Doctoral Thesis in Theoretical Chemistry and Biology

# Efficient Calculation of Nonlinear Spectroscopic Properties within the Time-Dependent Density Functional Theory Approximation 

KARAN AHMADZADEH



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#### Abstract

This thesis introduces a novel computational scheme tailored for efficient calculations of nonlinear spectroscopic observables. First, a derivation and implementation of an algorithm designed to harness the linearity of the Fock matrix construction in calculating two-photon absorption cross-sections within the self-consistent field approximation is presented. Subsequently, this computational scheme is extended to the density functional theory approximation for functionals belonging to the generalized gradient approximation. Lastly the derivation and implementation of the nonlinear exchange-correlation kernel for functionals belonging to the meta generalized gradient approximation are presented for the first time.

Collectively, the advancements presented in this thesis contribute new methodologies and insights to the computational realm of nonlinear spectroscopic calculations, offering the potential for large-scale theoretical spectroscopy calculations at the level of density functional theory.


## Svensk sammanfattning

Denna avhandling introducerar en ny beräkningsmetod skräddarsydd för effektiva beräkningar av icke-linjära spektroskopiska observabler. Först presenteras en härledning och implementering av en algoritm utformad för att utnyttja lineariteten i Fock-matrixkonstruktionen vid beräkning av två-fotons absorptions tvärsnitt inom ramen för "the self-consistent field approximation". Därefter utvidgas denna beräkningmethod till nivån av "density functional theory" för funktionaler som tillhör den generaliserade gradientapproximationen. Slutligen presenteras härledningen och implementeringen av den icke-linjära "exchange-correlation kernelen" för funktionaler som tillhör meta-generaliserade gradientapproximationen för första gången.

Sammantaget bidrar de framsteg som presenteras i denna avhandling med nya metoder och insikter för beräkningen av för icke-linjära spektroskopiska beräkningar, vilket erbjuder potentialen för storskaliga teoretiska spektroskopiberäkningar.

## Acknowledgements

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## Papers

Paper I 71
VeloxChem: A Python-driven density-functional theory program for spectroscopy simulations in high-performance computing environments

Paper II 73
Efficient implementation of isotropic cubic response functions for two-photon absorption cross sections within the self-consistent field approximation

## Paper III 75

Efficient Kohn-Sham density-functional theory implementation of isotropic spectroscopic observables associated with quadratic response functions

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Efficient Kohn-Sham density-functional theory implementation of isotropic spectroscopic observables associated with cubic response functions going beyond the generalized gradient approximation

Paper V 79
Benchmarking Two-Photon Absorption Cross-Sections: A Comparative study going beyond the generalized gradient approximation

Author's contributions 80
In Paper I, I contributed to the software. In Paper II, I performed all the calculations, derived and implemented the tensor-average method, conceptualized the subspace extraction technique, and wrote the manuscript. In Paper III, I handled all calculations, derived all equations, conceptualized the proof establishing the generalizability of the tensor-average method in the context of density functional theory, and authored the manuscript. For Paper IV, I derived all equations, implemented the methods, and wrote the manuscript. In Paper V, I conducted all the calculations and wrote the manuscript.

## INTRODUCTION

## Background and motivation

Computational chemistry has emerged as an indispensable tool for the exploration of chemical systems and the prediction of their properties, playing a crucial role in advancing our understanding of molecular phenomena and driving innovations in various fields such as materials science ${ }^{1,2}$, drug discovery ${ }^{3-5}$, and catalysis ${ }^{6}$. At its core, computational chemistry seeks to find approximate solutions to the Schrödinger equation ${ }^{7}$. This partial differential equation is typically recast into a linear algebraic matrix equation by projecting it onto a finite-dimensional space spanned by a set of known basis functions. Leveraging variational principles reformulates the problem of solving the Schrödinger equation into a routine task in numerical analysis. In variational methods, the objective is to determine the wave function parameters by enforcing the approximate wave function to adhere to constraints that align with the exact solution. In this procedure, the fundamental operations that constitute the building blocks of any quantum chemistry software can, as mentioned above, be divided between linear algebra operations and integral evaluations. The linear algebra operations predominantly consist of tensor contractions, matrix diagonalizations, and matrix inversions. In the design of efficient modern large-scale computer algorithms for approximate solutions of the Schrödinger equation, there are mainly three performanceoriented aspects to consider. First, the number of operations needed, that is, the computational cost. Second, the storage demand required to handle and store final and intermediate tensors and integrals. Lastly, optimizing parallel processing capabilities and adeptly managing both aggregated and distributed memory resources to ensure effective scaling on state-of-the-art High-Performance Computing (HPC) systems. In this thesis, a widely adopted computational strategy for approximating the solution to the Schrödinger equation is the Hartree-Fock approximation ${ }^{8-11}$. Within this approximation, the wave function is represented as a single Slater determinant. The Slater determinant in turn is constructed from a set of molecular orbitals composed of linear combinations of a finite set of N known atomic basis functions and their corresponding coefficients, which serve as the variational parameters. The Rayleigh-Ritz variational principle, together with a single Slater determinant ansatz, yields a matrix pseudo eigenvalue equation known as the Hartree-Fock equation. Solving the Hartree-Fock equation involves constructing the Fock matrix and diagonalizing it iteratively to obtain a converged set of eigenvalues and variational parameters. In fact, the efficiency of a Hartree-Fock implementation is centered around the construction and the diagonalization of the Fock matrix ${ }^{12-14}$. The HF method's computational complexity formally scales with the number of basis functions N as $O\left(N^{4}\right)$. In practice, this means that for the most demanding step, a
doubling of the number of basis functions would imply a 16-fold increase in the number of basic mathematical operations for that step alone. This scaling primarily arises from two key steps associated with the Fock matrix construction:

- The evaluation of the two-electron integrals, represented as a rank 4 tensor.
- The subsequent matrix-tensor contraction between the density matrix and the two-electron integral tensor for the Fock matrix construction.

Both these steps formally scale as $O\left(N^{4}\right)$. In the early days of computational chemistry the two-electron integral tensors were typically calculated only once in the atomic orbital basis and stored for use in all subsequent Fock matrix constructions. However, this approach quickly encountered memory bottlenecks as the number of unique integrals to store grows as $O\left(\frac{N^{4}}{8}\right)^{14}$. In modern computational schemes, other strategies are employed due to memory constraints, and the two-electron integral tensor is typically never stored in memory. Instead, the two-electron integrals are constructed and immediately contracted with the density matrix for the Fock matrix construction. This strategy is referred to as a direct integral approach ${ }^{15,16}$ and often leads to a significant reduction in memory requirements, making calculations for large systems tractable. Yet, the savings in memory demands gained by employing a direct approach come at the cost of requiring multiple re-evaluations of the two-electron integral tensors, which significantly increase the number of mathematical operations required. This has far-reaching consequences when going beyond the time-independent case to the approximate solution of the timedependent Schrödinger equation for the simulation of light-matter interactions. Within the framework of time-dependent Hartree-Fock theory and linear and non-linear response, the corrections to the Fock matrix in the presence of the field emerge as a central component of the mathematical formalism ${ }^{17}$. In fact, the most computationally demanding step is again found to be the construction of a large number of auxiliary Fock matrices. This necessitates efforts to minimize the number Fock matrix constructions. In this context, a two-electron code with a small memory footprint would enable the use of parallel construction of large numbers of Fock matrices created from a single evaluation of the set of two-electron integrals. To make maximal use of each two-electron integral evaluation, the fact that the auxiliary Fock matrices represent linear transformations acting on the density matrices with the two-electron integrals as the transformation tensor can be used to design an efficient algorithm. This allows for a computational scheme with a small memory footprint that potentially can scale to very large systems. The explicit goal of this thesis is to present a new efficient computational scheme exploiting the linearity in the two-electron integral contractions and exchange-correlation kernel integrations required for the simulation of non-linear spectroscopic observables.

# THE SEMI-CLASSICAL APPROXIMATION OF LIGHT MATER INTERACTIONS 

## Linear and non-linear susceptibilities

## MAXWELL'S EQUATIONS

The semi-classical approximation is a modelling approach in which the medium is treated quantum mechanically through the Schrödinger equation, while the electromagnetic radiation is described as a classical electromagnetic wave using Maxwell's equations ${ }^{18}$. A natural starting point for our discussion on light-matter interactions within the semi-classical approach is, therefore, the set of coupled differential equations known as Maxwell's equations, which synthesize Gauss's law for electricity, Gauss's law for magnetism, Faraday's law of electromagnetic induction, and Ampere's law. Before Maxwell, the laws governing electricity and magnetism were considered distinct. Maxwell formulated a set of equations that unified the electric $\boldsymbol{F}(r, t)$ and the magnetic $\boldsymbol{H}(r, t)$ vector fields. His equations demonstrated that a changing electric field could induce a magnetic field, and a changing magnetic field could induce an electric field. This interplay between the two fields gives rise to electromagnetic waves ${ }^{19}$.

