coefficients c_i, which can only decrease the number of specifying constants.

To illustrate this final step towards obtaining the form of atomic polarizabilities, an example of $X^2_{\alpha\beta,\gamma,\delta}$ follows. This polarizability has to be invariant under interchange of $\alpha \leftrightarrow \beta$ and $\gamma \leftrightarrow \delta$ indices. The expression (3.69) is symmetric in those indices only if $c_2 = c_3$. Now the condition of the trace $X^2_{\alpha\alpha,\gamma,\delta} = 0$ reads

$$X^2_{\alpha\alpha,\gamma,\delta} = c_1\delta_{\alpha\alpha}\delta_{\gamma\delta} + 2c_2\delta_{\alpha\gamma}\delta_{\alpha\delta} = (3c_1 + 2c_2)\delta_{\gamma\delta} = 0 \tag{3.71}$$

and has to be satisfied for any γ, δ. This gives

$$c_2 = -\frac{3}{2}c_1 \tag{3.72}$$

Therefore, the components of the atomic polarizability are

$$X^2_{\alpha\beta,\gamma,\delta} = c_1\left(\delta_{\alpha\beta}\delta_{\gamma\delta} - \frac{3}{2}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})\right) \tag{3.73}$$

This satisfies all required conditions (trivial, trace, isotropy) and has only one degree of freedom or specifying constant.

This rather tedious procedure can implemented in Maple [75] (Appendix B.1) and it gives the following results for all even rank atomic polarizabilities up to the sixth degree

$$X^1_{\alpha,\beta} = c_1 \delta_{\alpha\beta} \tag{3.74}$$

$$X^0_{\alpha\beta} = 0 \tag{3.75}$$

$$X^3_{\alpha,\beta,\gamma,\delta} = c_1 \left(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}\right) \tag{3.76}$$

$$X^2_{\alpha\beta,\gamma,\delta} = c_1 \left(\delta_{\alpha\beta}\delta_{\gamma\delta} - \tfrac{3}{2}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})\right) \tag{3.77}$$

$$X^1_{\alpha\beta,\gamma\delta} = c_1 \left(\delta_{\alpha\beta}\delta_{\gamma\delta} - \tfrac{3}{2}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})\right) \tag{3.78}$$

$$X^1_{\alpha\beta\gamma,\delta} = 0 \tag{3.79}$$

$$X^0_{\alpha\beta\gamma\delta} = 0 \tag{3.80}$$

$$\begin{aligned} X^5_{\alpha,\beta,\gamma,\delta,\varepsilon,\zeta} = c_1 (&\delta_{\gamma\delta}\delta_{\beta\varepsilon}\delta_{\alpha\zeta} + \delta_{\gamma\delta}\delta_{\beta\zeta}\delta_{\alpha\varepsilon} + \delta_{\alpha\delta}\delta_{\gamma\beta}\delta_{\zeta\varepsilon} \\ &+\delta_{\alpha\beta}\delta_{\delta\varepsilon}\delta_{\gamma\zeta} + \delta_{\alpha\beta}\delta_{\delta\zeta}\delta_{\gamma\varepsilon} + \delta_{\beta\delta}\delta_{\alpha\varepsilon}\delta_{\gamma\zeta} \\ &+\delta_{\beta\delta}\delta_{\alpha\zeta}\delta_{\gamma\varepsilon} + \delta_{\beta\delta}\delta_{\gamma\alpha}\delta_{\zeta\varepsilon} + \delta_{\alpha\delta}\delta_{\beta\zeta}\delta_{\gamma\varepsilon} \\ &+\delta_{\alpha\delta}\delta_{\beta\varepsilon}\delta_{\gamma\zeta} + \delta_{\gamma\alpha}\delta_{\delta\zeta}\delta_{\beta\varepsilon} + \delta_{\gamma\alpha}\delta_{\delta\varepsilon}\delta_{\beta\zeta} \\ &+\delta_{\gamma\beta}\delta_{\delta\zeta}\delta_{\alpha\varepsilon} + \delta_{\gamma\beta}\delta_{\delta\varepsilon}\delta_{\alpha\zeta} + \delta_{\gamma\delta}\delta_{\alpha\beta}\delta_{\zeta\varepsilon}) \end{aligned} \tag{3.81}$$

$$\begin{aligned} X^4_{\alpha\beta,\gamma,\delta,\varepsilon,\zeta} = c_1 \Big(&-\tfrac{4}{3}\delta_{\alpha\beta}\left(\delta_{\delta\varepsilon}\delta_{\gamma\zeta} + \delta_{\delta\zeta}\delta_{\gamma\varepsilon} + \delta_{\gamma\delta}\delta_{\varepsilon\zeta}\right) \\ &+\delta_{\gamma\delta}\delta_{\beta\varepsilon}\delta_{\alpha\zeta} + \delta_{\gamma\delta}\delta_{\beta\zeta}\delta_{\alpha\varepsilon} + \delta_{\alpha\delta}\delta_{\gamma\beta}\delta_{\zeta\varepsilon} \\ &+\delta_{\beta\delta}\delta_{\alpha\varepsilon}\delta_{\gamma\zeta} + \delta_{\beta\delta}\delta_{\alpha\zeta}\delta_{\gamma\varepsilon} + \delta_{\beta\delta}\delta_{\gamma\alpha}\delta_{\zeta\varepsilon} \\ &+\delta_{\alpha\delta}\delta_{\beta\zeta}\delta_{\gamma\varepsilon} + \delta_{\alpha\delta}\delta_{\beta\varepsilon}\delta_{\gamma\zeta} + \delta_{\gamma\alpha}\delta_{\delta\zeta}\delta_{\beta\varepsilon} \\ &+\delta_{\gamma\alpha}\delta_{\delta\varepsilon}\delta_{\beta\zeta} + \delta_{\gamma\beta}\delta_{\delta\zeta}\delta_{\alpha\varepsilon} + \delta_{\gamma\beta}\delta_{\delta\varepsilon}\delta_{\alpha\zeta}) \end{aligned} \tag{3.82}$$

$$\begin{aligned} X^3_{\alpha\beta,\gamma\delta,\varepsilon,\zeta} = &\left(-c_1 - \tfrac{3}{2}c_2\right)\left(\delta_{\gamma\delta}\delta_{\beta\varepsilon}\delta_{\alpha\zeta} + \delta_{\gamma\delta}\delta_{\beta\zeta}\delta_{\alpha\varepsilon} + \delta_{\alpha\beta}\delta_{\delta\varepsilon}\delta_{\gamma\zeta}\right. \\ &\left.+\delta_{\alpha\beta}\delta_{\delta\zeta}\delta_{\gamma\varepsilon}\right) + \left(\tfrac{3}{4}c_1 + \tfrac{9}{8}c_2\right)\left(\delta_{\beta\delta}\delta_{\alpha\varepsilon}\delta_{\gamma\zeta} + \delta_{\beta\delta}\delta_{\alpha\zeta}\delta_{\gamma\varepsilon}\right. \end{aligned}$$

$$
\begin{gathered}
+\delta_{\alpha\delta}\delta_{\beta\zeta}\delta_{\gamma\varepsilon} + \delta_{\alpha\delta}\delta_{\beta\varepsilon}\delta_{\gamma\zeta} + \delta_{\gamma\alpha}\delta_{\delta\zeta}\delta_{\beta\varepsilon} \\
+\delta_{\gamma\alpha}\delta_{\delta\varepsilon}\delta_{\beta\zeta} + \delta_{\gamma\beta}\delta_{\delta\zeta}\delta_{\alpha\varepsilon} + \delta_{\gamma\beta}\delta_{\delta\varepsilon}\delta_{\alpha\zeta}) \\
+c_1\left(\delta_{\alpha\delta}\delta_{\gamma\beta}\delta_{\zeta\varepsilon} + \delta_{\beta\delta}\delta_{\gamma\alpha}\delta_{\zeta\varepsilon}\right) + c_2\delta_{\gamma\delta}\delta_{\alpha\beta}\delta_{\zeta\varepsilon}
\end{gathered}
\tag{3.83}
$$

$$
\begin{gathered}
X^2_{\alpha\beta,\gamma\delta,\varepsilon\zeta} = c_1\,(\delta_{\gamma\delta}\delta_{\beta\varepsilon}\delta_{\alpha\zeta} + \delta_{\gamma\delta}\delta_{\beta\zeta}\delta_{\alpha\varepsilon} + \delta_{\alpha\delta}\delta_{\gamma\beta}\delta_{\zeta\varepsilon} \\
+\delta_{\alpha\beta}\delta_{\delta\varepsilon}\delta_{\gamma\zeta} + \delta_{\alpha\beta}\delta_{\delta\zeta}\delta_{\gamma\varepsilon} + \delta_{\beta\delta}\delta_{\gamma\alpha}\delta_{\zeta\varepsilon} \\
-\tfrac{3}{4}\,(\delta_{\beta\delta}\delta_{\alpha\varepsilon}\delta_{\gamma\zeta} + \delta_{\beta\delta}\delta_{\alpha\zeta}\delta_{\gamma\varepsilon} + \delta_{\alpha\delta}\delta_{\beta\zeta}\delta_{\gamma\varepsilon} \\
+\delta_{\alpha\delta}\delta_{\beta\varepsilon}\delta_{\gamma\zeta} + \delta_{\gamma\alpha}\delta_{\delta\zeta}\delta_{\beta\varepsilon} + \delta_{\gamma\alpha}\delta_{\delta\varepsilon}\delta_{\beta\zeta} \\
+\delta_{\gamma\beta}\delta_{\delta\zeta}\delta_{\alpha\varepsilon} + \delta_{\gamma\beta}\delta_{\delta\varepsilon}\delta_{\alpha\zeta}) - \tfrac{4}{3}\delta_{\alpha\beta}\delta_{\gamma\delta}\delta_{\varepsilon\zeta}\Big)
\end{gathered}
\tag{3.84}
$$

$$
\begin{gathered}
X^3_{\alpha\beta\gamma,\delta,\varepsilon,\zeta} = c_1\,(\delta_{\alpha\delta}\delta_{\gamma\beta}\delta_{\zeta\varepsilon} + \delta_{\alpha\beta}\delta_{\delta\varepsilon}\delta_{\gamma\zeta} + \delta_{\alpha\beta}\delta_{\delta\zeta}\delta_{\gamma\varepsilon} \\
+\delta_{\beta\delta}\delta_{\gamma\alpha}\delta_{\zeta\varepsilon} + \delta_{\gamma\alpha}\delta_{\delta\zeta}\delta_{\beta\varepsilon} + \delta_{\gamma\alpha}\delta_{\delta\varepsilon}\delta_{\beta\zeta} \\
+\delta_{\gamma\beta}\delta_{\delta\zeta}\delta_{\alpha\varepsilon} + \delta_{\gamma\beta}\delta_{\delta\varepsilon}\delta_{\alpha\zeta} + \delta_{\gamma\delta}\delta_{\alpha\beta}\delta_{\zeta\varepsilon} \\
-\tfrac{5}{2}\,(\delta_{\gamma\delta}\delta_{\beta\varepsilon}\delta_{\alpha\zeta} + \delta_{\gamma\delta}\delta_{\beta\zeta}\delta_{\alpha\varepsilon} + \delta_{\beta\delta}\delta_{\alpha\varepsilon}\delta_{\gamma\zeta} \\
+\delta_{\beta\delta}\delta_{\alpha\zeta}\delta_{\gamma\varepsilon} + \delta_{\alpha\delta}\delta_{\beta\zeta}\delta_{\gamma\varepsilon} + \delta_{\alpha\delta}\delta_{\beta\varepsilon}\delta_{\gamma\zeta}))
\end{gathered}
\tag{3.85}
$$

$$
\begin{gathered}
X^2_{\alpha\beta\gamma,\delta\varepsilon,\zeta} = c_1\,(\delta_{\alpha\delta}\delta_{\gamma\beta}\delta_{\zeta\varepsilon} + \delta_{\alpha\beta}\delta_{\delta\varepsilon}\delta_{\gamma\zeta} + \delta_{\alpha\beta}\delta_{\delta\zeta}\delta_{\gamma\varepsilon} \\
+\delta_{\beta\delta}\delta_{\gamma\alpha}\delta_{\zeta\varepsilon} + \delta_{\gamma\alpha}\delta_{\delta\zeta}\delta_{\beta\varepsilon} + \delta_{\gamma\alpha}\delta_{\delta\varepsilon}\delta_{\beta\zeta} \\
+\delta_{\gamma\beta}\delta_{\delta\zeta}\delta_{\alpha\varepsilon} + \delta_{\gamma\beta}\delta_{\delta\varepsilon}\delta_{\alpha\zeta} + \delta_{\gamma\delta}\delta_{\alpha\beta}\delta_{\zeta\varepsilon} \\
-\tfrac{5}{2}\,(\delta_{\gamma\delta}\delta_{\beta\varepsilon}\delta_{\alpha\zeta} + \delta_{\gamma\delta}\delta_{\beta\zeta}\delta_{\alpha\varepsilon} + \delta_{\beta\delta}\delta_{\alpha\varepsilon}\delta_{\gamma\zeta} \\
+\delta_{\beta\delta}\delta_{\alpha\zeta}\delta_{\gamma\varepsilon} + \delta_{\alpha\delta}\delta_{\beta\zeta}\delta_{\gamma\varepsilon} + \delta_{\alpha\delta}\delta_{\beta\varepsilon}\delta_{\gamma\zeta}))
\end{gathered}
\tag{3.86}
$$

$$
\begin{gathered}
X^1_{\alpha\beta\gamma,\delta\varepsilon\zeta} = c_1\,(\delta_{\alpha\delta}\delta_{\gamma\beta}\delta_{\zeta\varepsilon} + \delta_{\alpha\beta}\delta_{\delta\varepsilon}\delta_{\gamma\zeta} + \delta_{\alpha\beta}\delta_{\delta\zeta}\delta_{\gamma\varepsilon} \\
+\delta_{\beta\delta}\delta_{\gamma\alpha}\delta_{\zeta\varepsilon} + \delta_{\gamma\alpha}\delta_{\delta\zeta}\delta_{\beta\varepsilon} + \delta_{\gamma\alpha}\delta_{\delta\varepsilon}\delta_{\beta\zeta} \\
+\delta_{\gamma\beta}\delta_{\delta\zeta}\delta_{\alpha\varepsilon} + \delta_{\gamma\beta}\delta_{\delta\varepsilon}\delta_{\alpha\zeta} + \delta_{\gamma\delta}\delta_{\alpha\beta}\delta_{\zeta\varepsilon} \\
-\tfrac{5}{2}\,(\delta_{\gamma\delta}\delta_{\beta\varepsilon}\delta_{\alpha\zeta} + \delta_{\gamma\delta}\delta_{\beta\zeta}\delta_{\alpha\varepsilon} + \delta_{\beta\delta}\delta_{\alpha\varepsilon}\delta_{\gamma\zeta} \\
+\delta_{\beta\delta}\delta_{\alpha\zeta}\delta_{\gamma\varepsilon} + \delta_{\alpha\delta}\delta_{\beta\zeta}\delta_{\gamma\varepsilon} + \delta_{\alpha\delta}\delta_{\beta\varepsilon}\delta_{\gamma\zeta}))
\end{gathered}
\tag{3.87}
$$

$$
X^2_{\alpha\beta\gamma\delta,\varepsilon,\zeta} = 0 \tag{3.88}
$$

$$X^1_{\alpha\beta\gamma\delta,\varepsilon\zeta} = 0 \tag{3.89}$$

$$X^1_{\alpha\beta\gamma\delta\varepsilon,\zeta} = 0 \tag{3.90}$$

$$X^0_{\alpha\beta\gamma\delta\varepsilon\zeta} = 0 \tag{3.91}$$

Here c_1 and c_2 are different in every equation; they are meant to designate the specifying constant for each atomic polarizability separately. Some of these equations can be found in [2, 10].

It is interesting that certain even rank atomic polarizabilities turned out to be zero after all those conditions applied. Of course, this was rather expected in the cases of all permanent multipoles ($X^0_{\dots}$), but it is a non-trivial result for the others, for example $X^1_{\alpha\beta\gamma\delta,\varepsilon\zeta}$.

Another interesting fact is that some atomic polarizability tensors have the same component definition. This is the case for $X^2_{\alpha\beta,\gamma,\delta}$ and $X^1_{\alpha\beta,\gamma\delta}$; $X^3_{\alpha\beta\gamma,\delta,\varepsilon,\zeta}$, $X^2_{\alpha\beta\gamma,\delta\varepsilon,\zeta}$ and $X^1_{\alpha\beta\gamma,\delta\varepsilon\zeta}$.

And finally, atomic polarizability $X^3_{\alpha\beta,\gamma\delta,\varepsilon,\zeta}$ is the only one up to the sixth degree with more that one specifying constant (Table 3.1).