## Maxwell's Equations in Free Space

$$
\begin{align*}
& \nabla \cdot \boldsymbol{F}=0, \\
& \nabla \cdot \boldsymbol{H}=0, \\
& \nabla \times \boldsymbol{F}=-\mu_{0} \frac{\partial \boldsymbol{H}}{\partial t},  \tag{2.1}\\
& \nabla \times \boldsymbol{H}=\epsilon_{0} \frac{\partial \boldsymbol{F}}{\partial t}
\end{align*}
$$

The constants $\epsilon_{0}$ and $\mu_{0}$ represent the electric and magnetic permittivity of free space, respectively. They describe the inherent properties of a vacuum with respect to electric and magnetic fields, determining both the strength of the electric and magnetic forces in the vacuum and the speed of light within $\mathrm{it}^{20}$. Using the vector identity

$$
\begin{equation*}
\nabla \times(\nabla \times \boldsymbol{F})=\nabla(\nabla \cdot \boldsymbol{F})-\nabla^{2} \boldsymbol{F} \tag{2.2}
\end{equation*}
$$

alongside Maxwell's equations, we can derive the wave equation that describes how the electric and magnetic components of electromagnetic waves propagate in free space. Here, we present the wave equation for the electric field component:

$$
\begin{equation*}
\nabla^{2} \boldsymbol{F}-\frac{1}{\epsilon_{0} \mu_{0}} \frac{\partial^{2} \boldsymbol{F}}{\partial t^{2}}=0 \tag{2.3}
\end{equation*}
$$

In this model, every medium has its own permittivity and permeability, and these quantities reflect how the material responds to the field. In a material, the electric field can cause the charges to displace and the dipoles within it to reorient. To accommodate a material's response in Maxwell's equations, the electric displacement field $\boldsymbol{D}$ is introduced

$$
\begin{gather*}
\boldsymbol{D}=\epsilon_{0} \boldsymbol{F}+\boldsymbol{P}  \tag{2.4}\\
\boldsymbol{B}=\mu_{0} \boldsymbol{H}+\mu_{0} \boldsymbol{M} \tag{2.5}
\end{gather*}
$$

where, $\boldsymbol{P}$ is the polarization density vector, which represents the alignment of the electric dipoles within the material ${ }^{21}$. The polarization vector has a unit of $C / m^{2}$ and can be interpreted as the dipole moment per unit volume. In the absence of free charges and currents, Maxwell's equations in a medium take the following form

## Maxwell's equations in matter

$$
\begin{align*}
& \nabla \cdot \boldsymbol{D}=0 \\
& \nabla \cdot \boldsymbol{B}=0 \\
& \nabla \times \boldsymbol{F}=-\frac{\partial \boldsymbol{B}}{\partial t}  \tag{2.6}\\
& \nabla \times \boldsymbol{H}=\frac{\partial \boldsymbol{D}}{\partial t}
\end{align*}
$$

The wave equation derived from this set of coupled equations describes the propagation of electromagnetic waves within a material, accounting for the material's polarization.

$$
\begin{equation*}
\nabla^{2} \boldsymbol{F}-\frac{1}{\epsilon \mu} \frac{\partial^{2} \boldsymbol{F}}{\partial t^{2}}=0 \tag{2.7}
\end{equation*}
$$

where $\epsilon$ and $\mu$ are now the electric and magnetic permittivity of the material, respectively. A valid solution to the wave equation takes the form

$$
\begin{equation*}
F_{i}(t)=\frac{1}{2} \sum_{k}\left(F_{i}\left(\omega_{k}\right) e^{-i \omega_{k} t}+F_{i}\left(-\omega_{k}\right) e^{i \omega_{k} t}\right) \tag{2.8}
\end{equation*}
$$

where $F_{i}^{*}\left(\omega_{k}\right)=F_{i}\left(-\omega_{k}\right)$, ensuring that $F_{i}(t)$ is a real function of time.

## THE POLARIZATION

The polarization represents the response of the material due to the electric field and is in general a dynamic quantity that is a function of time. Furthermore, the polarization will in general not be instantaneous in the sense that the current state of the polarization depends on the history of the applied electric field ${ }^{22,23}$. We can model the response of the material as a series of convolutions ${ }^{24,25}$ between the electric field
and the electric susceptibility $\chi$, known as a Volterra series

$$
\begin{align*}
P_{i}(t) & =\epsilon_{0} \int_{-\infty}^{t} \chi_{i j}^{(1)}(t-\tau) F_{j}(\tau) d \tau \\
& +\epsilon_{0} \frac{1}{2} \int_{-\infty}^{t} \int_{-\infty}^{t} \chi_{i j k}^{(2)}\left(t-\tau_{1}, t-\tau_{2}\right) F_{j}\left(\tau_{1}\right) F_{k}\left(\tau_{2}\right) d \tau_{1} d \tau_{2}  \tag{2.9}\\
& +\epsilon_{0} \frac{1}{6} \int_{-\infty}^{t} \int_{-\infty}^{t} \int_{-\infty}^{t} \chi_{i j k l}^{(3)}\left(t-\tau_{1}, t-\tau_{2}, t-\tau_{3}\right) \\
& F_{j}\left(\tau_{1}\right) F_{k}\left(\tau_{2}\right) F_{l}\left(\tau_{3}\right) d \tau_{1} d \tau_{2} d \tau_{3}+\ldots
\end{align*}
$$

In this expression, $\tau$ signifies the time delay between the input and the response, while the time difference $(t-\tau)$ represents the interval between when the input was applied and the moment we are observing the response. The integration over all possible values of $\tau$ captures the system's response at time $t$, accounting for all interactions up until time $t$. The susceptibilities, denoted by $\chi$, are generally tensors and characterize the material's propensity to become polarized in response to an applied electric field. Both the polarization and the susceptibilities, as well as the electric fields, are all real functions within the time domain. To avoid the integrations associated with the convolutions, we can employ the convolution theorem. This theorem allows us to represent the convolutions in the frequency domain as products of the Fourier transforms of the susceptibilities and electric fields. Leveraging the convolution theorem, we get that the Fourier component of the polarization can be expressed as ${ }^{24}$

$$
\begin{equation*}
P_{i}^{(n)}\left(\omega_{\sigma}\right)=\epsilon_{0} \chi_{i j k . .}^{(n)}\left(-\omega_{\sigma} ; \omega_{1}, \omega_{2} \ldots \omega_{n}\right) F_{j}\left(\omega_{1}\right) F_{k}\left(\omega_{2}\right) \ldots \tag{2.10}
\end{equation*}
$$

where $\omega_{\sigma}=\sum_{k} \omega_{k}$. The trade-off for this simplification is that, in general, Fourier components are complex ${ }^{26}$. Furthermore, since the polarization in the time-domain is a continuous, periodic, and real function, we can utilize the inverse Fourier transform to rewrite the polarization in the time-domain as the sum

$$
\begin{equation*}
P_{i}^{(n)}(t)=\frac{1}{2} \sum_{k}\left(P_{i}^{(n)}\left(\omega_{k}\right) e^{-i \omega_{k} t}+P_{i}^{(n)}\left(-\omega_{k}\right) e^{i \omega_{k} t}\right) \tag{2.11}
\end{equation*}
$$

where $P_{i}^{(n)}\left(\omega_{k}\right)$ and $P_{i}^{(n)}\left(-\omega_{k}\right)$ are, in general, complex numbers, which satisfy the relation $\left(P_{i}^{(n)}\left(\omega_{k}\right)\right)^{*}=P_{i}^{(n)}\left(-\omega_{k}\right)$. Since the Fourier component of the polarization in general are complex numbers, we can decompose them into real and imaginary parts as follows

$$
\begin{equation*}
P_{i}^{(n)}(\omega)={ }^{\mathbb{R}} P^{(n)}(\omega)+i{ }^{\mathbb{I}} P^{(n)}(\omega) \tag{2.12}
\end{equation*}
$$

where ${ }^{\mathbb{R}} P^{(n)}(\omega)$ and ${ }^{\mathbb{I}} P^{(n)}(\omega)$ are the real and imaginary components respectively. The complex Fourier coefficients of the polarization can be represented in terms of its magnitude and phase as

$$
\begin{equation*}
P_{i}^{(n)}(\omega)=\left|P_{i}^{(n)}(\omega)\right| e^{i \phi(\omega)} \tag{2.13}
\end{equation*}
$$

where $\phi(\omega)$ represents the phase difference between the response and the perturbing fields and depends on the magnitude of the real and imaginary parts through the 2 -argument arctangent function

$$
\begin{equation*}
\phi(\omega)=\operatorname{atan} 2\left(\frac{{ }^{\mathbb{I}} P^{(n)}(\omega)}{\mathbb{R}^{\mathbb{R}} P^{(n)}(\omega)}\right) \tag{2.14}
\end{equation*}
$$

The magnitude of the Fourier component of the polarization is then given by

$$
\begin{equation*}
\left|P_{i}^{(n)}(\omega)\right|=\sqrt{\left(\mathbb{R}^{(n)}(\omega)\right)^{2}+\left({ }^{\mathbb{I}} P^{(n)}(\omega)\right)^{2}} \tag{2.15}
\end{equation*}
$$

The phase shift between the polarization and the field is tied to the time delay between the field and the polarization. Generally, a delay in the time domain manifests as a phase shift when observing the system's response in the frequency domain. This understanding is vital when analyzing periodic phenomena, as it allows us to decompose the system's response into a periodic component that is in-phase with the field and another component that is $\frac{\pi}{2}$ out of phase with the electric field at a given frequency. Applying Eq.(2.11) and Eq.(2.12), together with the identities

$$
\begin{equation*}
\cos (x)=\frac{e^{i x}+e^{-i x}}{2}, ; \sin (x)=\frac{e^{i x}-e^{-i x}}{2 i} \tag{2.16}
\end{equation*}
$$

we get that each frequency component of the polarization can be decomposed into two periodic terms that are $\frac{\pi}{2}$ out of phase:

$$
\begin{equation*}
P(t)=\sum_{k}\left({ }^{\mathbb{R}} P^{(n)}\left(\omega_{k}\right) \cos \left(\omega_{k} t\right)+{ }^{\mathbb{I}} P^{(n)}\left(\omega_{k}\right) \sin \left(\omega_{k} t\right)\right) \tag{2.17}
\end{equation*}
$$

If there is no time delay between the field and the material's polarization, then there is no phase shift, and the Fourier coefficient of the polarization is real, ${ }^{\mathbb{I}} P^{(n)}(\omega)=0$ (see Fig.2.2). Conversely, if the polarization is shift by a quarter of its period, $T / 4$, it becomes entirely out of phase with the field, resulting in a phase difference of $\frac{\pi}{2}$. In this case, the polarization's Fourier coefficient is completely imaginary, ${ }^{\mathbb{R}} P^{(n)}(\omega)=0$ (see Fig.2.3). In the subsequent sections, it will be seen that it is the time derivative of the polarization that needs to be in phase with the electric field for optimal energy transfer between a medium and the electric field.

## Mathematical Framework for Orientational Averaging

In the study of various physical processes such as the interaction of radiation with matter, experiments are often conducted with matter in a liquid or gas phase. In order to relate the results of such experiments to theory, the random orientation of the molecules must be taken into account when deriving expressions for observables. This is usually achieved by deriving the corresponding result for a system with a fixed orientation and then forming a rotational mean value.

This section is devoted to the orientational averaging required to connect the calculated polarization to the experimentally observed polarization. A natural starting point is therefore the Volterra series of the time-dependent dipole moment in the molecular frame

$$
\begin{align*}
\mu_{\alpha}(t) & =\int_{-\infty}^{t} \alpha_{\alpha \beta}(t-\tau) F_{\alpha}(\tau) d \tau \\
& +\frac{1}{2} \int_{-\infty}^{t} \int_{-\infty}^{t} \beta_{\alpha \beta \gamma}\left(t-\tau_{1}, t-\tau_{2}\right) F_{\alpha}\left(\tau_{1}\right) F_{\beta}\left(\tau_{2}\right) d \tau_{1} d \tau_{2}  \tag{2.18}\\
& +\frac{1}{6} \int_{-\infty}^{t} \int_{-\infty}^{t} \int_{-\infty}^{t} \gamma_{\alpha \beta \gamma \delta}\left(t-\tau_{1}, t-\tau_{2}, t-\tau_{3}\right) \\
& F_{\alpha}\left(\tau_{1}\right) F_{\beta}\left(\tau_{2}\right) F_{\gamma}\left(\tau_{3}\right) d \tau_{1} d \tau_{2} d \tau_{3}+\ldots
\end{align*}
$$

where $\alpha, \beta, \gamma$ are the polarizability, the hyperpolarizability and the second-order non-linear hyperpolarizabiity. We get that in frequency domain each Fourier component of the the corrections of the dipole moment, analogously to Eq. (2.10), are given by

$$
\begin{equation*}
\mu_{\alpha}^{(n)}\left(\omega_{\sigma}\right)=R_{\alpha \beta \gamma . .}^{(n)}\left(-\omega_{\sigma} ; \omega_{1}, \omega_{2} \ldots \omega_{n}\right) F_{\beta}\left(\omega_{1}\right) F_{\gamma}\left(\omega_{2}\right) \ldots \tag{2.19}
\end{equation*}
$$

where $R$ denotes a general hyperpolarizability of order $n$. The connection between the molecular properties and the materials polarization is through the effective susceptibility

$$
\begin{equation*}
P_{i}^{(n)}\left(\omega_{\sigma}\right)=\epsilon_{0} \chi_{i j k . .}^{(n) \text { eff }}\left(-\omega_{\sigma} ; \omega_{1}, \omega_{2} \ldots \omega_{n}\right) F_{j}\left(\omega_{1}\right) F_{k}\left(\omega_{2}\right) \ldots \tag{2.20}
\end{equation*}
$$

The effective susceptibility is obtained by taking the orientational average of $R$

$$
\begin{equation*}
\chi_{i j k . .}^{(n) \text { eff }}\left(-\omega_{\sigma} ; \omega_{1}, \omega_{2} \ldots \omega_{n}\right)=\mathcal{N} \sum_{\alpha \beta \gamma \ldots} R_{\alpha \beta \gamma . .}^{(n)}\left\langle p_{i \alpha} p_{j \beta} p_{k \gamma . .}\right\rangle \tag{2.21}
\end{equation*}
$$

where $\mathcal{N}$ is the number density and $p_{i \alpha}$ are the directional cosines between the lab and molecular coordinate systems. The orientational average of the directional cosines are given by

$$
\begin{equation*}
\left\langle p_{i \alpha} p_{j \beta} p_{k \gamma . .}\right\rangle=\frac{1}{8 \pi^{2}} \int_{0}^{\pi} \int_{0}^{2 \pi} \int_{0}^{2 \pi} p_{i \alpha} p_{j \beta} p_{k \gamma .} \sin (\theta) d \theta d \phi d \psi \tag{2.22}
\end{equation*}
$$

where $\theta$ is the polar angle, $\phi$ is the azimuthal angle and $\psi$ is the rotation angle about a particular molecular axis. We are primarily interested in the second and fourth-order terms which are given by the expressions ${ }^{27-29}$

$$
\begin{gather*}
\left\langle p_{i \alpha} p_{j \beta}\right\rangle=\frac{1}{3} \delta_{i j} \delta_{\alpha \beta}  \tag{2.23}\\
\left\langle p_{i \alpha} p_{j \beta} p_{k \gamma} p_{l \delta}\right\rangle=\frac{1}{30} \delta_{i j} \delta_{k l}\left(4 \delta_{\alpha \beta} \delta_{\gamma \delta}-\delta_{\alpha \gamma} \delta_{\beta \delta}-\delta_{\alpha \delta} \delta_{\beta \gamma}\right) \\
+\frac{1}{30} \delta_{i k} \delta_{j l}\left(4 \delta_{\alpha \gamma} \delta_{\beta \delta}-\delta_{\alpha \beta} \delta_{\gamma \delta}-\delta_{\alpha \delta} \delta_{\beta \gamma}\right)  \tag{2.24}\\
+\frac{1}{30} \delta_{i l} \delta_{j k}\left(4 \delta_{\alpha \delta} \delta_{\gamma \delta}-\delta_{\alpha \gamma} \delta_{\beta \delta}-\delta_{\alpha \beta} \delta_{\gamma \delta}\right)
\end{gather*}
$$

## Conservation of energy and the Poynting theorem

The Poynting theorem, a fundamental principle in electromagnetism, embodies the concept of energy conservation in electromagnetic systems. Once the Fourier components of the polarization are known, the Poynting theorem allows us to calculate the energy exchange between the radiation field and the material, bridging the spatial flow of electromagnetic energy with the work done on charges within the material. Utilizing the vector identity

$$
\begin{equation*}
\nabla \cdot(\boldsymbol{F} \times \boldsymbol{H})=(\nabla \times \boldsymbol{F}) \cdot \boldsymbol{H}-(\nabla \times \boldsymbol{H}) \cdot \boldsymbol{F} \tag{2.25}
\end{equation*}
$$

in conjunction with Maxwell's equations, we arrive at the Poynting theorem ${ }^{30}$ :

$$
\begin{equation*}
\nabla \cdot(\boldsymbol{F} \times \boldsymbol{H})=-\frac{\partial U}{\partial t}-\boldsymbol{F} \cdot \frac{\partial \boldsymbol{P}}{\partial t}-\mu_{0} \boldsymbol{H} \cdot \frac{\partial \boldsymbol{M}}{\partial t} \tag{2.26}
\end{equation*}
$$

This differential form of the equation describes the conservation of electromagnetic energy within a small differential volume. The rate of energy flow across the volume's boundaries is given by the divergence of $\boldsymbol{S}=\boldsymbol{F} \times \boldsymbol{H}$, also known as the Poynting vector ${ }^{31}$ which describes the instantaneous rate of energy transfer per unit area due to the electromagnetic fields. U is the electromagnetic energy density, representing the quantity of energy stored in the electric and magnetic fields within the differential volume. The last two terms on the right-hand side signify the work exerted on the electric and magnetic dipoles in the material by the respective fields. To link the Poynting theorem with the intensity loss of the electric field within the differential volume, we can express it in terms of the Poytnting vector as ${ }^{32}$

$$
\begin{equation*}
\nabla \cdot \boldsymbol{S}=-\frac{\partial U}{\partial t}-\boldsymbol{F} \cdot \frac{\partial \boldsymbol{P}}{\partial t}-\mu_{0} \boldsymbol{H} \cdot \frac{\partial \boldsymbol{M}}{\partial t} \tag{2.27}
\end{equation*}
$$

The time average of the Poynting vector, $\boldsymbol{S}$, is referred to as the field's intensity, $I$, or the average power per unit area ${ }^{21}$. If there is a continuous inflow of light through the boundary surface into the enclosed volume, and a portion of the energy in the electromagnetic field is absorbed, then the energy flux exiting the boundary of the volume will be less than what is entering it. In this scenario, the time average of the gradient of the Poynting vector will be negative, indicating a loss of intensity. Simultaneously, the energy density stored within the electromagnetic field in the differential volume is presumed to remain constant. If the electric field within the volume is doing work on the dipoles in the material, the second term in the right hand side in the Poynting equation will be non-zero. Consequently, we get the expression

$$
\begin{equation*}
\nabla I^{(n)}=-\frac{1}{T} \int_{0}^{T} \boldsymbol{F}(t) \cdot \frac{\partial \boldsymbol{P}^{(n)}(t)}{\partial t} d t \tag{2.28}
\end{equation*}
$$

which relates the intensity loss of light within the material to the work done on the dipoles of the material. As an illustration, we see that in