Based on results (3.74–3.91) it is now fairly simple to derive a relations between different components of each atomic polarizability. Suppose we want to derive the relations for $X^1_{\alpha,\beta}$. First we expand the term in ground-state energy (3.24) *without* inserting the isotropic form (3.74), simplifying it only by using trivial symmetries

$$-\tfrac{1}{2!}X^1_{\alpha,\beta}E_\alpha E_\beta = -\tfrac{1}{2!}\left(X^1_{x,x}E_x^2 + X^1_{y,y}E_y^2 + X^1_{z,z}E_z^2\right. \tag{3.92}$$

$$\left.+2X^1_{x,y}E_xE_y + 2X^1_{x,z}E_xE_z + 2X^1_{y,z}E_yE_z\right) \tag{3.93}$$

Then we compare it to the same term expanded by *using* the isotropic form (3.74)

$$-\frac{1}{2!}X^1_{\alpha,\beta}E_\alpha E_\beta = -\frac{1}{2!}c_1\delta_{\alpha,\beta}E_\alpha E_\beta = -\frac{1}{2!}c_1\left(E_x^2 + E_y^2 + E_z^2\right) \tag{3.94}$$

This immediately suggests zero components ($X^1_{x,y}, \ldots$) and that the relation between non-zero components is

$$X^1_{x,x} = X^1_{y,y} = X^1_{z,z} \tag{3.95}$$

By repeating this same procedure for all atomic polarizabilities up to the sixth order we get the following relations

$$X^3_{x,x,x,x} = X^3_{y,y,y,y} = X^3_{z,z,z,z} = 3X^3_{x,x,y,y} = 3X^3_{y,y,z,z} = 3X^3_{x,x,z,z} \tag{3.96}$$

$$\begin{aligned} X^2_{xx,x,x} &= X^2_{yy,y,y} = X^2_{zz,z,z} = -2X^2_{xx,y,y} = -2X^2_{xx,z,z} \\ &= -2X^2_{yy,z,z} = \frac{4}{3}X^2_{xy,x,y} = \frac{4}{3}X^2_{xz,x,z} = \frac{4}{3}X^2_{yz,y,z} \end{aligned} \tag{3.97}$$

$$\begin{aligned} X^1_{xx,xx} &= X^1_{yy,yy} = X^1_{zz,zz} = -2X^1_{xx,yy} = -2X^1_{xx,zz} \\ &= -2X^1_{yy,zz} = \frac{4}{3}X^1_{xy,xy} = \frac{4}{3}X^1_{xz,xz} = \frac{4}{3}X^1_{yz,yz} \end{aligned} \tag{3.98}$$

$$X^5_{x,x,x,x,x,x} = 5X^5_{x,x,y,y,y,y} = 15X^5_{x,x,y,y,z,z} = \ldots \tag{3.99}$$

$$\begin{aligned} X^4_{xx,x,x,x,x} &= -2X^4_{xx,y,y,y,y} = 12X^4_{xx,x,x,y,y} = \frac{8}{3}X^4_{xy,x,y,y,y} \\ &= 8X^4_{xy,x,y,z,z} = -6X^4_{xx,y,y,z,z} = \ldots \end{aligned} \tag{3.100}$$

$$\begin{aligned} X^2_{xx,xx,xx} &= -2X^2_{xx,xx,yy} = \frac{8}{3}X^2_{xy,xy,xx} = \frac{16}{9}X^2_{xy,yz,xz} \\ &= X^2_{xx,yy,zz} = -\frac{4}{3}X^2_{xy,xy,zz} = \ldots \end{aligned} \tag{3.101}$$

$$\begin{aligned} X^3_{xxx,x,x,x} &= -2X^3_{xxy,y,y,y} = \frac{3}{2}X^3_{xxy,x,x,y} = -2X^3_{xxx,x,y,y} \\ &= -6X^3_{xxy,y,z,z} = \frac{12}{5}X^3_{xyz,x,y,z} = \ldots \end{aligned} \tag{3.102}$$

$$\begin{aligned} X^2_{xxx,xx,x} &= -2X^2_{xxx,yy,x} = -2X^2_{xxx,xy,y} = \frac{3}{2}X^2_{xxy,xx,y} \\ &= \frac{3}{2}X^2_{xxy,xy,x} = -6X^2_{xxy,zz,y} = \frac{12}{5}X^2_{xyz,xy,z} \\ &= -6X^2_{xxy,yz,z} = -2X^2_{xxy,yy,y} = \ldots \end{aligned} \tag{3.103}$$

$$\begin{aligned} X^1_{xxx,xxx} = \frac{12}{5}X^1_{xyz,xyz} = -6X^1_{xxy,yzz} &= -2X^1_{xxx,xyy} \\ &= \frac{3}{2}X^1_{xxy,xxy} = \dots \end{aligned} \tag{3.104}$$

Of course, the relations for polarizabilities of the second and fourth degree are the same as those published in [3].

The atomic polarizability $X^3_{\alpha\beta,\gamma\delta,\varepsilon,\zeta}$ has two specifying constants, and its components satisfy this system of equations

$$\begin{aligned} X^3_{xx,xx,x,x} &= 4c_1 + 4c_2 \\ X^3_{xx,xx,y,y} &= 2c_1 + c_2 \\ 16X^3_{xz,yz,x,y} &= 12c_1 + 18c_2 \\ 8X^3_{xy,yy,x,y} &= 4c_1 + 6c_2 \\ 8X^3_{xy,zz,x,y} &= -8c_1 - 12c_2 \\ 2X^3_{yy,zz,x,x} &= 2c_2 \\ 2X^3_{xx,yy,x,x} &= -4c_1 - 4c_2 \\ 4X^3_{xy,xy,z,z} &= 4c_1 \\ 4X^3_{xy,xy,y,y} &= 10c_1 + 9c_2, \dots \end{aligned} \tag{3.105}$$

Here and above the dots denote that the same relations hold also for equivalent components not explicitly written but easily obtain by every permutation of $[x, y, z]$ and, of course, by applying trivial symmetries. For example: $X^2_{xxy,zz,y} = X^2_{yyx,zz,x} = X^2_{xyy,zz,x}$. All atomic polarizability components which contain x, y or z odd times as a suffix are zeros.

The relations (3.95–3.105) are the main results of this chapter. We will see in the following chapter that they will provide us with different estimators of atomic polarizabilities. It will be seen that computing them all reduces the statistical error of the simulated quantities.

Chapter 4

Quantum Monte Carlo Estimators of Atomic Polarizabilities

4.1 Analytic Derivatives of Ground-State Energy

As it was shown in the previous chapter, polarizabilities are essentially various derivatives of the ground-state energy with respect to the electric tensors components evaluated at zero electric field. Estimating of atomic polarizabilities is therefore estimating of these derivatives.

One obvious method to do that would be to perform QMC simulation for several choices of $E_\alpha, E_{\alpha\beta}, \ldots$ and to get corresponding estimates of the ground-state energy. By doing this we would sample the shape of ground-state energy as a function of the electric field tensor components. Then we could estimate from this shape the derivatives around $\mathbf{E} = 0$ point to obtain estimates of polarizabilities. This method is called the method of *finite differences*, because we are using many small, but finite electric fields to explore the response of the system.

There are QMC methods which directly estimate derivatives of energy at the point of zero perturbation [63, 55]. The infinitesimal differential diffusion QMC [55] is based on analytical treatment of derivatives of the expectation value of the ground-state energy. Using the algorithm without physical branching, we can calculate the derivatives of the ground-state energy estimator directly and then just run a single simulation which will estimate all neccessary derivatives (polarizabilities).

In this method, the trial function Ψ is kept fixed, and the described algorithm is utilizing the fixed node approximation. As it was shown [51, 52, 53], under

these conditions the Hellmann-Feynman theorem holds true and can be used for overriding explicit evaluation of the first derivatives of the ground-state energy. This will keep our formulas relatively simple.

For example, to obtain an estimator of $X^1_{x,x}$ component we have to calculate

$$X^1_{x,x} = -\left.\frac{\partial^2 E(E_\alpha, E_{\alpha\beta}, \ldots)}{\partial E_x^2}\right|_{E_\alpha=0, E_{\alpha\beta}=0,\ldots} = -\left.\frac{\partial^2 \langle \mathrm{H} \rangle_e}{\partial E_x^2}\right|_{E_\alpha=0, E_{\alpha\beta}=0,\ldots} \tag{4.1}$$

where the Hamiltonian dependence on the electric field is given by (3.21).

Using the Hellmann-Feynman theorem we can write

$$X^1_{x,x} = -\left.\frac{\partial \langle \frac{\partial \mathrm{H}}{\partial E_x} \rangle_e}{\partial E_x}\right|_{E_\alpha=0, E_{\alpha\beta}=0,\ldots} = \left.\frac{\partial \langle \mu_x \rangle_e}{\partial E_x}\right|_{E_\alpha=0, E_{\alpha\beta}=0,\ldots} \tag{4.2}$$

It is important to note that in the last equation the energy estimator $\langle \mathrm{H} \rangle_e \equiv E_0$ which uses the past weights (or future weights) (2.42, 2.50 or 2.51) was effectively replaced by an estimator of a non-differential property $\langle \mu_x \rangle_e$ which uses the past-future weights (2.52).

After inserting the expression for the estimator of the expectation value of μ_x (2.52)

$$X^1_{x,x} = \frac{\partial}{\partial E_x} \left. \left(\frac{\sum\limits_{i,j} \mu_x(\mathbf{R}_{i,j}) w_{i,j}^{(p,f)}}{\sum\limits_{i,j} w_{i,j}^{(p,f)}} \right) \right|_{E_\alpha=0, E_{\alpha\beta}=0,\ldots} \tag{4.3}$$

we see that the only quantity which depends on the electric field tensors is the past-future weight $w_{i,j}^{(p,f)}$ *via* the perturbed Hamiltonian (3.21). By using the definitions of weights (2.41, 2.46, 2.48) we can write the past-future weight in the following form

$$\begin{aligned} w_{i,j}^{(p,f)} &= \exp\Big[-\tau \Big(\left\{ E_0^{loc} - E_T \right\}_{i,j} - \left\{ \mu_\alpha \right\}_{i,j} E_\alpha \\ &\quad -\frac{1}{3} \left\{ \Theta_{\alpha\beta} \right\}_{i,j} E_{\alpha\beta} - \frac{1}{15} \left\{ \Omega_{\alpha\beta\gamma} \right\}_{i,j} E_{\alpha\beta\gamma} - \ldots \Big) \Big] \end{aligned} \tag{4.4}$$

where τ is the simulation time-step ($\delta\tau$ in Chapter 2), E_0^{loc} is the unperturbed local energy

$$E_0^{loc} = \frac{\mathrm{H}_0\Psi}{\Psi} \tag{4.5}$$

and a new symbol $\{\}$ is introduced for a cummulative value of a quantity

$$\{a\}_{i,j} \equiv \sum_{k=0}^{L-1} \left(a(\mathbf{R}_{i,j+k}) + a(\mathbf{R}_{i,j-k})\right) \tag{4.6}$$

This symbol allows us to write the first derivative of the perturbed past-future weight (4.4) in the following compact form

$$\left.\frac{\partial w_{i,j}^{(p,f)}}{\partial E_x}\right|_{E_\alpha=0,E_{\alpha\beta}=0,\ldots} = \tau \{\mu_x\}_{i,j} W_{i,j}^{(p,f)} \tag{4.7}$$

where $W_{i,j}^{(p,f)}$ is the past-future weight for the *unpertubed* Hamiltonian defined as

$$W_{i,j}^{(p,f)} \equiv w_{i,j}^{(p,f)}\Big|_{E_\alpha=0,E_{\alpha\beta}=0,\ldots} = \exp\left[-\tau\left(\left\{E_0^{loc} - E_T\right\}_{i,j}\right)\right] \tag{4.8}$$

By using (4.7), the polarizability component (4.3) can be expressed as

$$\begin{aligned} X_{x,x}^1 &= \tau \frac{\sum_{i,j} \mu_x(\mathbf{R}_{i,j}) \{\mu_x\}_{i,j} W_{i,j}^{(p,f)}}{\sum_{i,j} W_{i,j}^{(p,f)}} \\ &\quad -\tau \frac{\sum_{i,j} \mu_x(\mathbf{R}_{i,j}) W_{i,j}^{(p,f)}}{\sum_{i,j} W_{i,j}^{(p,f)}} \frac{\sum_{i,j} \{\mu_x\}_{i,j} W_{i,j}^{(p,f)}}{\sum_{i,j} W_{i,j}^{(p,f)}} && (4.9) \\ &\equiv \tau\left(\langle \mu_x \{\mu_x\}\rangle_e - \langle \mu_x\rangle_e \langle\{\mu_x\}\rangle_e\right) && (4.10) \end{aligned}$$

The formula (4.9) is the QMC estimator of $X_{x,x}^1$ polarizability for a general system. From now on, (4.10) will be used as a shortcut for (4.9) and it will also be referred to as the estimator. In the next section we will show how this formula simplifies further when the system has spherical symmetry.

By the same procedure we can obtain QMC estimator for any polarizability component. For a higher degree polarizability the number of terms grows quite

fast and it becomes complicated. Therefore, it was done by using Maple computer algebra software (Appendx B.2).

One also has to keep track of all possible applications of the Hellmann-Feynman theorem which give us different estimators for the same component. For example there are two ways in the case of $X^2_{xx,x,x}$

$$X^2_{xx,x,x} = -3\,\frac{\partial^2 \langle \frac{\partial \mathrm{H}}{\partial E_{xx}} \rangle_e}{\partial E_x^2}\bigg|_{E_\alpha=0,E_{\alpha\beta}=0,\ldots} = -3\,\frac{\partial^2 \langle \frac{\partial \mathrm{H}}{\partial E_x} \rangle_e}{\partial E_{xx}\partial E_x}\bigg|_{E_\alpha=0,E_{\alpha\beta}=0,\ldots} \tag{4.11}$$

Therefore, we will end up with two different estimators. However, in some cases, such as $X^3_{x,x,y,y}$, this gives estimators differing only by a permutation of indices $[x, y, z]$.

4.2 Simplified Estimators of Atomic Polarizabilities up to the Sixth Degree

If the system is spherically symmetric (such as an atom), several terms in the QMC estimators will vanish. For example, the second term in (4.10) vanishes because $\langle \mu_x \rangle_e$ is the x-component of permanent dipole moment, which was shown to be zero for atoms (Chapter 3). Similarly, all permanent multipoles will vanish

$$\langle \mu_\alpha \rangle_e = 0 \tag{4.12}$$

$$\langle \Theta_{\alpha\beta} \rangle_e = 0 \tag{4.13}$$

$$\langle \Omega_{\alpha\beta\gamma} \rangle_e = 0, \ldots \tag{4.14}$$

If an expectation value of an operator is zero then the expectation value of a cummulative value of that operator also has to be zero. We can write

$$\langle \{\mu_\alpha\} \rangle_e = 0 \tag{4.15}$$

$$\langle \{\Theta_{\alpha\beta}\} \rangle_e = 0 \tag{4.16}$$

$$\langle \{\Omega_{\alpha\beta\gamma}\} \rangle_e = 0, \ldots \tag{4.17}$$

Straightforward generalization of this idea yields the following relations for expectation values of various products of dipole and quadrupole moments and their cummulative values. These are the only ones relevant to this work and are used for simplification of QMC polarizability estimators up to the sixth degree. They are [1]

$$\langle\{\mu_\alpha\}^k\rangle_e = 0;\ k = 1,3,5,\dots \tag{4.18}$$

$$\langle\mu_\alpha\{\mu_\beta\}^k\rangle_e = 0;\ \alpha\neq\beta, k = 0,1,2,3,\dots \tag{4.19}$$

$$\langle\{\mu_\alpha\}\{\mu_\beta\}^k\rangle_e = 0;\ \alpha\neq\beta, k = 0,1,2,3,\dots \tag{4.20}$$

$$\langle\{\mu_x\}\{\mu_y\}\{\mu_z\}\rangle_e = 0 \tag{4.21}$$

$$\langle\mu_\alpha\{\mu_\alpha\}^k\{\mu_\beta\}^l\rangle_e = 0;\ k,l = 1,3,5,\dots \tag{4.22}$$

$$\langle\mu_\alpha\{\mu_\beta\}\{\mu_\gamma\}\rangle_e = 0;\ \alpha\neq\beta\neq\gamma\neq\alpha \tag{4.23}$$

$$\langle\Theta_{\alpha\beta}\{\mu_\gamma\}\rangle_e = 0 \tag{4.24}$$

$$\langle\mu_\alpha\{\Theta_{\beta\gamma}\}\rangle_e = 0 \tag{4.25}$$

By using the spherical symmetry relations (4.12–4.25) all QMC polarizability estimators obtained by the procedure described in the previous section greatly simplify.

Resulting formulas for all non-equivalent [2] components of all atomic polarizabilities up to the sixth order are

$$X^1_{x,x} = \tau\langle\mu_x\{\mu_x\}\rangle_e \tag{4.26}$$

$$X^3_{x,x,x,x} = \tau^3(\langle\mu_x\{\mu_x\}^3\rangle_e - 3\langle\{\mu_x\}^2\rangle_e\langle\mu_x\{\mu_x\}\rangle_e) \tag{4.27}$$

$$X^3_{x,x,y,y} = \tau^3(\langle\mu_x\{\mu_x\}\{\mu_y\}^2\rangle_e - \langle\{\mu_y\}^2\rangle_e\langle\mu_x\{\mu_x\}\rangle_e) \tag{4.28}$$

---

[1] In these formulas we do not use the summation convention.