Fig.2.1, the electric field, polarization, and the time derivative of the polarization are depicted, along with the time average of their products, in the case of a monochromatic perturbation. In Fig.2.1, the polarization possesses both real and imaginary components, resulting in a response component that is out of phase with the perturbing field. In Fig.2.2, the Fourier component of the polarization is purely real, thus the response and the perturbing field are perfectly in phase with each other. Conversely, in Fig.2.3, the polarization is purely imaginary, in this scenario, the polarization and the perturbation are out of phase, while the time derivative of the response and the perturbation are in phase. From these three cases, it is evident that the average work done by the field on the material over a period is zero when the polarization is in phase with the perturbation. In remained of this section, we will see that it is the imaginary component, or the out-of-phase component of the polarization, that contributes to a net energy transfer between the material and the field. After expressing the polarization in terms of its inverse Fourier transform (as shown in Eq.(2.11)), we obtain

$$
\begin{equation*}
\frac{\partial P_{i}(t)}{\partial t}=-\sum_{a} \frac{i \omega_{a}}{2}\left(P_{i}^{(n)}\left(\omega_{a}\right) e^{-i \omega_{a} t}-P_{i}^{(n)}\left(-\omega_{a}\right) e^{i \omega_{a} t}\right) \tag{2.29}
\end{equation*}
$$

Substituting Eq.(2.29) into Eq.(2.28), we find that after time-averaging, the gradient of the intensity is given by the expression

$$
\begin{equation*}
\nabla I^{(n)}=-\sum_{a} \frac{i \omega_{a}}{2}\left(P_{i}^{(n)}\left(-\omega_{a}\right) F_{i}\left(\omega_{a}\right)-P_{i}^{(n)}\left(\omega_{a}\right) F_{i}\left(-\omega_{a}\right)\right) \tag{2.30}
\end{equation*}
$$

Therefore, to each order, the gradient of the intensity for each frequency of light is described by the expression

$$
\begin{equation*}
\nabla I^{(n)}(\omega)=-\frac{i \omega}{2}\left(P_{i}^{(n)}(-\omega) F_{i}(\omega)-P_{i}^{(n)}(\omega) F_{i}(-\omega)\right) \tag{2.31}
\end{equation*}
$$

Using the relation between the complex conjugates of the Fourier amplitudes and the negative frequencies, we find

$$
\begin{equation*}
\nabla I^{(n)}(\omega)=-\frac{i \omega}{2}\left(P_{i}^{*(n)}(\omega) F_{i}(\omega)-P_{i}^{(n)}(\omega) F_{i}^{*}(\omega)\right) \tag{2.32}
\end{equation*}
$$

If the medium is isotropic we get that the Fourier component of the polarization is related to the susceptibility as

$$
\begin{equation*}
P_{i}^{(n)}\left(\omega_{\sigma}\right)=\epsilon_{0} \chi_{i j \ldots}^{(n)} \text { eff }\left(-\omega_{\sigma} ; \omega_{1}, \ldots \omega_{n}\right) F_{j}\left(\omega_{1}\right) \ldots \tag{2.33}
\end{equation*}
$$

By employing Eq.(2.21) and Eq.(2.23), we find that the effective linear susceptibility in an isotropic medium is given by

$$
\begin{equation*}
\chi_{i j}^{(1)} \text { eff }(-\omega ; \omega)=\mathcal{N}\left\langle\alpha_{\alpha \beta}(-\omega ; \omega)\right\rangle=\frac{\mathcal{N}}{3} \alpha_{\alpha \beta}(-\omega ; \omega) \delta_{i j} \delta_{\alpha \beta} \tag{2.34}
\end{equation*}
$$



FIGURE 2.1: The phase relation between the response, its time derivative and the perturbation for a complex polarization Fourier coefficient


FIGURE 2.2: The phase relation between the response, its time derivative and the perturbation for an purley real polarization Fourier coefficient


FIGURE 2.3: The phase relation between the response, its time derivative and the perturbation for an purley imaginary polarization Fourier coefficient

As a result, we find that the first-order intensity gradient can be represented by the expression

$$
\begin{align*}
& \nabla I^{(1)}(\omega) \\
& =-\frac{i \omega \mathcal{N}}{6} \sum_{i j \alpha \beta}\left(\alpha_{\alpha \beta}^{*}(-\omega ; \omega) F_{j}^{*}(\omega) F_{i}(\omega)-\alpha_{\alpha \beta}(-\omega ; \omega) F_{j}(\omega) F_{i}^{*}(\omega)\right) \delta_{i j} \delta_{\alpha \beta} \\
& =-\frac{i \omega}{3 c \epsilon} \sum_{\alpha}\left(\alpha_{\alpha \alpha}^{*}(-\omega ; \omega)-\alpha_{\alpha \alpha}(-\omega ; \omega)\right) I(\omega) \\
& =-\frac{2 \omega}{3 c \epsilon} \sum_{\alpha}{ }^{\mathbb{I}} \alpha_{\alpha \alpha}(-\omega ; \omega) I(\omega) \tag{2.35}
\end{align*}
$$

where we have used the relation $I(\omega)=\frac{c \epsilon}{2} F(\omega) F^{*}(\omega)$. We thus find that the solution to the differential equation in Eq.(2.35) is given by terms of the form

$$
\begin{equation*}
I(\omega, z)=I_{0} e^{-\sigma(\omega) z} \tag{2.36}
\end{equation*}
$$



FIGURE 2.4: The predicted intensity as a function of the distance travelled within a material for a given frequency for two different values of $\sigma(\omega)$

The orientationally averaged tensor we obtained in Eq. (2.35) will be referred to as the isotropic average polarizability $\bar{\alpha}$

$$
\begin{equation*}
\bar{\alpha}(-\omega ; \omega)=\frac{1}{3} \sum_{\alpha} \alpha_{\alpha \alpha}(-\omega ; \omega) \tag{2.37}
\end{equation*}
$$

The same logic applies to the second-order correction to the intensity gradient, which will depend on the second hyperpolarizability. For linearly polarized light with fields of the same frequency, we find that the effective second hyperpolarizability for randomly oriented
molecules is given by the expression ${ }^{33}$

$$
\begin{align*}
\bar{\gamma}(-\omega ; \omega,-\omega, \omega)=\frac{1}{15} \sum_{\alpha, \beta}^{x, y, z} & \left(\gamma_{\alpha \alpha \beta \beta}(-\omega ; \omega,-\omega, \omega)\right. \\
& +\gamma_{\alpha \beta \alpha \beta}(-\omega ; \omega,-\omega, \omega)  \tag{2.38}\\
& \left.+\gamma_{\alpha \beta \beta \alpha}(-\omega ; \omega,-\omega, \omega)\right) .
\end{align*}
$$

Finally, we can then write the gradient of the intensity in an isotropic medium as the series ${ }^{34}$

$$
\begin{equation*}
\nabla I(\omega)=-\frac{2 \omega}{c \epsilon_{0}} \mathbb{I}_{\bar{\alpha}}(-\omega ; \omega) I(\omega)-\frac{4 \omega}{c^{2} \epsilon_{0}^{2}} \mathbb{I}_{\bar{\gamma}}(-\omega ; \omega,-\omega, \omega) I^{2}(\omega)+\cdots \tag{2.39}
\end{equation*}
$$

Using the coefficients in the intensity gradient expansion, we now define the one and two-photon cross sections as

The one and two-photon absorption cross-sections

$$
\begin{gather*}
\sigma(\omega)=\frac{2 \omega}{c \epsilon_{0}} \mathbb{I} \bar{\alpha}(-\omega ; \omega)  \tag{2.40}\\
\sigma^{(2)}(\omega)=\frac{4 \omega}{c^{2} \epsilon_{0}^{2}} \mathbb{I}_{\bar{\gamma}}(-\omega ; \omega,-\omega, \omega) \tag{2.41}
\end{gather*}
$$

In the coming sections, we will determine the explicit expressions for the polarizability of molecules in response to external electric field perturbations, utilizing the Schrödinger equation, and discuss how absorption spectra can be calculated efficiently.

## FOURIER-COMPONENT VARIATIONAL PERTURBATION THEORY

## The Dirac-Frenkel variational principle

The quantum system under consideration is described by the wave function $\Psi$, which in general is a time-dependent complex function. Its evolution in time is dictated by the time-dependent Schrödinger equation ${ }^{7}$

$$
\begin{equation*}
\left(\hat{H}(t)-i \hbar \frac{\partial}{\partial t}\right)|\Psi\rangle=0 \tag{3.1}
\end{equation*}
$$

Here, $\hat{H}$ represents the Hamiltonian operator, encapsulating the total energy of the system, including the interactions between the electrons and the nuclei and the interaction with the external field. In the context of solving the Schrödinger equation, we intend to use the Dirac-Frenkel variational principle to obtain approximate solutions to the Schrödinger equation. To do this, we will define the Lagrangian density, A, as

$$
\begin{equation*}
A[\Psi]=\langle\Psi|\left(\hat{H}(t)-i \hbar \frac{\partial}{\partial t}\right)|\Psi\rangle . \tag{3.2}
\end{equation*}
$$

A first observation is that the exact solution $\Psi$ makes the Lagrangian density stationary, in other words, for any small variations $\delta \Psi$ around $\Psi, \delta A=0$, where $\delta A$ is given by,

$$
\begin{equation*}
\delta A[\Phi]=\langle\delta \Phi|\left(\hat{H}(t)-i \hbar \frac{\partial}{\partial t}\right)|\Phi\rangle+\langle\Phi|\left(\hat{H}(t)-i \hbar \frac{\partial}{\partial t}\right)|\delta \Phi\rangle \tag{3.3}
\end{equation*}
$$

The logic is now that if an approximate solution $\Phi$ behaves similarly under small variation $\delta \Phi$, then $\Phi$ should be a good approximation to $\Psi$. The Dirac-Frenkel variational principle then proposes that one finds an approximate solution $\Phi$ by finding a wave-function for which small variations $\delta \Phi$ from $\Phi$ the Lagrangian density is stationary, that is that the changes to A to first-order should be zero. The wave function is in general complex and the variations $\delta \Phi$ and $\delta \Phi^{*}$ are independent variations. Instead of treating $\delta \Phi$ and $\delta \Phi^{*}$ as as independent variations we multiply the variation $\delta \Phi$ by i to get an orthogonal variation in the complex plane, $\left|\delta \Phi^{\prime}\right\rangle=i|\delta \Phi\rangle$ and get a second equation for the Lagrangian density ${ }^{35}$

$$
\begin{equation*}
\delta A[\Phi]^{\prime}=-i\langle\delta \Phi|\left(\hat{H}(t)-i \hbar \frac{\partial}{\partial t}\right)|\Phi\rangle+i\langle\Phi|\left(\hat{H}(t)-i \hbar \frac{\partial}{\partial t}\right)|\delta \Phi\rangle=0 \tag{3.4}
\end{equation*}
$$

combining Eq. (3.3) and Eq. (3.4) we see that a further condition is that both terms in Eq. (3.3) must be zero

$$
\begin{equation*}
\langle\delta \Phi|\left(\hat{H}(t)-i \hbar \frac{\partial}{\partial t}\right)|\Phi\rangle=0 \tag{3.5}
\end{equation*}
$$

$$
\begin{equation*}
\langle\Phi|\left(\hat{H}(t)-i \hbar \frac{\partial}{\partial t}\right)|\delta \Phi\rangle=0 \tag{3.6}
\end{equation*}
$$

Furthermore, we can write Eq. (3.6) in terms of the complex conjugate of Eq. (3.5) using the relation

$$
\begin{equation*}
\langle\Phi|\left(\hat{H}(t)-i \hbar \frac{\partial}{\partial t}\right)|\delta \Phi\rangle=\langle\delta \Phi|\left(\hat{H}(t)-i \hbar \frac{\partial}{\partial t}\right)|\Phi\rangle^{*}-i \frac{\partial}{\partial t}\langle\Phi \mid \delta \Phi\rangle \tag{3.7}
\end{equation*}
$$

The first expression on the right hand side of Eq. (3.7) being the complex conjugate of Eq. (3.5) is hence zero. Substituting this expression into Eq. (3.3) we get the condition

$$
\begin{equation*}
\delta A[\Phi]=-i \frac{\partial}{\partial t}\langle\Phi \mid \delta \Phi\rangle=0 \tag{3.8}
\end{equation*}
$$

In order to make use of Eq. (3.8) we introduce an ansatz for the wave function

$$
\begin{equation*}
|\Phi\rangle=e^{-i \Lambda(t)}|\bar{\Phi}\rangle . \tag{3.9}
\end{equation*}
$$

Here $|\bar{\Phi}\rangle$ is the phase isolated wave-function and depends on some set of parameters which we will call $\eta^{\omega}$ which are the Fourier components of the time-dependent wave-function parameter $\eta(t)$ and $\Lambda$ is a phase that also depends on $\eta(t)$. For now we have not specified the details of $\eta$, that will be discussed in section 3.3. Furthermore, we constrain the phase isolated wave function such that its norm is unity and that the first-order variation of the norm is zero for all times

$$
\begin{equation*}
\langle\bar{\Phi}(t) \mid \bar{\Phi}(t)\rangle=1, \delta\langle\bar{\Phi}(t) \mid \bar{\Phi}(t)\rangle=0 \tag{3.10}
\end{equation*}
$$

We then get that the we can rewrite Eq. (3.8) as ${ }^{36}$

$$
\begin{align*}
& \delta A[\Phi]=-i \sum_{n} \sum_{k} \frac{\partial}{\partial t}\left\langle\Phi(t) \left\lvert\, \frac{\partial \Phi(t)}{\partial \eta_{n}^{\omega_{k}}}\right.\right\rangle \\
& =-i \sum_{n} \sum_{k} \frac{\partial}{\partial t}\langle\bar{\Phi}(t)|\left(-i \frac{\partial \Lambda(t)}{\partial \eta_{n}^{\omega_{k}}}+\frac{\partial}{\partial \eta_{n}^{\omega_{k}}}\right)|\bar{\Phi}(t)\rangle  \tag{3.11}\\
& =\sum_{n} \sum_{k}\left(\frac{\partial^{2} \Lambda(t)}{\partial \eta_{n}^{\omega_{k}} \partial t}-i \frac{\partial}{\partial t}\left\langle\bar{\Phi}(t) \left\lvert\, \frac{\partial \bar{\Phi}(t)}{\partial \eta_{n}^{\omega_{k}}}\right.\right\rangle\right)=0
\end{align*}
$$

Substituting the ansatz for the wave-function in Eq. (3.9) into the Schrödinger equation, Eq. (3.1), we can define the quasi-energy ${ }^{37} \mathrm{Q}(\mathrm{t})$ as the time-derivative of the phase $\Lambda$

$$
\begin{equation*}
Q(t)=\frac{\partial \Lambda(t)}{\partial t}=\langle\bar{\Phi}(t)|\left(\hat{H}(t)-i \frac{\partial}{\partial t}\right)|\bar{\Phi}(t)\rangle \tag{3.12}
\end{equation*}
$$

The quasi-energy will as will be seen an important quantity in the coming sections when we attempt to derive expressions for the response properties. With use of the quasi-energy we then get an equation for the parameters $\eta$ for which the Lagrangian density is stationary

The phase-isolated Dirac-Frenkel variational principle

$$
\begin{equation*}
\delta A[\Phi]=\sum_{n} \sum_{k}\left(\frac{\partial Q(t)}{\partial \eta_{n}^{\omega_{k}}}-i \frac{\partial}{\partial t}\left\langle\bar{\Phi}(t) \left\lvert\, \frac{\partial \bar{\Phi}(t)}{\partial \eta_{n}^{\omega_{k}}}\right.\right\rangle\right)=0 \tag{3.13}
\end{equation*}
$$

Solving this equation for the parameters $\eta$ hence gives us a way to find approximate solutions to the time-dependent Schrödinger equation.

## Time-Averaged Quasi-Energy Variational Formulation

In the previous section, we discussed the Lagrangian density and the Dirac--Frenkel variational principle, and arrived at Eq.(3.13), from which we could, in principle, solve for the wave-function parameters $\eta(t)$, which would provide us the time evolution of the wave function. In this section, we will employ Fourier component variational perturbation theory to solve Eq.(3.13). We now consider a system subjected to a periodic time-dependent perturbation given by $V(t)=V(t+T)$, such that the system is characterized by the Hamiltonian,

$$
\begin{equation*}
\hat{H}(t)=\hat{H}_{0}+\hat{V}(t) \tag{3.14}
\end{equation*}
$$

Where we have separated the the Hamiltonian $\hat{H}_{0}$ which describes the unperturbed system and the perturbation operator represents the coupling between a time-dependant electric field from a laser that is small compared to the atomic field with the dipole moment of the molecule

$$
\begin{gather*}
\hat{V}(t)=-\hat{\boldsymbol{\mu}} \cdot \boldsymbol{F}(t)  \tag{3.15}\\
\hat{\boldsymbol{\mu}}=\left(\begin{array}{c}
\hat{\mu}_{x} \\
\hat{\mu}_{y} \\
\hat{\mu}_{z}
\end{array}\right), \boldsymbol{F}(t)=\left(\begin{array}{l}
F_{x}(t) \\
F_{y}(t) \\
F_{z}(t)
\end{array}\right) . \tag{3.16}
\end{gather*}
$$

Assuming that the perturbation is periodic, the perturbation operator can be written as the discrete Fourier series

$$
\begin{equation*}
\hat{V}(t)=-\sum_{k} \sum_{\alpha}^{x, y, z} \hat{\mu}_{\alpha}\left(F_{\alpha}\left(\omega_{k}\right) e^{-i \omega_{k} t}+F_{\alpha}\left(-\omega_{k}\right) e^{i \omega_{k} t}\right) \tag{3.17}
\end{equation*}
$$

Moreover, since the electric field is periodic and real, the Fourier components of the field are related as

$$
\begin{equation*}
F_{\alpha}^{\omega_{k}}=\left(F_{\alpha}^{-\omega_{k}}\right)^{*} . \tag{3.18}
\end{equation*}
$$

In the presence of this periodic perturbation, we expand the phaseisolated wave-function $\bar{\Phi}$ in a power series of the Fourier amplitudes of the field.

$$
\begin{align*}
|\bar{\Phi}(t, F)\rangle & =|\bar{\Phi}\rangle+\sum_{k} \sum_{\alpha}\left|\bar{\Phi}_{\alpha}^{(1)}\left(\omega_{k}\right)\right\rangle F_{\alpha}^{\omega_{k}} e^{-i \omega_{k} t} \\
& +\sum_{k, l} \sum_{\alpha, \beta}\left|\bar{\Phi}_{\alpha \beta}^{(2)}\left(\omega_{k}, \omega_{l}\right)\right\rangle F_{\alpha}^{\omega_{k}} F_{\beta}^{\omega_{l}} e^{-i\left(\omega_{k}+\omega_{l}\right) t}+. . \tag{3.19}
\end{align*}
$$