[2] The formulas are non-equivalent in the sense that none of them can be obtained from another one by a permutation of $[x,y,z]$.

$$\begin{aligned}
X^2_{xx,x,x} &= \tau^2\langle\mu_x\,\{\mu_x\}\,\{\Theta_{xx}\}\rangle_e \qquad (4.29)\\
&= \tau^2\langle\Theta_{xx}\,\{\mu_x\}^2\rangle_e \qquad (4.30)\\
X^2_{xx,y,y} &= \tau^2\langle\mu_y\,\{\mu_y\}\,\{\Theta_{xx}\}\rangle_e \qquad (4.31)\\
&= \tau^2\langle\Theta_{xx}\,\{\mu_y\}^2\rangle_e \qquad (4.32)\\
X^2_{xz,x,z} &= \tau^2\langle\mu_x\,\{\mu_z\}\,\{\Theta_{xz}\}\rangle_e \qquad (4.33)\\
&= \tau^2\langle\Theta_{xz}\,\{\mu_x\}\,\{\mu_z\}\rangle_e \qquad (4.34)
\end{aligned}$$

$$\begin{aligned}
X^1_{xx,xx} &= \tau\langle\Theta_{xx}\,\{\Theta_{xx}\}\rangle_e \qquad (4.35)\\
X^1_{xx,zz} &= \tau\langle\Theta_{xx}\,\{\Theta_{zz}\}\rangle_e \qquad (4.36)\\
X^1_{xz,xz} &= \tau\langle\Theta_{xz}\,\{\Theta_{xz}\}\rangle_e \qquad (4.37)
\end{aligned}$$

$$\begin{aligned}
X^5_{x,x,x,x,x} &= \tau^5(\langle\mu_x\,\{\mu_x\}^5\rangle_e + 30\langle\{\mu_x\}^2\rangle_e{}^2\langle\mu_x\,\{\mu_x\}\rangle_e\\
&\quad -5\langle\{\mu_x\}^4\rangle_e\langle\mu_x\,\{\mu_x\}\rangle_e - 10\langle\{\mu_x\}^2\rangle_e\langle\mu_x\,\{\mu_x\}^3\rangle_e) \qquad (4.38)\\
X^5_{x,x,z,z,z,z} &= \tau^5(\langle\mu_x\,\{\mu_x\}\,\{\mu_z\}^4\rangle_e - 6\langle\{\mu_z\}^2\rangle_e\langle\mu_x\,\{\mu_x\}\,\{\mu_z\}^2\rangle_e\\
&\quad +6\langle\{\mu_z\}^2\rangle_e{}^2\langle\mu_x\,\{\mu_x\}\rangle_e - \langle\{\mu_z\}^4\rangle_e\langle\mu_x\,\{\mu_x\}\rangle_e) \qquad (4.39)\\
&= \tau^5(\langle\mu_z\,\{\mu_x\}^2\,\{\mu_z\}^3\rangle_e - \langle\{\mu_x\}^2\rangle_e\langle\mu_z\,\{\mu_z\}^3\rangle_e\\
&\quad -3\langle\{\mu_x\}^2\,\{\mu_z\}^2\rangle_e\langle\mu_z\,\{\mu_z\}\rangle_e\\
&\quad -3\langle\{\mu_z\}^2\rangle_e\langle\mu_z\,\{\mu_x\}^2\,\{\mu_z\}\rangle_e\\
&\quad +6\langle\{\mu_x\}^2\rangle_e\langle\{\mu_z\}^2\rangle_e\langle\mu_z\,\{\mu_z\}\rangle_e) \qquad (4.40)\\
X^5_{x,x,y,y,z,z} &= \tau^5(\langle\mu_x\,\{\mu_x\}\,\{\mu_y\}^2\,\{\mu_z\}^2\rangle_e - \langle\{\mu_y\}^2\rangle_e\langle\mu_x\,\{\mu_x\}\,\{\mu_z\}^2\rangle_e\\
&\quad -\langle\{\mu_y\}^2\,\{\mu_z\}^2\rangle_e\langle\mu_x\,\{\mu_x\}\rangle_e\\
&\quad +2\langle\{\mu_y\}^2\rangle_e\langle\{\mu_z\}^2\rangle_e\langle\mu_x\,\{\mu_x\}\rangle_e\\
&\quad -\langle\{\mu_z\}^2\rangle_e\langle\mu_x\,\{\mu_x\}\,\{\mu_y\}^2\rangle_e) \qquad (4.41)
\end{aligned}$$

$$X^4_{xx,x,x,x,x} = \tau^4(\langle\Theta_{xx}\,\{\mu_x\}^4\rangle_e - 6\langle\{\mu_x\}^2\rangle_e\langle\Theta_{xx}\,\{\mu_x\}^2\rangle_e) \qquad (4.42)$$

$$
\begin{aligned}
&= \tau^4(\langle \mu_x \{\mu_x\}^3 \{\Theta_{xx}\}\rangle_e - 3\langle\{\mu_x\}^2\rangle_e\langle \mu_x \{\mu_x\} \{\Theta_{xx}\}\rangle_e \\
&\quad -3\langle \mu_x \{\mu_x\}\rangle_e\langle\{\mu_x\}^2 \{\Theta_{xx}\}\rangle_e) \qquad (4.43)
\end{aligned}
$$

$$
\begin{aligned}
X^4_{xx,y,y,y,y} &= \tau^4(\langle \mu_y \{\mu_y\}^3 \{\Theta_{xx}\}\rangle_e - 3\langle\{\mu_y\}^2\rangle_e\langle \mu_y \{\mu_y\} \{\Theta_{xx}\}\rangle_e \\
&\quad -3\langle \mu_y \{\mu_y\}\rangle_e\langle\{\mu_y\}^2 \{\Theta_{xx}\}\rangle_e) \qquad (4.44) \\
&= \tau^4(\langle \Theta_{xx} \{\mu_y\}^4\rangle_e - 6\langle\{\mu_y\}^2\rangle_e\langle \Theta_{xx} \{\mu_y\}^2\rangle_e) \qquad (4.45)
\end{aligned}
$$

$$
\begin{aligned}
X^4_{xx,x,x,y,y} &= \tau^4(\langle \mu_x \{\mu_x\} \{\mu_y\}^2 \{\Theta_{xx}\}\rangle_e - \langle \mu_x \{\mu_x\}\rangle_e\langle\{\mu_y\}^2 \{\Theta_{xx}\}\rangle_e \\
&\quad -\langle\{\mu_y\}^2\rangle_e\langle \mu_x \{\mu_x\} \{\Theta_{xx}\}\rangle_e) \qquad (4.46) \\
&= \tau^4(\langle \mu_y \{\mu_x\}^2 \{\mu_y\} \{\Theta_{xx}\}\rangle_e - \langle \mu_y \{\mu_y\}\rangle_e\langle\{\mu_x\}^2 \{\Theta_{xx}\}\rangle_e \\
&\quad -\langle\{\mu_x\}^2\rangle_e\langle \mu_y \{\mu_y\} \{\Theta_{xx}\}\rangle_e) \qquad (4.47) \\
&= \tau^4(\langle \Theta_{xx} \{\mu_x\}^2 \{\mu_y\}^2\rangle_e - \langle\{\mu_x\}^2\rangle_e\langle \Theta_{xx} \{\mu_y\}^2\rangle_e \\
&\quad -\langle\{\mu_y\}^2\rangle_e\langle \Theta_{xx} \{\mu_x\}^2\rangle_e) \qquad (4.48)
\end{aligned}
$$

$$
\begin{aligned}
X^4_{xz,x,z,z,z} &= \tau^4(\langle \mu_x \{\mu_z\}^3 \{\Theta_{xz}\}\rangle_e - 3\langle\{\mu_z\}^2\rangle_e\langle \mu_x \{\mu_z\} \{\Theta_{xz}\}\rangle_e) \qquad (4.49) \\
&= \tau^4(\langle \mu_z \{\mu_x\} \{\mu_z\}^2 \{\Theta_{xz}\}\rangle_e \\
&\quad -2\langle \mu_z \{\mu_z\}\rangle_e\langle\{\mu_x\} \{\mu_z\} \{\Theta_{xz}\}\rangle_e \\
&\quad -\langle\{\mu_z\}^2\rangle_e\langle \mu_z \{\mu_x\} \{\Theta_{xz}\}\rangle_e) \qquad (4.50) \\
&= \tau^4(\langle \Theta_{xz} \{\mu_x\} \{\mu_z\}^3\rangle_e - 3\langle\{\mu_z\}^2\rangle_e\langle \Theta_{xz} \{\mu_x\} \{\mu_z\}\rangle_e) \qquad (4.51)
\end{aligned}
$$

$$
\begin{aligned}
X^4_{xz,x,z,y,y} &= \tau^4(\langle \mu_x \{\mu_y\}^2 \{\mu_z\} \{\Theta_{xz}\}\rangle_e \\
&\quad -\langle\{\mu_y\}^2\rangle_e\langle \mu_x \{\mu_z\} \{\Theta_{xz}\}\rangle_e) \qquad (4.52) \\
&= \tau^4(\langle \mu_y \{\mu_x\} \{\mu_y\} \{\mu_z\} \{\Theta_{xz}\}\rangle_e \\
&\quad -\langle \mu_y \{\mu_y\}\rangle_e\langle\{\mu_x\} \{\mu_z\} \{\Theta_{xz}\}\rangle_e) \qquad (4.53) \\
&= \tau^4(\langle \Theta_{xz} \{\mu_x\} \{\mu_y\}^2 \{\mu_z\}\rangle_e \\
&\quad -\langle\{\mu_y\}^2\rangle_e\langle \Theta_{xz} \{\mu_x\} \{\mu_z\}\rangle_e) \qquad (4.54)
\end{aligned}
$$

$$
\begin{aligned}
X^4_{xx,y,y,z,z} &= \tau^4(\langle \mu_y \{\mu_y\} \{\mu_z\}^2 \{\Theta_{xx}\}\rangle_e - \langle \mu_y \{\mu_y\}\rangle_e\langle\{\mu_z\}^2 \{\Theta_{xx}\}\rangle_e \\
&\quad -\langle\{\mu_z\}^2\rangle_e\langle \mu_y \{\mu_y\} \{\Theta_{xx}\}\rangle_e) \qquad (4.55)
\end{aligned}
$$

$$\begin{aligned} &= \tau^4(\langle\Theta_{xx}\{\mu_y\}^2\{\mu_z\}^2\rangle_e - \langle\{\mu_z\}^2\rangle_e\langle\Theta_{xx}\{\mu_y\}^2\rangle_e \\ &\quad -\langle\{\mu_y\}^2\rangle_e\langle\Theta_{xx}\{\mu_z\}^2\rangle_e) \end{aligned} \tag{4.56}$$

$$X^3_{xx,xx,x,x} = \tau^3(\langle\mu_x\{\mu_x\}\{\Theta_{xx}\}^2\rangle_e - \langle\mu_x\{\mu_x\}\rangle_e\langle\{\Theta_{xx}\}^2\rangle_e) \tag{4.57}$$

$$= \tau^3(\langle\Theta_{xx}\{\mu_x\}^2\{\Theta_{xx}\}\rangle_e - \langle\{\mu_x\}^2\rangle_e\langle\Theta_{xx}\{\Theta_{xx}\}\rangle_e) \tag{4.58}$$

$$X^3_{xx,xx,y,y} = \tau^3(\langle\mu_y\{\mu_y\}\{\Theta_{xx}\}^2\rangle_e - \langle\mu_y\{\mu_y\}\rangle_e\langle\{\Theta_{xx}\}^2\rangle_e) \tag{4.59}$$

$$= \tau^3(\langle\Theta_{xx}\{\mu_y\}^2\{\Theta_{xx}\}\rangle_e - \langle\{\mu_y\}^2\rangle_e\langle\Theta_{xx}\{\Theta_{xx}\}\rangle_e) \tag{4.60}$$

$$X^3_{xz,yz,x,y} = \tau^3\langle\mu_x\{\mu_y\}\{\Theta_{xz}\}\{\Theta_{yz}\}\rangle_e \tag{4.61}$$

$$= \tau^3\langle\Theta_{xz}\{\mu_x\}\{\mu_y\}\{\Theta_{yz}\}\rangle_e \tag{4.62}$$

$$X^3_{xz,zz,x,z} = \tau^3\langle\Theta_{zz}\{\mu_x\}\{\mu_z\}\{\Theta_{xz}\}\rangle_e \tag{4.63}$$

$$= \tau^3\langle\mu_x\{\mu_z\}\{\Theta_{zz}\}\{\Theta_{xz}\}\rangle_e \tag{4.64}$$

$$= \tau^3\langle\mu_z\{\mu_x\}\{\Theta_{zz}\}\{\Theta_{xz}\}\rangle_e \tag{4.65}$$

$$= \tau^3\langle\Theta_{xz}\{\mu_x\}\{\mu_z\}\{\Theta_{zz}\}\rangle_e \tag{4.66}$$

$$X^3_{xz,yy,x,z} = \tau^3\langle\mu_x\{\mu_z\}\{\Theta_{yy}\}\{\Theta_{xz}\}\rangle_e \tag{4.67}$$

$$= \tau^3\langle\Theta_{yy}\{\mu_x\}\{\mu_z\}\{\Theta_{xz}\}\rangle_e \tag{4.68}$$

$$= \tau^3\langle\Theta_{xz}\{\mu_x\}\{\mu_z\}\{\Theta_{yy}\}\rangle_e \tag{4.69}$$

$$\begin{aligned} X^3_{xx,yy,z,z} &= \tau^3(\langle\mu_z\{\mu_z\}\{\Theta_{xx}\}\{\Theta_{yy}\}\rangle_e \\ &\quad -\langle\mu_z\{\mu_z\}\rangle_e\langle\{\Theta_{xx}\}\{\Theta_{yy}\}\rangle_e) \end{aligned} \tag{4.70}$$

$$= \tau^3(\langle\Theta_{xx}\{\mu_z\}^2\{\Theta_{yy}\}\rangle_e - \langle\{\mu_z\}^2\rangle_e\langle\Theta_{xx}\{\Theta_{yy}\}\rangle_e) \tag{4.71}$$

$$\begin{aligned} X^3_{xx,yy,y,y} &= \tau^3(\langle\mu_y\{\mu_y\}\{\Theta_{xx}\}\{\Theta_{yy}\}\rangle_e \\ &\quad -\langle\mu_y\{\mu_y\}\rangle_e\langle\{\Theta_{xx}\}\{\Theta_{yy}\}\rangle_e) \end{aligned} \tag{4.72}$$

$$= \tau^3(\langle\Theta_{xx}\{\mu_y\}^2\{\Theta_{yy}\}\rangle_e - \langle\{\mu_y\}^2\rangle_e\langle\Theta_{xx}\{\Theta_{yy}\}\rangle_e) \tag{4.73}$$

$$= \tau^3(\langle\Theta_{yy}\{\mu_y\}^2\{\Theta_{xx}\}\rangle_e - \langle\{\mu_y\}^2\rangle_e\langle\Theta_{yy}\{\Theta_{xx}\}\rangle_e) \tag{4.74}$$

$$X^3_{xz,xz,y,y} = \tau^3(\langle\mu_y\{\mu_y\}\{\Theta_{xz}\}^2\rangle_e - \langle\mu_y\{\mu_y\}\rangle_e\langle\{\Theta_{xz}\}^2\rangle_e) \tag{4.75}$$

$$= \tau^3(\langle \Theta_{xz}\,\{\mu_y\}^2\,\{\Theta_{xz}\}\rangle_e - \langle \{\mu_y\}^2\rangle_e \langle \Theta_{xz}\,\{\Theta_{xz}\}\rangle_e) \tag{4.76}$$

$$X^3_{xz,xz,z,z} = \tau^3(\langle \mu_z\,\{\mu_z\}\,\{\Theta_{xz}\}^2\rangle_e - \langle \mu_z\,\{\mu_z\}\rangle_e \langle \{\Theta_{xz}\}^2\rangle_e) \tag{4.77}$$

$$= \tau^3(\langle \Theta_{xz}\,\{\mu_z\}^2\,\{\Theta_{xz}\}\rangle_e - \langle \{\mu_z\}^2\rangle_e \langle \Theta_{xz}\,\{\Theta_{xz}\}\rangle_e) \tag{4.78}$$

$$X^2_{xx,xx,xx} = \tau^2\langle \Theta_{xx}\,\{\Theta_{xx}\}^2\rangle_e \tag{4.79}$$

$$X^2_{xx,yy,yy} = \tau^2\langle \Theta_{xx}\,\{\Theta_{yy}\}^2\rangle_e \tag{4.80}$$

$$= \tau^2\langle \Theta_{yy}\,\{\Theta_{xx}\}\,\{\Theta_{yy}\}\rangle_e \tag{4.81}$$

$$X^2_{xz,xz,xx} = \tau^2\langle \Theta_{xx}\,\{\Theta_{xz}\}^2\rangle_e \tag{4.82}$$

$$= \tau^2\langle \Theta_{xz}\,\{\Theta_{xx}\}\,\{\Theta_{xz}\}\rangle_e \tag{4.83}$$

$$X^2_{xy,yz,xz} = \tau^2\langle \Theta_{xz}\,\{\Theta_{xy}\}\,\{\Theta_{yz}\}\rangle_e \tag{4.84}$$

$$X^2_{xx,yy,zz} = \tau^2\langle \Theta_{xx}\,\{\Theta_{yy}\}\,\{\Theta_{zz}\}\rangle_e \tag{4.85}$$

$$X^2_{xy,xy,zz} = \tau^2\langle \Theta_{zz}\,\{\Theta_{xy}\}^2\rangle_e \tag{4.86}$$

$$= \tau^2\langle \Theta_{xy}\,\{\Theta_{zz}\}\,\{\Theta_{xy}\}\rangle_e \tag{4.87}$$