By substituting this expansion into the Dirac-Frenkel variational principle, as given in Eq.(3.13), and performing time-averaging, we find that the second term is zero

$$
\begin{align*}
& \frac{1}{T} \int_{0}^{T}-i \sum_{k . .} \sum_{i} \frac{\partial}{\partial t}\left\langle\bar{\Phi}(t) \left\lvert\, \frac{\partial \bar{\Phi}(t)}{\partial \eta_{i}^{\omega_{k}}}\right.\right\rangle d t= \\
& \sum_{m n} \sum_{k . .} \sum_{i} \omega_{\sigma}\left\langle\bar{\Phi}_{\alpha, . .}^{(n)}\left(\omega_{k}, . .\right) \left\lvert\, \frac{\partial \bar{\Phi}_{\alpha, . .}^{(m)}\left(\omega_{k}, . .\right)}{\partial \eta_{i}^{\omega_{k}}}\right.\right\rangle F_{\alpha}^{\omega_{k}} \cdot \cdot \frac{1}{T} \int_{0}^{T} e^{-i \omega_{\sigma} t} d t=0 \tag{3.20}
\end{align*}
$$

Here, $\omega_{\sigma}$ represents the sum of all the frequencies involved in each term. Consequently, after time-averaging, we can reformulate the Dirac-Frenkel variational principle of Eq.(3.13) as

$$
\begin{align*}
& \frac{1}{T} \sum_{n} \sum_{k} \int_{0}^{T}\left[\frac{\partial Q(t)}{\partial \eta_{n}^{\omega_{k}}}-i \frac{\partial}{\partial t}\left\langle\bar{\Phi}(t) \left\lvert\, \frac{\partial \bar{\Phi}(t)}{\left.\partial \eta_{n}^{\omega_{k}}\right\rangle}\right.\right\rangle\right] d t=0 \\
& \rightarrow \frac{1}{T} \sum_{n} \sum_{k} \int_{0}^{T} \frac{\partial Q(t)}{\partial \eta_{n}^{\omega_{k}}} d t=\sum_{n} \sum_{k} \frac{\partial}{\partial \eta_{n}^{\omega_{k}}} \frac{1}{T} \int_{0}^{T} Q(t) d t  \tag{3.21}\\
& =\sum_{n} \sum_{k} \frac{\partial Q_{T}}{\partial \eta_{n}^{\omega_{k}}}=0
\end{align*}
$$

We have thus found that, in the presence of the perturbation, the Fourier components of the system's time-dependent wave-function parameters are altered in a way that renders the time-averaged quasienergy stationary with respect to the electronic degrees of freedom.

## Parametric Representation of the Phase-Isolated Reference

## State

In this section, we will introduce the parametrizations used for the phase-isolated wave-function. We will employ an exponential parametrization in terms of an anti-Hermitian operator, which will ensure that the transformation preserves the norm of the wavefunction

$$
\begin{equation*}
|\bar{\Phi}(t)\rangle=e^{-\hat{\eta}(t)}|0\rangle . \tag{3.22}
\end{equation*}
$$

The anti-Hermitian operator $\hat{\eta}$ can be represented as an inner product of two vectors, where one vector contains the operators and one vector contains the wave-function parameters

$$
\hat{\eta}(t)=\left(\begin{array}{ll}
\hat{O}_{n}^{\dagger} & -\hat{O}_{n} \tag{3.23}
\end{array}\right)\binom{\eta_{n}(t)}{\eta_{n}^{*}(t)}
$$

In this exponential parametrization, we distinguish between two cases: a parametrization in terms of the exact eigenstates of the unperturbed Hamiltonian, which we refer to as a state-rotation parametrization, and one where we use a single Slater-determinant ansatz and excite between single-particle orbitals, which we will refer to as an orbital rotation parametrization. In the state-rotation parametrization,
we introduce the state-rotation operators ${ }^{38}$ :

$$
\begin{equation*}
\hat{R}_{n}^{\dagger}=\left|\Psi_{n}\right\rangle\left\langle\Psi_{0}\right|, \hat{R}_{n}=\left|\Psi_{0}\right\rangle\left\langle\Psi_{n}\right| \tag{3.24}
\end{equation*}
$$

that transforms the wave-function to the exact eigenstates of $\hat{H}_{0}$ :

$$
\begin{equation*}
\hat{R}_{n}^{\dagger}\left|\Psi_{0}\right\rangle=\left|\Psi_{n}\right\rangle \tag{3.25}
\end{equation*}
$$

The other parametrization mentioned above is the orbital rotation parametrization. In this approach, the starting point is a reference state Slater-determinant $\left|\Theta_{0}\right\rangle$ :

$$
\begin{equation*}
\left|\Theta_{0}\right\rangle=\Pi_{i}^{o c c} \hat{a}_{i}^{\dagger}|v a c\rangle \tag{3.26}
\end{equation*}
$$

where the operators $\hat{a}$ are defined with respect to a basis of spin orbitals that we have obtained by either conducting a Hartree-Fock (HF) or Density Functional Theory (DFT) self-consistent field (SCF) calculation. We can then generate excited state Slater determinants from this reference state by promoting electrons as in ${ }^{34}$

$$
\begin{equation*}
\hat{q}_{n}^{\dagger}\left|\Theta_{0}\right\rangle=\left|\Theta_{n}\right\rangle \tag{3.27}
\end{equation*}
$$

where each excited-state Slater-determinant represents a different configuration of electrons. We then express perturbations to the wavefunction in terms of single-particle excitations $\hat{q}_{n}^{\dagger}$ and de-excitation $\hat{q}_{n}$ between occupied and unoccupied orbitals

$$
\begin{equation*}
\hat{q}_{n}^{\dagger}=\hat{a}_{a}^{\dagger} \hat{a}_{i}, \hat{q}_{n}=\hat{a}_{i}^{\dagger} \hat{a}_{a} \tag{3.28}
\end{equation*}
$$

with indices $i, j, \ldots, a, b, \ldots$, and $p, q, \ldots$, we denote occupied, unoccupied, and general spin orbitals or spatial orbitals, respectively, whether the operators are accompanied with a spin index. We also introduce compound indices, $n, m, \ldots$, to denote pairs of orbital indices $a, i$.

## The time-dependent Hellmann-Feynman theorem

In this section, we will use the time-dependent Hellmann-Feynman theorem to derive explicit expressions for the Fourier components of the induced time-dependent dipole moment in terms of the response vectors presented in the previous section. Using the Baker-Campbell-Hausdorff expansion and the expression for the phase-isolated wave function given by Eq. (3.22), we can expand the time-dependent dipole moment in terms of the wave-function parameters as

$$
\begin{align*}
& \mu(t)=\langle 0| e^{\hat{\eta}(t)} \hat{\mu} e^{-\hat{\eta}(t)}|0\rangle \\
& =\langle 0| \hat{\mu}|0\rangle+\sum_{n}\langle 0|\left[\eta_{r}(t) \hat{R}_{n}^{\dagger}-\eta_{n}^{*}(t) \hat{R}_{n}, \hat{\mu}\right]|0\rangle \\
& +\frac{1}{2!} \sum_{n, m}\langle 0|\left[\eta_{r}(t) \hat{R}_{n}^{\dagger}-\eta_{n}^{*}(t) \hat{R}_{n},\left[\eta_{m}(t) \hat{R}_{m}^{\dagger}-\eta_{m}^{*}(t) \hat{R}_{m}, \hat{\mu}\right]\right]|0\rangle \\
& +\ldots \tag{3.29}
\end{align*}
$$

Time-averaging the dipole moment in Eq.(3.29) and projecting it onto $e^{-i \omega t}$ yields the Fourier coefficient

$$
\begin{equation*}
\mu_{\alpha}(-\omega)=\frac{1}{T} \int_{0}^{T} \mu(t) e^{-i \omega t} d t \tag{3.30}
\end{equation*}
$$

Substituting Eq.(3.29) into Eq.(3.30) and taking the derivative of the Fourier coefficient with respect to the wave-function parameters gives us the first and second-order derivatives

$$
\begin{gather*}
\left.\frac{d \mu_{\alpha}^{-\omega}}{d \eta_{n}^{\omega_{k}}}\right|_{\eta=0}=\left\langle\Psi_{0}\right|\left[\hat{R}_{n}, \hat{\mu}_{\alpha}\right]\left|\Psi_{0}\right\rangle \delta\left(\omega+\omega_{k}\right)  \tag{3.31}\\
\left.\frac{d^{2} \mu_{\alpha}^{-\omega}}{d \eta_{n}^{\omega_{k}} d \eta_{m}^{\omega_{l}}}\right|_{\eta=0}=\frac{1}{2} P_{n m}\left\langle\Psi_{0}\right|\left[\hat{R}_{n},\left[\hat{R}_{m}, \hat{\mu}_{\alpha}\right]\right]\left|\Psi_{0}\right\rangle \delta\left(\omega+\omega_{k}+\omega_{l}\right) \tag{3.32}
\end{gather*}
$$