$$\begin{aligned} X^3_{xxx,x,x,x} = {} & \tau^3(\langle \mu_x\,\{\mu_x\}^2\,\{\Omega_{xxx}\}\rangle_e - 2\langle \mu_x\,\{\mu_x\}\rangle_e \langle \{\mu_x\}\,\{\Omega_{xxx}\}\rangle_e \\ & -\langle \{\mu_x\}^2\rangle_e \langle \mu_x\,\{\Omega_{xxx}\}\rangle_e) \end{aligned} \tag{4.88}$$

$$= \tau^3(\langle \Omega_{xxx}\,\{\mu_x\}^3\rangle_e - 3\langle \{\mu_x\}^2\rangle_e \langle \Omega_{xxx}\,\{\mu_x\}\rangle_e) \tag{4.89}$$

$$\begin{aligned} X^3_{xxy,y,y,y} = {} & \tau^3(\langle \mu_y\,\{\mu_y\}^2\,\{\Omega_{xxy}\}\rangle_e - 2\langle \mu_y\,\{\mu_y\}\rangle_e \langle \{\mu_y\}\,\{\Omega_{xxy}\}\rangle_e \\ & -\langle \{\mu_y\}^2\rangle_e \langle \mu_y\,\{\Omega_{xxy}\}\rangle_e) \end{aligned} \tag{4.90}$$

$$= \tau^3(\langle \Omega_{xxy}\,\{\mu_y\}^3\rangle_e - 3\langle \{\mu_y\}^2\rangle_e \langle \Omega_{xxy}\,\{\mu_y\}\rangle_e) \tag{4.91}$$

$$\begin{aligned} X^3_{xxy,x,x,y} = {} & \tau^3(\langle \mu_x\,\{\mu_x\}\,\{\mu_y\}\,\{\Omega_{xxy}\}\rangle_e \\ & -\langle \mu_x\,\{\mu_x\}\rangle_e \langle \{\mu_y\}\,\{\Omega_{xxy}\}\rangle_e) \end{aligned} \tag{4.92}$$

$$= \tau^3(\langle \mu_y\,\{\mu_x\}^2\,\{\Omega_{xxy}\}\rangle_e - \langle \{\mu_x\}^2\rangle_e \langle \mu_y\,\{\Omega_{xxy}\}\rangle_e) \tag{4.93}$$

$$= \tau^3(\langle \Omega_{xxy}\,\{\mu_x\}^2\,\{\mu_y\}\rangle_e - \langle \{\mu_x\}^2\rangle_e \langle \Omega_{xxy}\,\{\mu_y\}\rangle_e) \tag{4.94}$$

$$X^3_{xxx,x,y,y} = \tau^3(\langle \mu_x\,\{\mu_y\}^2\,\{\Omega_{xxx}\}\rangle_e - \langle \{\mu_y\}^2\rangle_e \langle \mu_x\,\{\Omega_{xxx}\}\rangle_e) \tag{4.95}$$

$$= \tau^3(\langle\mu_y\{\mu_x\}\{\mu_y\}\{\Omega_{xxx}\}\rangle_e - \langle\mu_y\{\mu_y\}\rangle_e\langle\{\mu_x\}\{\Omega_{xxx}\}\rangle_e) \tag{4.96}$$

$$= \tau^3(\langle\Omega_{xxx}\{\mu_x\}\{\mu_y\}^2\rangle_e - \langle\{\mu_y\}^2\rangle_e\langle\Omega_{xxx}\{\mu_x\}\rangle_e) \tag{4.97}$$

$$X^3_{xxy,y,z,z} = \tau^3(\langle\mu_y\{\mu_z\}^2\{\Omega_{xxy}\}\rangle_e - \langle\{\mu_z\}^2\rangle_e\langle\mu_y\{\Omega_{xxy}\}\rangle_e) \tag{4.98}$$

$$= \tau^3(\langle\mu_z\{\mu_y\}\{\mu_z\}\{\Omega_{xxy}\}\rangle_e - \langle\mu_z\{\mu_z\}\rangle_e\langle\{\mu_y\}\{\Omega_{xxy}\}\rangle_e) \tag{4.99}$$

$$= \tau^3(\langle\Omega_{xxy}\{\mu_y\}\{\mu_z\}^2\rangle_e - \langle\{\mu_z\}^2\rangle_e\langle\Omega_{xxy}\{\mu_y\}\rangle_e) \tag{4.100}$$

$$X^3_{xyz,x,y,z} = \tau^3\langle\mu_x\{\mu_y\}\{\mu_z\}\{\Omega_{xyz}\}\rangle_e \tag{4.101}$$

$$= \tau^3\langle\Omega_{xyz}\{\mu_x\}\{\mu_y\}\{\mu_z\}\rangle_e \tag{4.102}$$

$$X^2_{xxx,xx,x} = \tau^2\langle\mu_x\{\Theta_{xx}\}\{\Omega_{xxx}\}\rangle_e \tag{4.103}$$

$$= \tau^2\langle\Theta_{xx}\{\mu_x\}\{\Omega_{xxx}\}\rangle_e \tag{4.104}$$

$$= \tau^2\langle\Omega_{xxx}\{\mu_x\}\{\Theta_{xx}\}\rangle_e \tag{4.105}$$

$$X^2_{xxx,yy,x} = \tau^2\langle\mu_x\{\Theta_{yy}\}\{\Omega_{xxx}\}\rangle_e \tag{4.106}$$

$$= \tau^2\langle\Theta_{yy}\{\mu_x\}\{\Omega_{xxx}\}\rangle_e \tag{4.107}$$

$$= \tau^2\langle\Omega_{xxx}\{\mu_x\}\{\Theta_{yy}\}\rangle_e \tag{4.108}$$

$$X^2_{xxx,xy,y} = \tau^2\langle\mu_y\{\Theta_{xy}\}\{\Omega_{xxx}\}\rangle_e \tag{4.109}$$

$$= \tau^2\langle\Theta_{xy}\{\mu_y\}\{\Omega_{xxx}\}\rangle_e \tag{4.110}$$

$$= \tau^2\langle\Omega_{xxx}\{\mu_y\}\{\Theta_{xy}\}\rangle_e \tag{4.111}$$

$$X^2_{xxy,xx,y} = \tau^2\langle\mu_y\{\Theta_{xx}\}\{\Omega_{xxy}\}\rangle_e \tag{4.112}$$

$$= \tau^2\langle\Theta_{xx}\{\mu_y\}\{\Omega_{xxy}\}\rangle_e \tag{4.113}$$

$$= \tau^2\langle\Omega_{xxy}\{\mu_y\}\{\Theta_{xx}\}\rangle_e \tag{4.114}$$

$$X^2_{xxy,xy,x} = \tau^2\langle\mu_x\{\Theta_{xy}\}\{\Omega_{xxy}\}\rangle_e \tag{4.115}$$

$$= \tau^2\langle\Theta_{xy}\{\mu_x\}\{\Omega_{xxy}\}\rangle_e \tag{4.116}$$

$$= \tau^2 \langle \Omega_{xxy} \{\mu_x\} \{\Theta_{xy}\} \rangle_e \tag{4.117}$$

$$X^2_{xxy,zz,y} = \tau^2 \langle \mu_y \{\Theta_{zz}\} \{\Omega_{xxy}\} \rangle_e \tag{4.118}$$

$$= \tau^2 \langle \Theta_{zz} \{\mu_y\} \{\Omega_{xxy}\} \rangle_e \tag{4.119}$$

$$= \tau^2 \langle \Omega_{xxy} \{\mu_y\} \{\Theta_{zz}\} \rangle_e \tag{4.120}$$

$$X^2_{xyz,xy,z} = \tau^2 \langle \mu_z \{\Theta_{xy}\} \{\Omega_{xyz}\} \rangle_e \tag{4.121}$$

$$= \tau^2 \langle \Theta_{xy} \{\mu_z\} \{\Omega_{xyz}\} \rangle_e \tag{4.122}$$

$$= \tau^2 \langle \Omega_{xyz} \{\mu_z\} \{\Theta_{xy}\} \rangle_e \tag{4.123}$$

$$X^2_{xxy,yz,z} = \tau^2 \langle \mu_z \{\Theta_{yz}\} \{\Omega_{xxy}\} \rangle_e \tag{4.124}$$

$$= \tau^2 \langle \Theta_{yz} \{\mu_z\} \{\Omega_{xxy}\} \rangle_e \tag{4.125}$$

$$= \tau^2 \langle \Omega_{xxy} \{\mu_z\} \{\Theta_{yz}\} \rangle_e \tag{4.126}$$

$$X^2_{xxy,yy,y} = \tau^2 \langle \mu_y \{\Theta_{yy}\} \{\Omega_{xxy}\} \rangle_e \tag{4.127}$$

$$= \tau^2 \langle \Theta_{yy} \{\mu_y\} \{\Omega_{xxy}\} \rangle_e \tag{4.128}$$

$$= \tau^2 \langle \Omega_{xxy} \{\mu_y\} \{\Theta_{yy}\} \rangle_e \tag{4.129}$$

$$X^1_{xxx,xxx} = \tau \langle \Omega_{xxx} \{\Omega_{xxx}\} \rangle_e \tag{4.130}$$

$$X^1_{xyz,xyz} = \tau \langle \Omega_{xyz} \{\Omega_{xyz}\} \rangle_e \tag{4.131}$$

$$X^1_{xxy,zzy} = \tau \langle \Omega_{xxy} \{\Omega_{zzy}\} \rangle_e \tag{4.132}$$

$$X^1_{yyy,xxy} = \tau \langle \Omega_{xxy} \{\Omega_{yyy}\} \rangle_e \tag{4.133}$$

$$= \tau \langle \Omega_{yyy} \{\Omega_{xxy}\} \rangle_e \tag{4.134}$$

$$X^1_{xxy,xxy} = \tau \langle \Omega_{xxy} \{\Omega_{xxy}\} \rangle_e \tag{4.135}$$

These formulas can be used to obtain estimators for every non-zero component of every atomic polarizability tensor up to the sixth degree. For example, $X^1_{xxz,yyz}$ can be obtained by permutation $[x, y, z] \to [x, z, y]$ applied to the formula (4.132).

It is also clear that for two components which are related by a valid interchange of indices (trivial symmetry) such as $X^1_{xxz,zyy}$ and $X^1_{xxz,yyz}$, the formulas

components	H-F multiplicity
$X^1_{x,x}, X^1_{y,y}, X^1_{z,z}$	1

Table 4.1: Different estimators and H-F multiplicity for $X^1_{\alpha,\beta}$

components	H-F multiplicity
$X^3_{x,x,x,x}, X^3_{y,y,y,y}, X^3_{z,z,z,z}$	1
$X^3_{x,x,y,y}, X^3_{x,x,z,z}, X^3_{y,y,z,z}$	2

Table 4.2: Different estimators and H-F multiplicity for $X^3_{\alpha,\beta,\gamma,\delta}$

are exactly the same. It would be meaningless to evaluate both of them in a simulation, because both would result in the same number.

In Tables 4.1–4.11 are listed components of each atomic polarizability, which are both non-zero and not related by trivial symmetries. For example, in Table 4.2 are not written the components $X^3_{x,y,x,y}$, $X^3_{x,y,y,x}$, $X^3_{y,x,x,y}$, $X^3_{y,x,y,x}$, $X^3_{y,y,x,x}$ because they are equivalent to the one already written ($X^3_{x,x,y,y}$), which we picked as a representant of them. By H-F multiplicity is meant the number of different estimators of a component due to the different applications of the Hellmann-Feynman theorem.

The total number of estimators for each polarizability is given in Table 4.12. In total there are 542 possible different non-equivalent estimators of atomic polarizabilities up to the sixth degree.

components	H-F multiplicity
$X^2_{xx,x,x}, X^2_{yy,y,y}, X^2_{zz,z,z}$	2
$X^2_{xx,y,y}, X^2_{xx,z,z}, X^2_{yy,z,z}, X^2_{yy,x,x}, X^2_{zz,x,x}, X^2_{zz,y,y}$	2
$X^2_{xy,x,y}, X^2_{yz,y,z}, X^2_{xz,x,z}$	3

Table 4.3: Different estimators and H-F multiplicity for $X^2_{\alpha\beta,\gamma,\delta}$

components	H-F multiplicity
$X^1_{xx,xx}, X^1_{yy,yy}, X^1_{zz,zz}$	1
$X^1_{xx,yy}, X^1_{xx,zz}, X^1_{yy,zz}$	2
$X^1_{xy,xy}, X^1_{yz,yz}, X^1_{xz,xz}$	1

Table 4.4: Different estimators and H-F multiplicity for $X^1_{\alpha\beta,\gamma\delta}$

components	H-F multiplicity
$X^5_{x,x,x,x,x,x}, X^5_{y,y,y,y,y,y}, X^5_{z,z,z,z,z,z}$	1
$X^5_{x,x,y,y,y,y}, X^5_{x,x,z,z,z,z}, X^5_{y,y,z,z,z,z},$ $X^5_{y,y,x,x,x,x}, X^5_{z,z,x,x,x,x}, X^5_{z,z,y,y,y,y}$	2
$X^5_{x,x,y,y,z,z}$	3

Table 4.5: Different estimators and H-F multiplicity for $X^5_{\alpha,\beta,\gamma,\delta,\epsilon,\zeta}$

components	H-F multiplicity
$X^4_{xx,x,x,x,x}, X^4_{yy,y,y,y,y}, X^4_{zz,z,z,z,z}$	2
$X^4_{xx,y,y,y,y}, X^4_{xx,z,z,z,z}, X^4_{yy,z,z,z,z},$ $X^4_{yy,x,x,x,x}, X^4_{zz,x,x,x,x}, X^4_{zz,y,y,y,y}$	2
$X^4_{xx,x,x,y,y}, X^4_{xx,x,x,z,z}, X^4_{yy,y,y,z,z},$ $X^4_{yy,y,y,x,x}, X^4_{zz,z,z,x,x}, X^4_{zz,z,z,y,y}$	3
$X^4_{xy,x,y,y,y}, X^4_{xy,y,x,x,x}, X^4_{xz,x,z,z,z},$ $X^4_{xz,z,x,x,x}, X^4_{yz,y,z,z,z}, X^4_{yz,z,y,y,y}$	3
$X^4_{xy,x,y,z,z}, X^4_{xz,x,z,y,y}, X^4_{yz,y,z,x,x}$	4
$X^4_{xx,y,y,z,z}, X^4_{yy,x,x,z,z}, X^4_{zz,x,x,y,y}$	3

Table 4.6: Different estimators and H-F multiplicity for $X^4_{\alpha\beta,\gamma,\delta,\epsilon,\zeta}$

components	H-F multiplicity
$X^3_{xx,xx,x,x}$, $X^3_{yy,yy,y,y}$, $X^3_{zz,zz,z,z}$	2
$X^3_{xx,xx,y,y}$, $X^3_{xx,xx,z,z}$, $X^3_{yy,yy,z,z}$, $X^3_{yy,yy,x,x}$, $X^3_{zz,zz,x,x}$, $X^3_{zz,zz,y,y}$	2
$X^3_{xz,yz,x,y}$, $X^3_{xz,xy,y,z}$, $X^3_{xy,yz,x,z}$	4
$X^3_{xy,yy,x,y}$, $X^3_{xy,xx,x,y}$, $X^3_{xz,xx,x,z}$, $X^3_{xz,zz,x,z}$, $X^3_{yz,yy,y,z}$, $X^3_{yz,zz,y,z}$	4
$X^3_{xy,zz,x,y}$, $X^3_{xz,yy,x,z}$, $X^3_{yz,xx,y,z}$	4
$X^3_{xx,yy,z,z}$, $X^3_{xx,zz,y,y}$, $X^3_{yy,zz,x,x}$	3
$X^3_{xx,yy,y,y}$, $X^3_{yy,xx,x,x}$, $X^3_{xx,zz,z,z}$, $X^3_{zz,xx,x,x}$, $X^3_{yy,zz,z,z}$, $X^3_{zz,yy,y,y}$	3
$X^3_{xy,xy,z,z}$, $X^3_{xz,xz,y,y}$, $X^3_{yz,yz,x,x}$	2
$X^3_{xy,xy,y,y}$, $X^3_{xy,xy,x,x}$, $X^3_{xz,xz,x,x}$, $X^3_{xz,xz,z,z}$, $X^3_{yz,yz,y,y}$, $X^3_{yz,yz,z,z}$	2

Table 4.7: Different estimators and H-F multiplicity for $X^3_{\alpha\beta,\gamma\delta,\varepsilon,\zeta}$

components	H-F multiplicity
$X^2_{xx,xx,xx}$, $X^2_{yy,yy,yy}$, $X^2_{zz,zz,zz}$	1
$X^2_{xx,xx,yy}$, $X^2_{xx,xx,zz}$, $X^2_{yy,yy,zz}$, $X^2_{yy,yy,xx}$, $X^2_{zz,zz,xx}$, $X^2_{zz,zz,yy}$	2
$X^2_{xy,xy,yy}$, $X^2_{xy,xy,xx}$, $X^2_{xz,xz,xx}$, $X^2_{xz,xz,zz}$, $X^2_{yz,yz,yy}$, $X^2_{yz,yz,zz}$	2
$X^2_{xy,yz,xz}$	3
$X^2_{xx,yy,zz}$	3
$X^2_{xy,xy,zz}$, $X^2_{xz,xz,yy}$, $X^2_{yz,yz,xx}$	2

Table 4.8: Different estimators and H-F multiplicity for $X^2_{\alpha\beta,\gamma\delta,\varepsilon\zeta}$

components	H-F multiplicity
$X^2_{xxx,x,x,x}$, $X^2_{yyy,y,y,y}$, $X^2_{zzz,z,z,z}$	2
$X^2_{xxy,y,y,y}$, $X^2_{xxz,z,z,z}$, $X^2_{yyx,x,x,x}$, $X^2_{yyz,z,z,z}$, $X^2_{zzx,x,x,x}$, $X^2_{zzy,y,y,y}$	2
$X^2_{xxy,x,x,y}$, $X^2_{xxz,x,x,z}$, $X^2_{yyx,y,y,x}$, $X^2_{yyz,y,y,z}$, $X^2_{zzx,z,z,x}$, $X^2_{zzy,z,z,y}$	3
$X^2_{xxx,x,y,y}$, $X^2_{xxx,x,z,z}$, $X^2_{yyy,y,x,x}$, $X^2_{yyy,y,z,z}$, $X^2_{zzz,z,x,x}$, $X^2_{zzz,z,y,y}$	3
$X^2_{xxy,y,z,z}$, $X^2_{xxz,z,y,y}$, $X^2_{yyx,x,z,z}$, $X^2_{yyz,z,x,x}$, $X^2_{zzx,x,y,y}$, $X^2_{zzy,y,x,x}$	3
$X^2_{xyz,x,y,z}$	4

Table 4.9: Different estimators and H-F multiplicity for $X^3_{\alpha\beta\gamma,\delta,\varepsilon,\zeta}$

components	H-F multiplicity
$X^2_{xxx,xx,x}, X^2_{yyy,yy,y}, X^2_{zzz,zz,z}$	3
$X^2_{xxx,yy,x}, X^2_{xxx,zz,x}, X^2_{yyy,xx,y}, X^2_{yyy,zz,y}, X^2_{zzz,xx,z}, X^2_{zzz,yy,z}$	3
$X^2_{xxx,xy,y}, X^2_{xxx,xz,z}, X^2_{yyy,xy,x}, X^2_{yyy,yz,z}, X^2_{zzz,xz,x}, X^2_{zzz,yz,y}$	3
$X^2_{xxy,xx,y}, X^2_{xxz,xx,z}, X^2_{yyx,yy,x}, X^2_{yyz,yy,z}, X^2_{zzx,zz,x}, X^2_{zzy,zz,y}$	3
$X^2_{xxy,xy,x}, X^2_{xxz,xz,x}, X^2_{yyx,xy,y}, X^2_{yyz,yz,y}, X^2_{zzx,xz,z}, X^2_{zzy,yz,z}$	3
$X^2_{xxy,zz,y}, X^2_{xxz,yy,z}, X^2_{yyx,zz,x}, X^2_{yyz,xx,z}, X^2_{zzx,yy,x}, X^2_{zzy,xx,y}$	3
$X^2_{xyz,xy,z}, X^2_{xyz,xz,z}, X^2_{xyz,yz,x}$	3
$X^2_{xxy,yz,z}, X^2_{xxz,yz,y}, X^2_{yyx,xz,z}, X^2_{yyz,xz,x}, X^2_{zzx,xy,y}, X^2_{zzy,xy,x}$	3
$X^2_{xxy,yy,y}, X^2_{xxz,zz,z}, X^2_{yyx,xx,x}, X^2_{yyz,zz,z}, X^2_{zzx,xx,x}, X^2_{zzy,yy,y}$	3

Table 4.10: Different estimators and H-F multiplicity for $X^2_{\alpha\beta\gamma,\delta\varepsilon,\zeta}$

components	H-F multiplicity
$X^1_{xxx,xxx}, X^1_{yyy,yyy}, X^1_{zzz,zzz}$	1
$X^1_{xyz,xyz}$	1
$X^1_{xxy,zzy}, X^1_{xxz,yyz}, X^1_{yyx,zzx}$	2
$X^1_{xxx,yyx}, X^1_{xxx,zzx}, X^1_{yyy,xxy}, X^1_{yyy,zzy}, X^1_{zzz,xxz}, X^1_{zzz,yyz}$	2
$X^1_{xxy,xxy}, X^1_{xxz,xxz}, X^1_{yyx,yyx}, X^1_{yyz,yyz}, X^1_{zzx,zzx}, X^1_{zzy,zzy}$	1

Table 4.11: Different estimators and H-F multiplicity for $X^1_{\alpha\beta\gamma,\delta\varepsilon\zeta}$

polarizability	number of estimators
$X^1_{\alpha,\beta}$	3
$X^3_{\alpha,\beta,\gamma,\delta}$	9
$X^2_{\alpha\beta,\gamma,\delta}$	27
$X^1_{\alpha\beta,\gamma\delta}$	12
$X^5_{\alpha,\beta,\gamma,\delta,\varepsilon,\zeta}$	18
$X^4_{\alpha\beta,\gamma,\delta,\varepsilon,\zeta}$	75
$X^3_{\alpha\beta,\gamma\delta,\varepsilon,\zeta}$	111
$X^2_{\alpha\beta,\gamma\delta,\varepsilon\zeta}$	39
$X^3_{\alpha\beta\gamma,\delta,\varepsilon,\zeta}$	76
$X^2_{\alpha\beta\gamma,\delta\varepsilon,\zeta}$	144
$X^1_{\alpha\beta\gamma,\delta\varepsilon\zeta}$	28
Total	542

Table 4.12: Number of different estimators

Chapter 5

Technical Details

5.1 Trial Functions

The choice of a trial function Ψ is very important for designing a quantum Monte Carlo simulation. For node-less systems the quality of the trial function affects the efficiency of the simulation, the variance of estimate. For systems with nodes the quality of Ψ affects the magnitude of the fixed-node error. Thus, in our simulations we use trial functions which satisfy some conditions characteristic of high quality: low variational ground-state energy, high overlap integral with the exact solution, among other criteria.

Of course, in the case of the hydrogen atom, the choice of Ψ is simple and straightforward. Hydrogen atom has an electronic Hamiltonian given by (atomic units)

$$\mathrm{H}_0 = -\frac{1}{2}\nabla^2 - \frac{1}{r} \tag{5.1}$$

and the corresponding Schrödinger equation can be analytically solved. The normalized ground-state wavefunction of the hydrogen atom is

$$\Psi(\mathbf{r}) = \frac{1}{\sqrt{\pi}}\exp(-r) \tag{5.2}$$

the drift vector field (2.29) is equal to

$$\mathbf{F} \equiv \frac{\nabla\Psi}{\Psi} = -\frac{\mathbf{r}}{r} \tag{5.3}$$

and the local energy (4.5) is a constant

$$E_0^{loc} \equiv \frac{\mathrm{H}_0\Psi}{\Psi} = -0.5 \tag{5.4}$$

This makes all weights (4.8) equal, and we don't have to calculate them. They can be set to one in all atomic polarizability estimators (4.26–4.135).

The exact ground-state solution of the Schrödinger equation for the helium atom with the Hamiltonian given by

$$\mathrm{H}_0 = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - 2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} \tag{5.5}$$

is not known. Any trial function is therefore an approximation to the exact solution.

We use a trial function which is a result of a sophisticated optimization of its variational energy [76, 77]. The symmetric spatial part of the trial function has the following form [1]

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Phi(1)\Phi(2)J_{SM} \tag{5.6}$$

where the atomic orbitals Φ are a linear combination of four Slater-type orbitals

$$\Phi = c_1\phi_{1s}(\zeta_{1s}) + c_2\phi_{2s}(\zeta_{2s}^1) + c_3\phi_{2s}(\zeta_{2s}^2) + c_4\phi_{3s}(\zeta_{3s}) \tag{5.7}$$

and J_{SM} is a Schmidt-Moskowitz electron correlation factor

$$J_{SM} = \exp\left[\sum_{k=1}^{9} g_k(\bar{r}_1^{m_k}\bar{r}_2^{n_k} + \bar{r}_2^{m_k}\bar{r}_1^{n_k})\bar{r}_{12}^{o_k}\right] \tag{5.8}$$

$$\bar{r}_i = \frac{br_i}{1+br_i}\ ;\ i = 1, 2 \tag{5.9}$$

$$\bar{r}_{12} = \frac{dr_{12}}{1+dr_{12}} \tag{5.10}$$

The values for all parameters $b, d, c_i, \zeta_{1s}, \zeta_{2s}^1, \zeta_{2s}^2, \zeta_{3s}$ and g_k, m_k, n_k, o_k are given in Table 5.1. We correct a misprint for one of the published parameter, c_4 in [76].

The corresponding drift and local energy are complicated functions of the configuration vector $\mathbf{R} \equiv [x_1, y_1, z_1, x_2, y_2, z_2]$ and were implemented by M. Snajdr

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[1] The spin part has the antisymmetric singlet form $(\alpha(1)\beta(2) - \alpha(2)\beta(1))/\sqrt(2)$.

par.	value	par.	value	par.	value	par.	value	par.	value
ζ_{1s}	1.526	g_1	0.5	m_1	0	n_1	0	o_1	1
c_1	1.348	g_2	-0.18	m_2	0	n_2	0	o_2	2
ζ_{2s}^1	1.757	g_3	-0.138	m_3	0	n_3	0	o_3	3
c_2	-0.366	g_4	-0.343	m_4	0	n_4	0	o_4	4
ζ_{2s}^2	2.88	g_5	0.623	m_5	2	n_5	0	o_5	0
c_3	-0.103	g_6	0.111	m_6	3	n_6	0	o_6	0
ζ_{3s}	5.229	g_7	-0.155	m_7	4	n_7	0	o_7	0
c_4	0.0226	g_8	-1.73	m_8	2	n_8	2	o_8	0
b	0.847	g_9	1.825	m_9	2	n_9	0	o_9	2
d	0.478								

Table 5.1: Parameters of the helium trial function

and available as "black box" computer procedures. The trial energy is chosen to be an estimate of the variational energy of the trial function

$$E_T = -2.903\,109 \text{ a. u.} \tag{5.11}$$

For comparison, the exact ground-state energy of the helium atom is $E_0 = -2.903\,72\ldots$ a. u. [76].

This trial function appears to be of very high quality. It recovers 99% of the correlation energy, gives very good variational expectation values of various non-differential operators [78], and we estimated its overlap with the unknown solution was estimated to be 0.999 957(8) [70].

However, the local energy for this trial function has singularities for a configuration of two electrons close to each other or one electron close to the nucleus. This would yield to an unusually large (or small) branching factor for the particle and it would affect $2L - 1$ succesive weights (Figure 2.1), potentially biasing estimates of the ground-state expectation values.

Thus, in the case of helium, any branching factor larger that some treshold value has to be truncated, but in a τ dependent manner, such that the truncation will statistically vanish in the limit $\tau \to 0$ [79].

Based on a trial run, which showed us the size of fluctuations of the local energy, we decided to truncate the exponent of the branching factor as follows

$$-\tau(E_{i,j}^{loc}-E_T)=\begin{cases}-\tau(E_{i,j}^{loc}-E_T) & \text{if } |\tau(E_{i,j}^{loc}-E_T)|\leq 0.5\tau_0\\ 0.5\tau_0\mathrm{sign}[-\tau(E_{i,j}^{loc}-E_T)] & \text{otherwise}\end{cases} \tag{5.12}$$

where τ_0 is the maximum time-step used in the simulation.

Similarily, the drift can be for some configurations a very large vector in the case of helium, which would "push" a particle very far away from a region of reasonable probability and potentially also cause a bias. We chose the following truncation

$$\tau\mathbf{F}=\begin{cases}\tau\mathbf{F} & \text{if } |\tau\mathbf{F}|\leq 2.7\tau_0\\ \frac{\tau\mathbf{F}}{|\tau\mathbf{F}|}2.7\tau_0 & \text{otherwise}\end{cases} \tag{5.13}$$

5.2 Design of the Simulation

The basic structure of the simulations is as described at the end of Chapter 2. The quantities we are going to directly estimate are the exact expectation values $\langle\mu_x\{\mu_x\}\rangle_e, \langle\mu_y\{\mu_y\}\rangle_e, \ldots, \langle\Omega_{zzx}\{\Omega_{zzx}\}\rangle_e, \langle\Omega_{zzy}\{\Omega_{zzy}\}\rangle_e$ required for all different estimators of atomic polarizabilities (Tables 4.1–4.11). There are 599 expectation values. After finishing each time-step, they will be combined according to the formulas (4.26–4.135) to obtain all 542 polaziability components estimates.

In order to do that, we have to evaluate on each iteration 15 multipole moments operators (3.9, 3.16, 3.17): μ_x, μ_y, μ_z, Θ_{xx}, Θ_{yy}, Θ_{xy}, Θ_{xz}, Θ_{yz}, Ω_{xxy}, Ω_{xxz}, Ω_{yyx}, Ω_{yyz}, Ω_{zzx}, Ω_{zzy}, Ω_{xyz}. All other components of multipole moments can be calculated from these using their traceless form; for example, $\Theta_{xx}=-\Theta_{yy}-\Theta_{zz}$ or $\Omega_{xxx}=-\Omega_{yyx}-\Omega_{zzx}$. We also have to store these values for each particle in the memory for $2L-1$ successive iterations to be able calculate their cummulative values (Chapter 2).

For verification purposes, in the case of He atom the simulation estimated also the ground-state energy and the overlap integral of the trial function with the exact solution. The output of the simulation was a set of 542 (and the energy and the overlap integral for He) estimates[2] of all polarizabilities components for all time-steps and all values of L ($542 \times N_T \times N_L$ values in total).

The simulation was dependent on an initial random number generator seed. Therefore, by running the same simulation for different seeds we could obtain output files containing uncorrelated estimates of polarizability components. This is especially advantegous when the simulations can be run *at once* on a parallel computer, which was the case.

A separate code was used to combine all available output files to get one file containing 542 estimates of all components *with* their standard deviations. Each quantity was averaged through the different independent files, the standard deviation corresponds to the dispersion of those independent values. These estimates were extrapolated by a suitable model (constant, linear, quadratic) to get the final $\tau \to 0$ intercept for each of 542 components and each value of initial L.

5.3 Combining Different Estimators

The objective of this work is to estimate all atomic polarizabilities up to the sixth degree for H and He atoms. In other words (Table 3.1), we have to estimate one specifying constant for $X^1_{\alpha,\beta}$, $X^3_{\alpha,\beta,\gamma,\delta}$, $X^2_{\alpha\beta,\gamma,\delta}$, $X^1_{\alpha\beta,\gamma\delta}$, $X^5_{\alpha,\beta,\gamma,\delta,\varepsilon,\zeta}$, $X^4_{\alpha\beta,\gamma,\delta,\varepsilon,\zeta}$, $X^2_{\alpha\beta,\gamma\delta,\varepsilon\zeta}$, $X^3_{\alpha\beta\gamma,\delta,\varepsilon,\zeta}$, $X^2_{\alpha\beta\gamma,\delta\varepsilon,\zeta}$, $X^1_{\alpha\beta\gamma,\delta\varepsilon\zeta}$ tensors and two for the $X^3_{\alpha\beta,\gamma\delta,\varepsilon,\zeta}$ tensor.

It is convenient to choose the specifying constants to be particular components of each given polarizability tensor. Natural choice is to estimate the following polarizability tensors components: $X^1_{x,x}$, $X^3_{x,x,x,x}$, $X^2_{xx,x,x}$, $X^1_{xx,xx}$, $X^5_{x,x,x,x,x,x}$, $X^4_{xx,x,x,x,x}$, $X^2_{xx,xx,xx}$, $X^3_{xxx,x,x,x}$, $X^2_{xxx,xx,x}$, $X^1_{xxx,xxx}$ and $X^3_{xx,xx,x,x}$, $X^3_{xx,xx,y,y}$ (that

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[2] Just the results of the estimators, not standard deviations

is, twelve quantities for an atom).

The reason why our simulation evaluates all 542 estimators is to decrease the statistical error. By using all of them in the way described below we decrease the variance of final polarizability estimates. The technique of keeping all the estimators separately during the τ extrapolation allows us to deal with the time-step bias of different estimators separately. It also accounts for differences in variances of different estimators.

The extrapolation procedure gives us 542 $\tau \rightarrow 0$ intercepts for each of N_L initial values of L. Now we need to combine them to get the final estimates of the twelve polarizabilities. The way this is done for all polarizabilities *except* $X^3_{xx,xx,x,x}$ and $X^3_{xx,xx,y,y}$ is simply to use all the spherical symmetry relations (3.95–3.104). The final estimate is then given by the variance-weighted average[3] of all relevant different estimators multiplied by a corresponding factor, as it is in the symmetry relations.

The final estimates of $X^3_{xx,xx,x,x}$ and $X^3_{xx,xx,y,y}$ require a special procedure of combining the different components of $X^3_{\alpha\beta,\gamma\delta,\varepsilon,\zeta}$. It is due to the fact that the polarizability has two specifying constants and its components satisfy a system of linear equations (3.105). Thus, its components are not related to each other just by a multiplicative constant, as it is for all other polarizabilities up to the sixth degree.