The Fourier coefficient of the dipole moment is a function of the wavefunction parameters, and we can consequently write the expansion of the Fourier component of the dipole moment as a Taylor expansion

$$
\begin{equation*}
\mu_{\alpha}(-\omega)=\left.\sum_{k, n} \frac{d \mu_{\alpha}^{-\omega}}{d \eta_{n}^{\omega_{k}}}\right|_{\eta=0} \eta_{n}^{\omega_{k}}+\left.\sum_{k l m n} \frac{d^{2} \mu_{\alpha}^{-\omega}}{d \eta_{n}^{\omega_{k}} d \eta_{m}^{\omega_{l}}}\right|_{\eta=0} \eta_{n}^{\omega_{k}} \eta_{m}^{\omega_{l}}+\cdots \tag{3.33}
\end{equation*}
$$

Utilizing this formula allows us to observe the alterations in the dipole moment's Fourier component as modifications are made to the parameters of the wave function. To illustrate, we can derive formulas to understand the variations in the dipole moment's Fourier component relative to an external electric field by calculating the derivative of the Fourier coefficient with respect to the field

$$
\begin{gather*}
\left.\frac{d \mu_{\alpha}^{-\omega}}{d F_{\beta}^{\omega_{k}}}\right|_{F=0}=\left.\frac{d \mu_{\alpha}^{-\omega}}{d \eta_{n}^{\omega_{k}}}\right|_{\eta=0} \frac{d \eta_{n}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}}  \tag{3.34}\\
\left.\frac{d^{2} \mu_{\alpha}^{-\omega}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{m}}}\right|_{F=0}=\left.\frac{d \mu_{\alpha}^{-\omega}}{d \eta_{n}^{\omega_{k}}}\right|_{\eta=0} \frac{d^{2} \eta_{n}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{m}}}+\left.\frac{d^{2} \mu_{\alpha}^{-\omega}}{d \eta_{n}^{\omega_{k}} d \eta_{m}^{\omega_{l}}}\right|_{\eta=0} \frac{d \eta_{n}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}} \frac{d \eta_{n}^{\omega_{l}}}{d F_{\gamma}^{\omega_{l}}} \tag{3.35}
\end{gather*}
$$

The second-order derivatives have two pathways: one is related to the simultaneous change of a wave function parameter with respect to two fields, and the second term involves the separate change of different wave function parameters with respect to two distinct perturbations. In the section on non-linear response, we will discuss the differences between these two terms in greater detail. From these equations, it is apparent that we can estimate the rate of change of the Fourier component of the dipole moment with respect to the field if we know the rate of change of the Fourier components of the wave function parameters. Utilizing these derivatives, we can construct a
power series expansion of the Fourier component of the dipole moment with respect to the field

$$
\begin{align*}
\mu_{\alpha}^{F}(-\omega) & =\left.\sum_{k} \frac{d \mu_{\alpha}^{-\omega}}{d F_{\beta}^{\omega_{k}}}\right|_{F=0} F_{\beta}^{\omega_{k}}+\left.\frac{1}{2} \sum_{k, l} \frac{d^{2} \mu_{\alpha}^{-\omega}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}}}\right|_{F=0} F_{\beta}^{\omega_{k}} F_{\gamma}^{\omega_{l}} \\
& +\left.\frac{1}{6} \sum_{k, l, m} \frac{d^{3} \mu_{\alpha}^{-\omega}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}\right|_{F=0} F_{\beta}^{\omega_{k}} F_{\gamma}^{\omega_{l}} F_{\delta}^{\omega_{m}}+. . \tag{3.36}
\end{align*}
$$

By definition, the derivatives represent the polarizability and the hyperpolarizabilities.

The hyper polarizabilities

$$
\begin{align*}
& \alpha_{\alpha \beta}\left(-\omega ; \omega_{k}\right)=\left.\frac{d \mu_{\alpha}^{-\omega}}{d F_{\beta}^{\omega_{k}}}\right|_{F=0} \\
& \beta_{\alpha \beta \gamma}\left(-\omega ; \omega_{k}, \omega_{l}\right)=\left.\frac{d^{2} \mu_{\alpha}^{-\omega}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}}}\right|_{F=0},  \tag{3.3}\\
& \gamma_{\alpha \beta \gamma \delta}\left(-\omega ; \omega_{k}, \omega_{l}, \omega_{m}\right)=\left.\frac{d^{3} \mu_{\alpha}^{-\omega}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}\right|_{F=0}
\end{align*}
$$

After time averaging, the quasi-energy is a function of the Fourier amplitudes of the field through the operator $\hat{V}$ as well as the Fourier amplitudes of the wave function parameters in the phase isolated wave function, $Q_{T}\left(\eta^{\omega}, F^{\omega}\right)$. If we now consider how the timeaveraged quasi-energy changes with respect to the field, we obtain the time-dependent Hellman-Feynman theorem

## The time-dependent Hellmann-Feynmann theorem

$$
\begin{equation*}
\frac{d Q_{T}}{d F_{\alpha}^{\omega}}=\frac{\partial Q_{T}}{\partial F_{\alpha}^{\omega}}+\sum_{n} \frac{\partial Q_{T}}{\partial \eta_{n}^{\omega}} \frac{\partial \eta_{n}^{\omega}}{\partial F_{\alpha}^{\omega}}=\mu_{\alpha}(-\omega) \tag{3.38}
\end{equation*}
$$

The second term in the right hand side of Eq. (3.38) equals zero since the quasi-energy remains stationary with respect to the wave function parameters, as shown in Eq. (3.21). Moreover, the remaining term can be written in terms of the expected value of the timedependent dipole moment ${ }^{37}$

$$
\begin{align*}
\frac{\partial Q_{T}}{\partial F_{\alpha}^{\omega}} & =\frac{1}{T} \int_{0}^{T}\langle\bar{\Phi}(t)| \frac{\partial \hat{V}(t)}{\partial F_{\alpha}^{\omega}}|\bar{\Phi}(t)\rangle d t  \tag{3.39}\\
& =\frac{1}{T} \int_{0}^{T}\langle\bar{\Phi}(t)| \hat{\mu}_{\alpha}|\bar{\Phi}(t)\rangle e^{-i \omega t} d t
\end{align*}
$$

To obtain the Fourier coefficients of the time-dependent dipole moment, we expand the dipole moment using a power series.

$$
\begin{align*}
& \langle\bar{\Phi}(t)| \hat{\mu}_{\alpha}|\bar{\Phi}(t)\rangle=\mu_{\alpha}+\sum_{\beta} \sum_{k} \alpha_{\alpha \beta}\left(-\omega ; \omega_{k}\right) F_{\beta}^{\omega_{k}} e^{-i \omega_{k} t} \\
& +\frac{1}{2} \sum_{\beta, \gamma} \sum_{k, l} \beta_{\alpha \beta \gamma}\left(-\omega ; \omega_{k}, \omega_{l}\right) F_{\beta}^{\omega_{k}} F_{\gamma}^{\omega_{l}} e^{-i\left(\omega_{k}+\omega_{l}\right) t} \\
& +\frac{1}{6} \sum_{\beta, \gamma, \delta} \sum_{k, l, m} \gamma_{\alpha \beta \gamma \delta}\left(-\omega ; \omega_{k}, \omega_{l}, \omega_{m}\right) F_{\beta}^{\omega_{k}} F_{\gamma}^{\omega_{l}} F_{\delta}^{\omega_{m}} e^{-i\left(\omega_{k}+\omega_{l}+\omega_{m}\right) t} \\
& +\cdots \tag{3.40}
\end{align*}
$$

We then have that the field derivative of the time-averaged quasienergy is related to the Fourier components of the time-dependant dipole moment through a power series of the field amplitudes by combining Eq. (3.40) and Eq. (3.39)

$$
\begin{align*}
& \frac{d Q_{T}}{d F_{\alpha}^{\omega}}=\mu_{\alpha} \frac{1}{T} \int_{0}^{T} e^{-i \omega t} d t \\
& +\frac{1}{2} \sum_{\beta} \sum_{k} \alpha_{\alpha \beta}\left(-\omega ; \omega_{k}\right) F_{\beta}^{\omega_{k}} \frac{1}{T} \int_{0}^{T} e^{-i\left(\omega_{k}+\omega_{n}\right) t} d t \\
& +\frac{1}{6} \sum_{\beta, \gamma} \sum_{k, l} \beta_{\alpha \beta \gamma}\left(-\omega ; \omega_{k}, \omega_{l}\right) F_{\beta}^{\omega_{k}} F_{\gamma}^{\omega_{l}} \frac{1}{T} \int_{0}^{T} e^{-i\left(\omega_{k}+\omega_{l}+\omega\right) t} d t \\
& +\sum_{\beta, \gamma, \delta} \sum_{k, l, m} \gamma_{\alpha \beta \gamma \delta}\left(-\omega ; \omega_{k}, \omega_{l}, \omega_{m}\right) F_{\beta}^{\omega_{k}} F_{\gamma}^{\omega_{l}} F_{\delta}^{\omega_{m}} \frac{1}{T} \int_{0}^{T} e^{-i\left(\omega_{k}+\omega_{l}+\omega_{m}+\omega\right) t} d t \\
& +\cdots \tag{3.41}
\end{align*}
$$