The procedure is in essence estimating the two constants c_1, c_2 in the system (3.105) by using all 111 (Table 4.12) different estimators. That is done in three steps:

1. Calculate averages (and standard deviations) of all components related by a permutation. This corresponds to calculating averages of all estimators written on the same line in Table 4.7 (nine of them). By doing this, we will

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[3] That is the maximum likelihood estimator

obtain estimates of the left-hand sides of the system (3.105)

2. Because we have nine equations and two unknowns c_1 and c_2, there are $\frac{9!}{2!7!} = 36$ pairs of linear equations which can be uniquely solved for c_1, c_2. By evaluating all possible expressions from all those systems of two linear equations picked from the original system, we will get only 32 pairs of solutions, because 4 of the 36 systems are singular (they can be satisfied for any c_1 and c_2). Moreover, 8 of the 32 solutions for each constant are the same, because of the two equations in (3.105) which contain only one specifying constant. Therefore, we will end up with 25 unique estimates for c_1 and c_2.

3. Finally, we take the variance-wighted average of these twenty-five estimates for each of the two specifying constants and we use these to calculate $X^3_{xx,xx,x,x}$ and $X^3_{xx,xx,y,y}$ and their standard deviations by the first two equations of (3.105)

The simulations were programmed in C language (~6000 lines of code), and the extrapolation and combination of results was done by using a package of macros in Physica [80]. For the production runs we used 64 R12 000 processors (400 MHz) of host Borealis at the University of Alberta.

5.4 Initial Values of Simulation Parameters

According to the outline in Section 2.5, the first step of a QMC simulation is initialization of parameters, such as the number of particles and iterations, values of time-steps, etc. Of course, they affect the overall perfomance of the simulation.

For example, the CPU time spent by a simulation depends linearly on the initial number of particles N_{p0}, on the initial number of iterations N_{i0}, and roughly

parameter	H	He
number of particles N_{p0}	100	100
number of iterations N_{i0}	4000	6000
time-steps	0.1,...,0.6[0.1] a.u.	0.05,...,0.30[0.05] a.u.
stacks lengths L's	10,...,80[10]	10,...,50[10]

Table 5.2: Initial Values of Simulation Parameters

linearly on the maximum value among the initial L's. The dependence on the number of L's is not significant.

There is generally no applicable way to decide the values of the initial parameters. One has to take in account not only the resources of the hardware used, but—and this is extremely critical—also the suitability of a certain $\tau \to 0$ extrapolation model for a chosen set of time-steps [69] and values of L's. The aim is to use small L's which are still large enough to see vanishing finite L-bias of the estimates (see Figure 2.2).

In order to find the optimum values of the simulation parameters, several preliminary runs with carefully chosen trial values have to be run. By doing this, we decided to use the initial parameters as they are listed in Table 5.2. The table is related to *one* simulation for H and He, respectively. As it was already described above, it can be run several times with different random number generator seeds to get effectively a larger number of particles (iterations).

Chapter 6

Results and Conclusions

We invested roughly the same amount of CPU time for both H and He simulations: 1500 independent simulations (Section 5.4), each of which took approximately 10 hours on R12 000 processor running at 400 MHz (15 000 h=625 days on a single processor for each atom). The data from all the simulations were averaged (Section 5.2) and then $\tau \to 0$ extrapolated. In order to obtain estimates of atomic polarizabilities which are not biased by a particular extrapolation model[1], two natural models were chosen:

1. quadratic fit of values of a quantity X at *all six* chosen time-steps

$$X(\tau) \approx a + b\tau + c\tau^2 \tag{6.1}$$

2. linear fit of values of X at *the three smallest* time-steps

$$X(\tau) \approx a + b\tau \tag{6.2}$$

The $\tau = 0$ intercepts (coefficients a above) together with their standard deviations were combined (Section 5.3) and the first values with no finite-L-bias were found (Figure 2.2). The final results of both extrapolations were compared. In cases where the two estimates did not overlap within their standard deviations, an average of them and a corresponding standard deviation covering both values were chosen to be the final estimate. By doing this, we believe that we obtained $\tau \to 0$ extrapolation model bias-free estimates of the ground-state atomic polarizabilities of H and He atoms, Table 6.1.

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[1] The true τ-dependence of a polarizability is not known.

	H		He	
Polarizability	this work(QMC)	literature	this work(QMC)	literature[e]
$X^1_{x,x}$	4.499(2)	4.5[a]	1.385(2)	1.383192
$X^3_{x,x,x,x}$	1327(10)	1333.125[b]	40(3)	43.104
$X^2_{xx,x,x}$	-106.9(3)	-106.5[c]	-7.5(2)	-7.3267
$X^1_{xx,xx}$	15.06(3)	15[c,d]	2.42(2)	2.4451
$X^5_{x,x,x,x,x,x}$	$3.5(1) \times 10^6$	3533595.5[e]	$1.7(3) \times 10^4$	14937
$X^4_{xx,x,x,x,x}$	$-185(4) \times 10^3$	-188092.12[e]	$-1.6(2) \times 10^3$	-1605.8
$X^3_{xx,xx,x,x}$	$12.0(1) \times 10^3$	12032.25[f]	210(23)	213.79
$X^3_{xx,xx,y,y}$	$5.09(4) \times 10^3$	5112.0938[g]	90(9)	90.633
$X^2_{xx,xx,xx}$	-455(6)	-459[e]	-17(1)	-17.964
$X^3_{xxx,x,x,x}$	$7.32(9) \times 10^3$	7357.5[c]	134(12)	128.65
$X^2_{xxx,xx,x}$	-808(7)	-810[e]	-29(1)	-30.507
$X^1_{xxx,xxx}$	131.8(7)	131.25[d]	10.4(4)	10.6204

[a] Ref. [81], [b] Ref. [18], [c] Ref. [82, 83], [d] Ref. [84].
[e] Ref. [26], [f] Ref. [85], [g] Ref. [86]

Table 6.1: Ground-state electrostatic polarizabilities of H and He (a.u.)

The case of the hydrogen atom is very special, because this simple system can be treated analytically and the literature values of polarizabilities are *exact*. In other words, for the hydrogen atom, QMC estimates can not possibly compete with the accuracy of the perturbation methods. Nevertheless, it is useful to investigate the efficiency of the method, where in this case we have the luxury of the trial function equal to the exact solution, hence all the past-future weights are ones. The only source of variance in this case are the cummulative values of multipole moments and their products, see (4.26–4.135).

All QMC results cover the reference values within their statistical error. The precision of the results is related to the number of perturbations involved in the definition of the polarizabilities (3.24). For example, the results for $X^1_{x,x}$, $X^2_{xx,x,x}$, $X^1_{xx,xx}$, $X^1_{xxx,xxx}$ have four significant digits; $X^3_{x,x,x,x}$, $X^4_{xx,x,x,x,x}$, $X^3_{xx,xx,x,x}$, $X^3_{xx,xx,y,y}$, $X^2_{xxx,xx,x}$ have three, and the rest of the polarizabilities estimates have two significant digits. This hypothesis is supported by the example of $X^5_{x,x,x,x,x,x}$

with two significant digits—this is an outcome of six dipole moments and their cummulative values entering the formulas (4.38–4.41). The other results with rather low precision are $X^2_{xx,xx,xx}$, $X^3_{xxx,x,x,x}$ and possibly $X^2_{xxx,xx,x}$, all due to the mixing of three quadrupole moments, octupole moment with three dipole moments and octupole, quadrupole and dipole moment, respectively.

In the case of the helium atom, there is clear increase in the standard deviations of the results in comparison with the hydrogen atom. This is because of the additional noise of the past-future weights now entering every QMC estimator (4.26–4.135). Again, all the helium polarizability estimates cover the reference values within the statistical error. Assuming that the results from [26] are very accurate, we can conclude that the $\tau \to 0$ extrapolation model bias was successfully removed by combining the linear and quadratic model. Because of that decrease of the precision of helium polarizabilities (except $X^1_{x,x}$), some of the higher order ones have only one to two significant digits. The worst case is again the $X^5_{x,x,x,x,x,x}$ polarizability, with approximately 18% relative error.

In summary, we applied the infinitesimal differential QMC techique to estimate all atomic polarizabilities up to the sixth degree. We derived all independent QMC estimators of the non-zero polarizabilities and developed a procedure to combine them according to the symmetry relations in order to increase the efficiency of the simulation and to decrease the statistical errors of the estimates. Finally, we successfully used these theoretical results to estimate the atomic polarizabilities of H and He atoms, using two $\tau \to 0$ extrapolation models to obtained unbiased results.

The presented quantum Monte Carlo technique promises to be a very powerful *ab initio* method to estimate polarizabilities of larger systems, although the results would suffer from a bias due to the fixed-node approximation. For larger atoms, the technique can be applied without further changes. In the case

of molecules, the algebra behind the molecular polarizability tensors is somehow more complex and corresponding modifications are neccessary. Non-electronic effects would also have to be included, such as vibrational and rotational corrections.

The quality of the used trial function affects the variance of expectation values of properties, and it is expected to increase for many fermion systems. One source of this variance is the fluctuating past-future weights. An attractive solution to this problem is to assume that the trial function is sufficiently close to the unknown exact solution so that all past-future weights are equal to one. Although this would certainly bias the estimates, the statistical error would considerably decrease, and they may still provide useful approximates of the polarizabilities.

Appendix A

Units of Polarizabilities

The conversion factors from atomic units to SI units for polarizabilities in Table 3.1 are based on fundamental constants from www.nist.gov/srd/online.htm : A=$5.29177208 \times 10^{-11}$ m, Q = $1.60217646 \times 10^{-19}$ C, U = $4.3597438 \times 10^{-18}$ J for 1.a.u. of the length, charge and energy, respectively.

The conversion factor of a polarizability, which is defined as a coefficient in (3.23, 3.24) contracted with k electric field components, l electric gradient components, m electric hyper-gradient components, etc, is given by [71]

$$A^{k+2l+3m+\ldots} \times U^{1-k-l-m-\ldots} \times Q^{k+l+m+\ldots} \tag{A.1}$$

Appendix B

Maple Worksheets Listings

This appendix contains listings of two Maple worksheets which were used to calculate the component definitions of atomic polarizability tensors and formulas for QMC polarizabilities estimators. They are available on the web at abraham.chem.brocku.ca/~mhornik/index.html, where they can be also downloaded (there are more worksheets related to this thesis than the following two). They run under Maple V Release 5, Version 5.00 [75].

Although several brief remarks are provided through the codes, these listings are not meant to be very explanatory (the worksheets are only a tool, not the objectives of this thesis). The author simply wanted to have an available hardcopy of two most important Maple worksheets used in this work. Without them the derivation of isotropic tensor definitions and the QMC estimators of polarizabilities would have been almost impossible and extensively tedious task.

To maintain the width of the listings, too long lines were broken even though in the code the lines are not broken. The rule is that every symbol ">" represents a new line.

B.1 Isotropic Polarizability Tensors

The following Maple worksheet was used to derive the component definitions of isotropic polarizability tensors (3.74–3.91).

The first part is preliminary—it defines procedures for generating all possible products of two and three Kronecker's deltas, represented by grouped sets of

given indices (for example, $\delta_{\alpha\beta}\delta_{\gamma\delta}$ is represented by a set $\{\{\alpha,\beta\},\{\gamma,\delta\}\}$) and auxiliary procedures which operates on sets

```
> restart;unprotect(gamma);
> allDoubles:=proc(basis)
> local i,j,result;
> result:={};
> for i in basis do
>  for j in basis do
>   if not(i=j) then
>    result:=result union {{i,j}};
>   fi;
>  od;
> od;
> result;
> end;
> deltaDoubles:=proc(basis)
> local doubleBasis,i,j,result;
> result:={};
> doubleBasis:=allDoubles(basis);
> for i in doubleBasis do
>  for j in doubleBasis do
>   if nops(i union j)=(nops(i)+nops(j)) then
>    result:=result union {{i,j}};
>   fi;
>  od;
> od;
> result;
> end;
```

```
> deltaTriples:=proc(basis)
> local doubleBasis,i,j,k,result;
> result:={};
> doubleBasis:=allDoubles(basis);
> for i in doubleBasis do
>  for j in doubleBasis do
>   for k in doubleBasis do
>    if nops(i union j union k)=(nops(i)+nops(j)+nops(k)) then
>     result:=result union {{i,j,k}};
>    fi;
>   od;
>  od;
> od;
> result;
> end;
> setToList:=proc(set)
> local result,i;
> result:=[];
> for i in set do
>  result:=[op(result),i];
> od;
> result;
> end;
> makeExpression:=proc(list)
> local result,i;
> result:=0;
> for i from 1 to nops(list) do
>  result:=result + C[i]*K[op(i,list)];
```

```
> od;
> result;
> end;
> interchangeSet:=proc(l1,l2)
> local result,i;
> result:={};
> for i from 1 to nops(l1) do
>  result:=result union {op(i,l1)=op(i,l2),op(i,l2)=op(i,l1)};
> od;
> result;
> end;
> interchange:=proc(l1,l2,what)
> subs(interchangeSet(l1,l2), what);
> end;
```

The following procedures apply given trivial symmetries and vanishing trace equation and identify all left specifying constants

```
> symmetryRelation:=proc(l1,l2,list,cList)
> local changedList,i,j,result;result:={};
> changedList:=interchange(l1,l2,list);
> for i from 1 to nops(list) do
>  for j from 1 to nops(changedList) do
>   if op(i,list)=op(j,changedList) then
>    #print(C[i]=C[j]);
>    result:=result union {op(i,cList)=op(j,cList)};
>   fi;
>  od;
> od;
> result;
```

```
> end;
> createCList:=proc(list)
> local result, i;
> result:=[];
> for i from 1 to nops(list) do
>  result:=[op(result),C[i]];
> od;
> result;
> end;
> buildExpression:=proc(cList,iList)
> local result, i;
> result:=0;
> for i from 1 to nops(cList) do
>  result:=result + op(i,cList) * K[op(i, iList)];
> od;
> result;
> end;
> changeCListViaSymmetry:=proc(l1,l2,iList,cList)
> local result, symmetrySet,i;
> result:=cList;
> symmetrySet:=symmetryRelation(l1,l2,iList,cList);#print(symmetrySet);
> for i in symmetrySet do
>  result:=subs({i}, result);
> od;
> result;
> end;
> contractList:=proc(s1,s2,iList)
> subs({s1=s2},iList);
```

```
> end;
> traceEquation:=proc(s1,s2,iList,cList)
> local leftOver,leftOverCList,i,j,k,temp,temp2,temp3,
        replacement,couple,doneTerms,express,resultSet,NE;
> leftOver:=contractList(s1,s2,iList);
> leftOverCList:=cList;
> #print(`simplifying 3 contractions:`);
> for i from 1 to nops(leftOver) do
>  temp:=op(i,leftOver);
>  for j from 1 to nops(temp) do
>   temp2:=op(j,temp);
>   if nops(temp2)=1 then
>    #print(`found in `, i, temp);
>    temp:=temp minus {temp2};
>    leftOver:=subsop(i=temp,leftOver);
>    leftOverCList:=subsop(i=3*op(i,leftOverCList),leftOverCList);
>    break;
>   fi;
>  od;
> od;
> #print(`3-contractions completed.`);
> #print(`simplifying 1-1 contraction:`);
> for i from 1 to nops(leftOver) do
>  temp:=op(i,leftOver);#print(`term `,temp);
>  couple:={};
>  for j from 1 to nops(temp) do
>   temp2:=op(j,temp);
>   if member(s2, temp2) then
```

```
>    couple:=couple union {temp2};
>   fi;
>  od;
>  if not(couple={}) then
>   #print(‘match found: ‘,op(couple));
>   replacement:=(op(1,couple)
        minus {s2}) union (op(2,couple) minus {s2});
>   temp:=temp minus {op(1,couple)};
>   temp:=temp minus {op(2,couple)};
>   temp:=temp union {replacement};
>   leftOver:=subsop(i=temp,leftOver);
>  fi;
> od;
> #print(leftOver);
> #print(leftOverCList);
> #print(buildExpression(leftOverCList,leftOver)=0);
> #print(‘building the equations for coefficients‘);
> resultSet:={};
> doneTerms:={};
> NE:= nops({seq(op(i,leftOver),i=1..nops(leftOver))});
> for i from 1 to NE do
>  #print(‘choosing the ‘,i,‘-th term‘);
>  j:=1;while member(op(j,leftOver), doneTerms) do j:=j+1; od;
>  #print(‘j = ‘,j,op(j,leftOver),‘chosen‘);
>  express:=0;
>  for k from 1 to nops(leftOver) do
>   if (op(k,leftOver)=op(j,leftOver)) then
>    express:=express+op(k,leftOverCList);
```

```
>   fi;
>  od;
>  resultSet:=resultSet union {express=0};
>  doneTerms:=doneTerms union {op(j,leftOver)};
> od;
> resultSet;
> end;
> allIndexSymm:=proc(list)
> global lD,lC;
> local i;
> for i in list do
>  lC:=changeCListViaSymmetry(op(1,i),op(2,i),lD,lC);
> od;
> lC;
> end;
> allTraceSymm:=proc(list)
> global lD, lC;
> local i,resultSet;
> resultSet:={};
> for i in list do
>  resultSet:=resultSet union traceEquation(op(1,i),op(2,i),lD, lC);
> od;
> resultSet;
> end;
```

The following set of instructions calculates the component definition of atomic $X^1_{\alpha\beta,\gamma\delta}$ polarizability

```
> #The forth order X_ab_cd
> basis:={alpha,beta,gamma,delta};
```

```
> lD:=setToList(deltaDoubles(basis));
> lC:=createCList(lD);
> #index symmetries (give the structure of the tensor(meaning))
> allIndexSymm([[[alpha],[beta]],[[gamma],[delta]],
   [[alpha,beta],[gamma,delta]]]);
> #trace equations
> allTraceSymm([[alpha,beta],[gamma,delta]]);
> solve(%);(subs(%, buildExpression(lC,lD)));
```

The last line will produce this output

$$\{C_1 = -\tfrac{3}{2}C_3, C_3 = C_3\} \tag{B.1}$$

$$-\tfrac{3}{2}C_3K_{\{\{\alpha,\delta\},\{\gamma,\beta\}\}} - \tfrac{3}{2}C_3K_{\{\{\beta,\delta\},\{\gamma,\alpha\}\}} + C_3K_{\{\{\gamma,\delta\},\{\alpha,\beta\}\}} \tag{B.2}$$

where the first line is a result of previous simplifications and the second line corresponds to definition (3.78).

The rest of the worksheet is a similar code for calculating definitions of polarizability tensors of the sixth order

```
> #The sixth order X_a_b_c_d_e_f
> basis:={alpha,beta,gamma,delta,mu,nu};
> lD:=setToList(deltaTriples(basis));
> lC:=createCList(lD);
> #index symmetries (give the structure of the tensor(meaning))
> allIndexSymm([[[alpha],[beta]],[[alpha],[gamma]],
   [[alpha],[delta]],[[alpha],[mu]]]);
> buildExpression(lC,lD);
> #X_ab_c_d_e_f
> lC:=createCList(lD);
> #index symmetries (give the structure of the tensor(meaning))
> allIndexSymm([[[alpha],[beta]],[[gamma],[delta]],[[gamma],[mu]],
```

```
   [[gamma],[nu]],[[delta],[mu]],[[delta],[nu]],[[mu],[nu]]]);
> #trace symmetry
> allTraceSymm([[alpha,beta]]);
> solve(%);(subs(%, buildExpression(lC,lD)));
> #X_ab_cd_e_f
> lC:=createCList(lD);
> #index symmetries (give the structure of the tensor(meaning))
> allIndexSymm([[[alpha],[beta]],[[gamma],[delta]],[[alpha,beta],
   [gamma,delta]],[[mu],[nu]]]);
> #traces
> allTraceSymm([[alpha,beta],[gamma,delta]]);
> solve(%);(subs(%, buildExpression(lC,lD)));
> #X_ab_cd_ef
> lC:=createCList(lD);
> allIndexSymm([[[alpha],[beta]],[[gamma],[delta]],[[mu],[nu]],
   [[alpha,beta],[gamma,delta]],[[gamma,delta],[mu,nu]],
   [[alpha,beta],[mu,nu]]]);
> allTraceSymm([[alpha,beta],[gamma,delta],[mu,nu]]);
> solve(%);(subs(%, buildExpression(lC,lD)));
> #X_abc_d_e_f
> lC:=createCList(lD);
> allIndexSymm([[[alpha],[beta]],[[beta],[gamma]],[[alpha],
   [gamma]],[[delta],[mu]],[[mu],[nu]],[[delta],[nu]]]);
> allTraceSymm([[alpha,beta],[beta,gamma],[alpha,gamma]]);
> solve(%);(subs(%, buildExpression(lC,lD)));
> #X_abc_de_f
> lC:=createCList(lD);
> allIndexSymm([[[alpha],[beta]],[[beta],[gamma]],[[alpha],[gamma]],
```

```
    [[delta],[mu]]]);
> allTraceSymm([[alpha,beta],[beta,gamma],[alpha,gamma],[delta,mu]]);
> solve(%);(subs(%, buildExpression(lC,lD)));
> #X_abc_def
> lC:=createCList(lD);
> allIndexSymm([[[alpha],[beta]],[[beta],[gamma]],[[alpha],[gamma]],
    [[delta],[mu]],[[mu],[nu]],[[delta],[nu]],[[alpha,beta,gamma],
    [delta,mu,nu]]]);
> allTraceSymm([[alpha,beta],[beta,gamma],[alpha,gamma],[mu,delta],
    [mu,nu],[delta,nu]]);
> solve(%);(subs(%, buildExpression(lC,lD)));
> #X_abcd_e_f (ZERO??)
> lC:=createCList(lD);
> allIndexSymm([[[alpha],[beta]],[[alpha],[gamma]],[[alpha],[delta]],
    [[beta],[gamma]],[[beta],[delta]],[[gamma],[delta]],[[mu],[nu]]]);
> allTraceSymm([[alpha,beta],[alpha,gamma],[alpha,delta],[beta,gamma]
    ,[beta,delta],[gamma,delta]]);
> solve(%);(subs(%, buildExpression(lC,lD)));
> #X_abcd_ef (ZERO??)
> lC:=createCList(lD);
> allIndexSymm([[[alpha],[beta]],[[alpha],[gamma]],[[alpha],[delta]],
    [[beta],[gamma]],[[beta],[delta]],[[gamma],[delta]],[[mu],[nu]]]);
> allTraceSymm([[alpha,beta],[alpha,gamma],[alpha,delta],[beta,gamma],
    [beta,delta],[gamma,delta],[mu,nu]]);
> solve(%);(subs(%, buildExpression(lC,lD)));
> #X_abcde_f
> lC:=createCList(lD);
> allIndexSymm([[[alpha],[beta]],[[alpha],[gamma]],[[alpha],[delta]],
```

```
  [[alpha],[mu]],[[beta],[gamma]],[[beta],[delta]],[[beta],[mu]],
  [[gamma],[delta]],[[gamma],[mu]],[[delta],[mu]]]);
> #it looks like a zero??
> allTraceSymm([[alpha,beta]]);
> #yes, this is ZERO!
> solve(%);(subs(%, buildExpression(1C,1D)));
```

B.2 Atomic Polarizabilities Formulas

This Maple worksheet produces all quantum Monte Carlo estimators of all non-equivalent components of atomic polarizabilities up to the sixth order. If the spherical symmetry simplification procedures are turned off, it will calculate estimators for a general system with no symmetry.

First, the worksheet defines the perturbed Hamiltonian, its cumulative value, the past-future weight and a procedure for generating any Hellmann-Feynman derivative of the ground-state energy

```
> restart:
> h[i] := h0[i]-mu[x][i]*F[x]-mu[y][i]*F[y]-mu[z][i]*F[z]
  -1/3*theta[zz][i]*F[zz]-1/3*theta[xx][i]*F[xx]-1/3*theta[yy][i]*F[yy]
  -2/3*theta[xz][i]*F[xz]-2/3*theta[yz][i]*F[yz]-2/3*theta[xy][i]*F[xy]
  -1/15*Omega[xxx][i]*F[xxx]-1/15*Omega[yyy][i]*F[yyy]
  -3/15*Omega[xxy][i]*F[xxy]-3/15*Omega[zzy][i]*F[zzy]
  -6/15*Omega[xyz][i]*F[xyz];
> Ch[i]:=-{mu[x]}[i]*F[x]-{mu[y]}[i]*F[y]-{mu[z]}[i]*F[z]
  -1/3*{theta[zz]}[i]*F[zz]-1/3*{theta[xx]}[i]*F[xx]
  -1/3*{theta[yy]}[i]*F[yy]-2/3*{theta[xz]}[i]*F[xz]
  -2/3*{theta[yz]}[i]*F[yz]-2/3*{theta[xy]}[i]*F[xy]
  -1/15*{Omega[xxx]}[i]*F[xxx]-1/15*{Omega[yyy]}[i]*F[yyy]
  -3/15*{Omega[xxy]}[i]*F[xxy]-3/15*{Omega[zzy]}[i]*F[zzy]
```

```
  -6/15*{Omega[xyz]}[i]*F[xyz];
> w[i]:=omega[i]*exp(-tau*Ch[i]);
> VarSeq:=[F[x],F[y],F[z],F[zz],F[xx],F[yy],F[xy],F[xz],F[yz],F[xxx],
           F[yyy],F[xxy],F[zzy],F[xyz]];
> Zeroes:={seq(op(i,VarSeq)=0,i=1..nops(VarSeq))};
> HFDerivative:=proc(x)
> Sum(diff(h[i], x)*w[i], i)/Sum(w[i],i);
> end;
> readlib(coeftayl);
```

Then it contains definitions of all important spherical symmetries, which will be used to simplify a raw result of differentiation

```
> DipoleSymmetries1:={Sum(mu[z][i]*omega[i],i)=0,
   Sum({mu[z]}[i]*omega[i],i)=0,Sum({mu[z]}[i]^3*omega[i],i)=0,
   Sum(mu[x][i]*omega[i],i)=0,Sum({mu[x]}[i]*omega[i],i)=0,
   Sum({mu[x]}[i]^3*omega[i],i)=0,
   Sum(mu[x][i]*{mu[x]}[i]^2*omega[i],i)=0,
   Sum(mu[z][i]*{mu[z]}[i]^2*omega[i],i)=0,Sum(mu[y][i]*omega[i],i)=0,
   Sum({mu[y]}[i]*omega[i],i)=0,Sum({mu[y]}[i]^3*omega[i],i)=0,
   Sum(mu[y][i]*{mu[y]}[i]^2*omega[i],i)=0};
> DipoleSymmetries2:={Sum(mu[x][i]*{mu[y]}[i]*omega[i],i)=0,
   Sum(mu[y][i]*{mu[x]}[i]*omega[i],i)=0,
   Sum(mu[x][i]*{mu[z]}[i]*omega[i],i)=0,
   Sum(mu[z][i]*{mu[x]}[i]*omega[i],i)=0,
   Sum(mu[y][i]*{mu[z]}[i]*omega[i],i)=0,
   Sum(mu[z][i]*{mu[y]}[i]*omega[i],i)=0,
   Sum({mu[x]}[i]*{mu[y]}[i]*omega[i],i)=0,
   Sum({mu[x]}[i]*{mu[z]}[i]*omega[i],i)=0,
   Sum({mu[y]}[i]*{mu[z]}[i]*omega[i],i)=0};
```

```
> DipoleSymmetries3:={Sum(mu[x][i]*{mu[y]}[i]^2*omega[i],i)=0,
   Sum(mu[y][i]*{mu[x]}[i]^2*omega[i],i)=0,
   Sum(mu[x][i]*{mu[z]}[i]^2*omega[i],i)=0,
   Sum(mu[z][i]*{mu[x]}[i]^2*omega[i],i)=0,
   Sum(mu[y][i]*{mu[z]}[i]^2*omega[i],i)=0,
   Sum(mu[z][i]*{mu[y]}[i]^2*omega[i],i)=0,
   Sum({mu[x]}[i]*{mu[y]}[i]^2*omega[i],i)=0,
   Sum({mu[y]}[i]*{mu[x]}[i]^2*omega[i],i)=0,
   Sum({mu[x]}[i]*{mu[z]}[i]^2*omega[i],i)=0,
   Sum({mu[z]}[i]*{mu[x]}[i]^2*omega[i],i)=0,
   Sum({mu[y]}[i]*{mu[z]}[i]^2*omega[i],i)=0,
   Sum({mu[z]}[i]*{mu[y]}[i]^2*omega[i],i)=0,
   Sum({mu[x]}[i]*{mu[y]}[i]*{mu[z]}[i]*omega[i],i)=0};
> DipoleSymmetries4:={Sum(mu[x][i]*{mu[x]}[i]*{mu[y]}[i]*omega[i],i)=0,
   Sum(mu[y][i]*{mu[y]}[i]*{mu[x]}[i]*omega[i],i)=0,
   Sum(mu[x][i]*{mu[x]}[i]*{mu[z]}[i]*omega[i],i)=0,
   Sum(mu[z][i]*{mu[z]}[i]*{mu[x]}[i]*omega[i],i)=0,
   Sum(mu[y][i]*{mu[y]}[i]*{mu[z]}[i]*omega[i],i)=0,
   Sum(mu[z][i]*{mu[z]}[i]*{mu[y]}[i]*omega[i],i)=0,
   Sum(mu[x][i]*{mu[y]}[i]*{mu[z]}[i]*omega[i],i)=0,
   Sum(mu[y][i]*{mu[x]}[i]*{mu[z]}[i]*omega[i],i)=0,
   Sum(mu[z][i]*{mu[x]}[i]*{mu[y]}[i]*omega[i],i)=0};
> DipoleSymmetries:=DipoleSymmetries1 union DipoleSymmetries2
   union DipoleSymmetries3 union DipoleSymmetries4;
> QuadrupoleSymmetries1:={Sum(theta[zz][i]*omega[i],i)=0,
   Sum({theta[zz]}[i]*omega[i],i)=0,Sum(theta[xz][i]*omega[i],i)=0,
   Sum({theta[xz]}[i]*omega[i],i)=0,Sum(theta[xx][i]*omega[i],i)=0,
   Sum({theta[xx]}[i]*omega[i],i)=0,Sum(theta[yz][i]*omega[i],i)=0,
```

```
  Sum({theta[yz]}[i]*omega[i],i)=0,Sum(theta[yy][i]*omega[i],i)=0,
  Sum({theta[yy]}[i]*omega[i],i)=0,Sum(theta[xy][i]*omega[i],i)=0,
  Sum({theta[xy]}[i]*omega[i],i)=0};
> QuadrupoleSymmetries2:={Sum(theta[xz][i]*omega[i]*{mu[x]}[i],i)=0,
  Sum(theta[xz][i]*omega[i]*{mu[y]}[i],i)=0,
  Sum(theta[xz][i]*omega[i]*{mu[z]}[i],i)=0,
  Sum(theta[xy][i]*omega[i]*{mu[x]}[i],i)=0,
  Sum(theta[xy][i]*omega[i]*{mu[y]}[i],i)=0,
  Sum(theta[xy][i]*omega[i]*{mu[z]}[i],i)=0,
  Sum(theta[yz][i]*omega[i]*{mu[x]}[i],i)=0,
  Sum(theta[yz][i]*omega[i]*{mu[y]}[i],i)=0,
  Sum(theta[yz][i]*omega[i]*{mu[z]}[i],i)=0};
> QuadrupoleSymmetries3:={Sum(mu[x][i]*{theta[xx]}[i]*omega[i],i)=0,
  Sum(mu[y][i]*{theta[xx]}[i]*omega[i],i)=0,
  Sum(mu[z][i]*{theta[xx]}[i]*omega[i],i)=0,
  Sum(mu[x][i]*{theta[yy]}[i]*omega[i],i)=0,
  Sum(mu[y][i]*{theta[yy]}[i]*omega[i],i)=0,
  Sum(mu[z][i]*{theta[yy]}[i]*omega[i],i)=0,
  Sum(mu[x][i]*{theta[zz]}[i]*omega[i],i)=0,
  Sum(mu[y][i]*{theta[zz]}[i]*omega[i],i)=0,
  Sum(mu[z][i]*{theta[zz]}[i]*omega[i],i)=0,
  Sum(mu[x][i]*{theta[xy]}[i]*omega[i],i)=0,
  Sum(mu[y][i]*{theta[xy]}[i]*omega[i],i)=0,
  Sum(mu[z][i]*{theta[xy]}[i]*omega[i],i)=0,
  Sum(mu[x][i]*{theta[yz]}[i]*omega[i],i)=0,
  Sum(mu[y][i]*{theta[yz]}[i]*omega[i],i)=0,
  Sum(mu[z][i]*{theta[yz]}[i]*omega[i],i)=0,
  Sum(mu[x][i]*{theta[xz]}[i]*omega[i],i)=0,
```

```
  Sum(mu[y][i]*{theta[xz]}[i]*omega[i],i)=0,
  Sum(mu[z][i]*{theta[xz]}[i]*omega[i],i)=0};
> QuadrupoleSymmetries4:={Sum(theta[xx][i]*{mu[x]}[i]*omega[i],i)=0,
  Sum(theta[xx][i]*{mu[y]}[i]*omega[i],i)=0,
  Sum(theta[xx][i]*{mu[z]}[i]*omega[i],i)=0,
  Sum(theta[yy][i]*{mu[x]}[i]*omega[i],i)=0,
  Sum(theta[yy][i]*{mu[y]}[i]*omega[i],i)=0,
  Sum(theta[yy][i]*{mu[z]}[i]*omega[i],i)=0,
  Sum(theta[zz][i]*{mu[x]}[i]*omega[i],i)=0,
  Sum(theta[zz][i]*{mu[y]}[i]*omega[i],i)=0,
  Sum(theta[zz][i]*{mu[z]}[i]*omega[i],i)=0};
> QuadrupoleSymmetries:=QuadrupoleSymmetries1
  union QuadrupoleSymmetries2 union QuadrupoleSymmetries3
  union QuadrupoleSymmetries4;
> OctupoleSymmetries:={Sum(Omega[xxx][i]*omega[i],i)=0,
  Sum({Omega[xxx]}[i]*omega[i],i)=0,Sum(Omega[yyy][i]*omega[i],i)=0,
  Sum({Omega[yyy]}[i]*omega[i],i)=0,Sum(Omega[xxy][i]*omega[i],i)=0,
  Sum({Omega[xxy]}[i]*omega[i],i)=0,Sum(Omega[xyz][i]*omega[i],i)=0,
  Sum({Omega[xyz]}[i]*omega[i],i)=0,Sum(Omega[zzy][i]*omega[i],i)=0,
  Sum({Omega[zzy]}[i]*omega[i],i)=0};
> Symmetries:=DipoleSymmetries union QuadrupoleSymmetries
  union OctupoleSymmetries:
> ApplySphericalSymmetry:=proc(term)
> global Symmetries;
> #simplify(term, Symmetries);
> simplify(simplify(simplify(term,DipoleSymmetries),
  QuadrupoleSymmetries),OctupoleSymmetries);
> end;
```

Now follows a procedure, which does all the operations: for a given list of electric field tensor components, it calculates all possible Hellmann-Feynman derivatives and then it differentiate these derivatives further to obtain the polarizability estimator. Finally, it applies all the spherical symmetries to obtain the estimator for atoms (a multiplicative correction factor is required)

```
> MakeAllFormulae:=proc(VList,Correct)
>  local i, HFVars,DegList,Derivative,
        TaylorList,OriginalDegree,Result,myZeroes;
   global VarSeq;
>  myZeroes:=[seq(0,i=1..nops(VarSeq))];
>  HFVars:={}:
>  DegList:=[seq(0,i=1..nops(VarSeq))]:
>  for i from 1 to nops(VList) do
>   if (member(op(i,VList),VarSeq,’pos’)) then
>   DegList:=subsop(pos=(op(pos,DegList)+1), DegList):
>   HFVars:=HFVars union {op(pos, VarSeq)}:
>   fi:
>  od:
>  #print(HFVars, DegList);
>  if (HFVars<>{}) then
>   for i from 1 to nops(HFVars) do
>    #APPLY THE H-F TH.
>    print(‘Hellmann-Feynman via‘, op(i, HFVars)):
>    Derivative:=eval(HFDerivative(op(i, HFVars))):
>    member(op(i, HFVars), VarSeq,’pos’):
>    OriginalDegree:=op(pos,DegList):
>    TaylorList:=subsop(pos=(OriginalDegree-1), DegList):
>    #Result:=1/OriginalDegree*coeftayl(Derivative,
```

```
     [F[x],F[z],F[zz],F[xx],F[xz],F[zzz]]=[0,0,0,0,0,0], TaylorList):
>    Result:=1/OriginalDegree*coeftayl(Derivative,
                                   VarSeq=myZeroes, TaylorList):
>    print(subs(Sum(omega[i],i)=1,
     taylor(expand(ApplySphericalSymmetry(Correct*Result)),tau,10))):
>   od:
>  else
>   print('ERROR:Impossible to apply the Hellmann-Feynman theorem...'):
>  fi:
> end:
```

For example, the QMC estimator of $X^1_{x,x}$ can be now obtained by

```
> MakeAllFormulae([F[x],F[x]],-2!);
```

which will produce the following output

$$Hellmann - Feynman\ via, F_x$$

$$\frac{\sum\limits_i \mu_{x_i}\omega_i\{\mu_{x_i}\}}{\sum\limits_i \omega_i}\tau \tag{B.3}$$

and this is nothing else than the result (4.26). The next code calculates all required formulas of QMC polarizabilities estimators up to the sixth degree

```
> MakeAllFormulae([F[x],F[x],F[x],F[x]], -4!);
> MakeAllFormulae([F[x],F[x],F[y],F[y]], -4!/6);
> MakeAllFormulae([F[xx],F[x],F[x]], -2!*3);
> MakeAllFormulae([F[xx],F[y],F[y]], -2!*3);
> MakeAllFormulae([F[xz],F[x],F[z]], -2!*3/4);
> MakeAllFormulae([F[xx],F[xx]],-2!*3^2);
> MakeAllFormulae([F[zz],F[xx]],-2!*3^2/2);
> MakeAllFormulae([F[xz],F[xz]],-2!*3^2/4);
> MakeAllFormulae([F[x],F[x],F[x],F[x],F[x],F[x]], -6!);
```

```
> MakeAllFormulae([F[x],F[x],F[z],F[z],F[z],F[z]], -6!/15);
> MakeAllFormulae([F[x],F[x],F[y],F[y],F[z],F[z]], -6!/90);
> MakeAllFormulae([F[xx],F[x],F[x],F[x],F[x]],-4!*3);
> MakeAllFormulae([F[xx],F[y],F[y],F[y],F[y]],-4!*3);
> MakeAllFormulae([F[xx],F[x],F[x],F[y],F[y]],-4!*3/6);
> MakeAllFormulae([F[xz],F[x],F[z],F[z],F[z]],-4!*3/8);
> MakeAllFormulae([F[xz],F[x],F[z],F[y],F[y]],-4!*3/24);
> MakeAllFormulae([F[xx],F[y],F[y],F[z],F[z]],-4!*3/6);
> MakeAllFormulae([F[xx],F[xx],F[x],F[x]],-2!*2!*3^2);
> MakeAllFormulae([F[xx],F[xx],F[y],F[y]],-2!*2!*3^2);
> MakeAllFormulae([F[xz],F[yz],F[x],F[y]],-2!*2!*3^2/16);
> MakeAllFormulae([F[xz],F[zz],F[x],F[z]],-2!*2!*3^2/8);
> MakeAllFormulae([F[xz],F[yy],F[x],F[z]],-2!*2!*3^2/8);
> MakeAllFormulae([F[xx],F[yy],F[z],F[z]],-2!*2!*3^2/2);
> MakeAllFormulae([F[xx],F[yy],F[y],F[y]],-2!*2!*3^2/2);
> MakeAllFormulae([F[xz],F[xz],F[y],F[y]],-2!*2!*3^2/4);
> MakeAllFormulae([F[xz],F[xz],F[z],F[z]],-2!*2!*3^2/4);
> MakeAllFormulae([F[xx],F[xx],F[xx]],-3!*3^3);
> MakeAllFormulae([F[xx],F[yy],F[yy]],-3!*3^3/3);
> MakeAllFormulae([F[xz],F[xz],F[xx]],-3!*3^3/12);
> MakeAllFormulae([F[xy],F[yz],F[xz]],-3!*3^3/48);
> MakeAllFormulae([F[xx],F[yy],F[zz]],-3!*3^3/6);
> MakeAllFormulae([F[xy],F[xy],F[zz]],-3!*3^3/12);
> MakeAllFormulae([F[xxx],F[x],F[x],F[x]],-3!*15);
> MakeAllFormulae([F[xxy],F[y],F[y],F[y]],-3!*15/3);
> MakeAllFormulae([F[xxy],F[x],F[x],F[y]],-3!*15/9);
> MakeAllFormulae([F[xxx],F[x],F[y],F[y]],-3!*15/3);
> MakeAllFormulae([F[xxy],F[y],F[z],F[z]],-3!*15/9);
```

```
> MakeAllFormulae([F[xyz],F[x],F[y],F[z]],-3!*15/36);
> MakeAllFormulae([F[xxx],F[xx],F[x]],-45);
> MakeAllFormulae([F[xxx],F[yy],F[x]],-45);
> MakeAllFormulae([F[xxx],F[xy],F[y]],-45/2);
> MakeAllFormulae([F[xxy],F[xx],F[y]],-45/3);
> MakeAllFormulae([F[xxy],F[xy],F[x]],-45/6);
> MakeAllFormulae([F[xxy],F[zz],F[y]],-45/3);
> MakeAllFormulae([F[xyz],F[xy],F[z]],-45/12);
> MakeAllFormulae([F[xxy],F[yz],F[z]],-45/6);
> MakeAllFormulae([F[xxy],F[yy],F[y]],-45/3);
> MakeAllFormulae([F[xxx],F[xxx]],-2!*15^2);
> MakeAllFormulae([F[xyz],F[xyz]],-2!*15^2/36);
> MakeAllFormulae([F[xxy],F[zzy]],-2!*15^2/18);
> MakeAllFormulae([F[yyy],F[xxy]],-2!*15^2/6);
> MakeAllFormulae([F[xxy],F[xxy]],-2!*15^2/9);
```

If we want, we can use this worksheet to calculate polarizabilities estimators of any degree, for example the eight order $X^7_{z,z,z,z,z,z,z,z}$ atomic polarizability estimator would be obtained by

```
> MakeAllFormulae([F[z],F[z],F[z],F[z],F[z],F[z],F[z],F[z]],-8!);
```

Bibliography

[1] R. W. Boyd, *Nonlinear Optics*, Academic Press, Inc., San Diego, 1992.

[2] A. D. Buckingham, Adv. Chem. Phys. **12**, 107 (1967).

[3] A. D. McLean and M. Yoshimine, J. Chem. Phys. **47**, 1927 (1967).

[4] A. D. Buckingham and J. A. Pople, Proc. Phys. Soc. **68**, 905 (1955).

[5] S. J. Cyvin, J. E. Rauch, and J. C. Decius, J. Chem. Phys. **43**, 4083 (1965).

[6] J. F. Ward and G. H. C. New, Phys. Rev. **185**, 57 (1969).

[7] J. F. Ward and C. K. Miller, Phys. Rev. A **19**, 826 (1979).

[8] A. Takahashi, Phys. Rev. B **56**, 3792 (1997).

[9] R. Luyckx, P. Coulon, and H. N. W. Lekkerkerker, Chem. Phys. Lett. **48**, 187 (1977).

[10] K. L. Ç. Hunt, Chem. Phys. Lett. **70**, 336 (1980).

[11] S. L. Price, A. J. Stone, and M. Alderton, Molec. Phys. **52**, 987 (1984).

[12] X. Li, K. L. C. Hunt, J. Pipin, and D. M. Bishop, J. Chem. Phys. **105**, 10954 (1996).

[13] M. H. Champagne, X. Li, and K. L. C. Hunt, J. Chem. Phys. **112**, 1893 (2000).

[14] A. D. Buckingham, J. Chem. Phys. **30**, 1580 (1959).

[15] T. M. Miller and B. Bederson, Adv. At. Mol. Phys. **13**, 1 (1977).

[16] D. Gugan and G. W. Michel, Molec. Phys. **39**, 783 (1980).

[17] T. M. Miller and B. Bederson, Adv. At. Mol. Phys. **25**, 37 (1988).

[18] G. L. Sewell, Proc. Camb. Phil. Soc. **45**, 678 (1949).

[19] W. Kolos and L. Wolniewicz, J. Chem. Phys. **46**, 1426 (1967).

[20] M. N. Grasso, K. T. Chung, and R. P. Hurst, Phys. Rev. **167**, 1 (1968).

[21] W. D. Robb, M. R. Meadows, T. Burnett, and G. Doolen, Phys. Rev. A **15**, 1063 (1977).

[22] J. Rychlewski, Molec. Phys. **41**, 833 (1980).

[23] A. J. Thakkar, J. Chem. Phys. **75**, 4496 (1981).

[24] R. D. Amos, Chem. Phys. Lett. **88**, 89 (1982).

[25] D. M. Bishop and B. Lam, Chem. Phys. Lett. **120**, 69 (1985).

[26] D. M. Bishop and J. Pipin, Chem. Phys. Lett. **236**, 15 (1995).

[27] V. A. Gani and V. M. Weinberg, Hydrogen atom in crossed external fields reexamined by the moment method, xxx.lanl.gov/abs/physics/9808041, 1998.

[28] W. Bartowiak and J. Lipiński, Chem. Phys. Lett. **292**, 92 (1998).

[29] V. E. Ingamells, M. G. Papadopoulos, and A. J. Sadlej, Chem. Phys. **260**, 1 (2000).

[30] S. G. Raptis, M. G. Papadopoulos, and A. J. Sadlej, Phys. Chem. Chem. Phys. **2**, 3393 (2000).

[31] P. Sitz and R. Yaris, J. Chem. Phys. **49**, 3546 (1968).

[32] R. M. Glover and F. Weinhold, J. Chem. Phys. **65**, 4913 (1976).

[33] R. M. Glover and F. Weinhold, J. Chem. Phys. **66**, 191 (1977).

[34] D. M. Bishop and L. M. Cheung, J. Chem. Phys. **72**, 5125 (1980).

[35] J. Rychlewski, Chem. Phys. Lett. **73**, 135 (1980).

[36] L. J. Bartolotti, J. Chem. Phys. **73**, 3666 (1980).

[37] D. M. Bishop and L. M. Cheung, J. Chem. Phys. **76**, 2492 (1982).

[38] J. Rychlewski, J. Chem. Phys. **78**, 7252 (1983).

[39] M. Jaszuński and B. O. Roos, Molec. Phys. **52**, 1209 (1984).

[40] D. M. Bishop and B. Lam, J. Chem. Phys. **88**, 3398 (1988).

[41] D. M. Bishop and B. Lam, Molec. Phys. **62**, 721 (1987).

[42] D. M. Bishop and J. Pipin, J. Chem. Phys. **91**, 3549 (1989).

[43] N. K. Rahman, A. Rizzo, and D. L. Yeager, Chem. Phys. Lett. **166**, 565 (1990).

[44] D. M. Bishop, J. Pipin, and S. M. Cybulski, Phys. Rev. A **43**, 4845 (1991).

[45] M. Rérat, M. Mérawa, and C. Pouchan, Phys. Rev. A **45**, 6263 (1992).

[46] B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry*, volume 1 of *World Scientific Lecture and Course Notes in Chemistry*, World Scientific Publishing Co. Pte. Ltd., Singapore, 1994.

[47] J. B. Anderson, Int. Rev. Phys. Chem. **14**, 85 (1995).

[48] D. M. Ceperley and L. Mitas, Adv. Chem. Phys. **93**, 1 (1996).

[49] M. P. Nightingale and C. J. Umrigar, Adv. Chem. Phys. **105**, 65 (1999).

[50] A. Lüchow and J. B. Anderson, Annu. Rev. Phys. Chem. **51**, 501 (2000).

[51] F. Schautz and H.-J. Flad, J. Chem. Phys. **110**, 11700 (1999).

[52] K. C. Huang, R. J. Needs, and G. Rajagopal, J. Chem. Phys. **112**, 4419 (2000).

[53] F. Schautz and H.-J. Flad, J. Chem. Phys. **112**, 4421 (2000).

[54] M. Caffarel, M. Rérat, and C. Pouchan, Phys. Rev. A **47**, 3704 (1993).

[55] J. Vrbik and S. M. Rothstein, J. Chem. Phys. **96**, 2071 (1992).

[56] M. Caffarel and O. Hess, Phys. Rev. A **43**, 2139 (1991).

[57] R. Assaraf and M. Caffarel, J. Chem. Phys. **113**, 4028 (2000).

[58] P. Langfelder, S. M. Rothstein, and J. Vrbik, J. Chem. Phys. **107**, 8525 (1997).

[59] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipies in Fortran: the Art of Scientific Computing*, chapter 19, page 818, Press Syndicate of the University of Cambidge, 2nd edition, 1992.

[60] S. M. Rothstein and J. Vrbik, J. Chem. Phys. **87**, 1902 (1987).

[61] P. J. Reynolds and D. M. Ceperley, J. Chem. Phys. **77**, 5593 (1982).

[62] D. M. Ceperley and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics*, 2nd edition, Springer-Verlag, Berlin, New York, page 145, 1986.

[63] M. Caffarel and P. Claverie, J. Chem. Phys. **88**, 1088 (1988).

[64] P. Langfelder, Calculation of nondifferential properties for atomic ground states, Master's thesis, Brock University, 1997.

[65] A. L. L. East, S. M. Rothstein, and J. Vrbik, J. Chem. Phys. **89**, 4880 (1988).

[66] R. Assaraf, M. Caffarel, and A. Khelif, Phys. Rev. E **61**, 4566 (2000).

[67] P. J. Reynolds, J. Chem. Phys. **92**, 2118 (1990).

[68] A. L. L. East, S. M. Rothstein, and J. Vrbik, J. Chem. Phys. **92**, 2120 (1990).

[69] J. Vrbik and S. M. Rothstein, Int. J. Quant. Chem. **29**, 461 (1986).

[70] M. Hornik, M. Snajdr, and S. M. Rothstein, J. Chem. Phys. **113**, 3496 (2000).

[71] C. E. Dykstra, Ab initio *Calculation of the Structures and Properties of Molecules*, chapter 7, Elsevier, Amsterdam, 1988.

[72] D. E. Stogryn and A. P. Stogryn, Molec. Phys. **11**, 371 (1966).

[73] C. G. Gray, Can. J. Phys. **54**, 505 (1976).

[74] C. G. Gray and B. W. N. Lo, Chem. Phys. **14**, 73 (1976).

[75] B. Char et al., *Maple V Language Reference Manual*, Springer-Verlag. New York, Berlin, 1991.

[76] M. Snajdr, J. R. Dwyer, and S. M. Rothstein, J. Chem. Phys. **111**, 9971 (1999).

[77] M. Snajdr, Histogram filtering as a tool in variational Monte Carlo optimization, Master's thesis, Brock University, 1999.

[78] M. Snajdr and S. M. Rothstein, J. Chem. Phys. **112**, 4935 (2000).

[79] M. F. DePasquale, S. M. Rothstein, and J. Vrbik, J. Chem. Phys. **89**, 3629 (1988).

[80] J. L. Chuma, *Physica Reference Manual*, TRIUMF, 1998.

[81] I. Waller, Z. Physik **38**, 635 (1926).

[82] C. A. Coulson, Proc. Roy. Soc. Edin. A **61**, 20 (1941).

[83] A. D. Buckingham, C. A. Coulson, and J. T. Lewis, Proc. Phys. Soc. A **69**, 639 (1956).

[84] A. Dalgarno, Advan. Phys. **11**, 281 (1962).

[85] A. D. Buckingham and K. L. Clarke, Chem. Phys. Lett. **57**, 321 (1978).

[86] P. W. Fowler, K. L. C. Hunt, H. M. Kelly, and A. J. Sadlej, J. Chem. Phys. **100**, 2932 (1994).