We therefore, get that the Fourier component of the dipole moment that oscillates at frequency $\omega$ is given by the following power series

$$
\begin{aligned}
& \frac{d Q_{T}}{d F_{\alpha}^{\omega}}=\sum_{\beta} \sum_{k} \alpha_{\alpha \beta}\left(-\omega ; \omega_{k}\right) F_{\beta}^{\omega_{k}} \delta\left(\omega_{k}+\omega\right) \\
& +\frac{1}{2} \sum_{\beta, \gamma} \sum_{k, l} \beta_{\alpha \beta \gamma}\left(-\omega ; \omega_{k}, \omega_{l}\right) F_{\beta}^{\omega_{k}} F_{\gamma}^{\omega_{l}} \delta\left(\omega_{k}+\omega_{l}+\omega\right) \\
& +\frac{1}{6} \sum_{\beta, \gamma, \delta} \sum_{k, l, m} \gamma_{\alpha \beta \gamma \delta}\left(-\omega ; \omega_{k}, \omega_{l}, \omega_{m}\right) F_{\beta}^{\omega_{k}} F_{\gamma}^{\omega_{l}} F_{\delta}^{\omega_{m}} \delta\left(\omega_{k}+\omega_{l}+\omega_{m}+\omega\right)
\end{aligned}
$$

$$
\begin{equation*}
+\cdots \tag{3.42}
\end{equation*}
$$

where the polarizabilites are defined as the rate of change of the dipole moment with respect to the field evaluated at zero field strength so as to give the intrinsic property of the molecule

The hyper polarizabilities in terms of the quasi-energy

$$
\begin{align*}
& \alpha_{\alpha \beta}\left(-\omega ; \omega_{k}\right)=\left.\frac{d^{2} Q_{T}}{d F_{\alpha}^{\omega} d F_{\beta}^{\omega_{k}}}\right|_{F=0}, \\
& \beta_{\alpha \beta \gamma}\left(-\omega ; \omega_{k}, \omega_{l}\right)=\left.\frac{d^{3} Q_{T}}{d F_{\alpha}^{\omega} d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}}}\right|_{F=0},  \tag{3.43}\\
& \gamma_{\alpha \beta \gamma \delta}\left(-\omega ; \omega_{k}, \omega_{l}, \omega_{m}\right)=\left.\frac{d^{4} Q_{T}}{d F_{\alpha}^{\omega} d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}\right|_{F=0} .
\end{align*}
$$

Employing a vector formalism allows us to derive concise expressions for the field derivatives of the quasi-energy, as will be demonstrated below. In terms of the parameter vector of Eq. (3.23), which had two blocks

$$
\begin{equation*}
\boldsymbol{\eta}=\binom{\eta_{n}}{\eta_{n}^{*}} . \tag{3.44}
\end{equation*}
$$

where the upper block is referred to as the excitation block, and the lower segment as the de-excitation block we can derive explicit formulas for hyperpolarizabilities as higher-order field derivatives of the quasi-energy

$$
\begin{align*}
\alpha_{\alpha \beta}\left(-\omega ; \omega_{k}\right) & =\frac{\partial^{2} Q_{T}}{\partial F_{\alpha}^{\omega} \partial \boldsymbol{\eta}^{\omega_{k}}} \frac{d \boldsymbol{\eta}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}},  \tag{3.45}\\
\beta_{\alpha \beta \gamma}\left(-\omega ; \omega_{k}, \omega_{l}\right) & =\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{\omega} \partial \boldsymbol{\eta}^{\omega_{k}} \partial \boldsymbol{\eta}^{\omega_{l}}} \frac{d \boldsymbol{\eta}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}} \frac{d \boldsymbol{\eta}^{\omega_{l}}}{d F_{\gamma}^{\omega_{l}}} \\
& +\frac{\partial^{2} Q_{T}}{\partial F_{\alpha}^{\omega} \partial \boldsymbol{\eta}^{\omega_{k}, \omega_{l}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{k}, \omega_{l}}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}}} .  \tag{3.46}\\
\gamma_{\alpha \beta \gamma \delta}\left(-\omega ; \omega_{k}, \omega_{l}, \omega_{m}\right)= & \frac{\partial^{4} Q_{T}}{\partial F_{\alpha}^{\omega} \partial \boldsymbol{\eta}^{\omega_{k}} \partial \boldsymbol{\eta}^{\omega_{l}}} \frac{d \boldsymbol{\eta}_{l}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}} \frac{d \boldsymbol{\eta}^{\omega_{l}}}{d F_{\gamma}^{\omega_{l}}} \frac{d \boldsymbol{\eta}^{\omega_{m}}}{d F_{\delta}^{\omega_{m}}} \\
& +\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{\omega} \partial \boldsymbol{\eta}^{\omega_{k}, \omega_{l}} \partial \boldsymbol{\eta}^{\omega_{m}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{k}, \omega_{l}}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}}} \frac{d \boldsymbol{\eta}_{m}}{d F_{\delta}^{\omega_{m}}} \\
& +\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{\omega} \partial \boldsymbol{\eta}^{\omega_{l}, \omega_{m}} \partial \boldsymbol{\eta}^{\omega_{m}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{l}, \omega_{m}}}{d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}} \frac{d \boldsymbol{\eta}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}} \\
& +\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{\omega} \partial \boldsymbol{\eta}^{\omega_{k}, \omega_{m}} \partial \boldsymbol{\eta}^{\omega_{l}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{k}, \omega_{m}}}{d F_{\beta}^{\omega_{k}} d F_{\delta}^{\omega_{m}}} \frac{d \boldsymbol{\eta}^{\omega_{l}}}{d F_{\gamma}^{\omega_{l}}} \\
& +\frac{\partial^{2} Q_{T}}{\partial F_{\alpha}^{\omega} \partial \boldsymbol{\eta}^{\omega_{k}, \omega_{k}, \omega_{l}}} \frac{d^{3} \boldsymbol{\eta}^{\omega_{k}, \omega_{l}, \omega_{m}}}{d F_{\beta}^{\omega_{k}}} \frac{d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}{} . \tag{3.47}
\end{align*}
$$

Leveraging the equation $\frac{\partial Q_{T}}{\partial F_{\alpha}^{\omega}}=\mu_{\alpha}(-\omega)$ enables us to express the derivatives more explicitly in terms of dipole moment derivatives

$$
\begin{equation*}
\alpha_{\alpha \beta}\left(-\omega ; \omega_{k}\right)=\frac{\partial \mu_{\alpha}^{-\omega}}{\partial \boldsymbol{\eta}^{\omega_{k}}} \frac{d \boldsymbol{\eta}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}}, \tag{3.48}
\end{equation*}
$$

$$
\left.\begin{array}{rl}
\beta_{\alpha \beta \gamma}\left(-\omega ; \omega_{k}, \omega_{l}\right) & =\frac{\partial^{2} \mu_{\alpha}^{-\omega}}{\partial \boldsymbol{\eta}^{\omega_{k}} \partial \boldsymbol{\eta}^{\omega_{l}}} \frac{d \boldsymbol{\eta}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}} \frac{d \boldsymbol{\eta}^{\omega_{l}}}{d F_{\gamma}^{\omega_{l}}} \\
& +\frac{\partial \mu_{\alpha}^{-\omega}}{\partial \boldsymbol{\eta}^{\omega_{k}, \omega_{l}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{k}, \omega_{l}}}{d F_{\beta}^{\omega_{k}}} d F_{\gamma}^{\omega_{l}}
\end{array}\right] \begin{aligned}
\gamma_{\alpha \beta \gamma \delta}\left(-\omega ; \omega_{k}, \omega_{l}, \omega_{m}\right) & =\frac{\partial^{3} \mu_{\alpha}^{-\omega}}{\partial \boldsymbol{\eta}^{\omega_{k}} \partial \boldsymbol{\eta}^{\omega_{l}}} \frac{d \boldsymbol{\eta}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}} \frac{d \boldsymbol{\eta}^{\omega_{l}}}{d F_{\gamma}^{\omega_{l}}} \frac{d \boldsymbol{\eta}^{\omega_{m}}}{d F_{\delta}^{\omega_{m}}} \\
& +\frac{\partial^{2} \mu_{\alpha}^{-\omega}}{\partial \boldsymbol{\eta}^{\omega_{k}, \omega_{l}} \partial \boldsymbol{\eta}_{m}^{\omega_{m}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{k}, \omega_{l}}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}}} \frac{d \boldsymbol{\eta}^{\omega_{m}}}{d F_{\delta}^{\omega_{m}}} \\
& +\frac{\partial^{2} \mu_{\alpha}^{-\omega}}{\partial \boldsymbol{\eta}^{\omega_{l}, \omega_{m}} \partial \boldsymbol{\eta}^{\omega_{m}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{l}, \omega_{m}}}{d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}} \frac{d \boldsymbol{\eta}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}} \\
& +\frac{\partial^{2} \mu_{\alpha}^{-\omega}}{\partial \boldsymbol{\eta}^{\omega_{k}, \omega_{m}} \partial \boldsymbol{\eta}^{\omega_{l}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{k}, \omega_{m}}}{d F_{\beta}^{\omega_{k}} d F_{\delta m}^{\omega_{m}}} \frac{d \boldsymbol{\eta}_{l}}{d F_{\gamma}^{\omega_{l}}}  \tag{3.50}\\
& +\frac{\partial \mu_{\alpha}^{-\omega}}{\partial \boldsymbol{\eta}^{\omega_{k}, \omega_{k}, \omega_{l}}} \frac{d^{3} \boldsymbol{\eta}_{k}^{\omega_{k}, \omega_{l}, \omega_{m}}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}} .
\end{aligned}
$$

To summarize this section, we have demonstrated that the dipole moment is indirectly affected by an external perturbation. This perturbation modulates the wave-function parameters, allowing the Fourier component of the dipole moment to be estimated via a Taylor expansion centered around the reference state. Through this expansion, we can analyze the variations in the Fourier component of the dipole moment as a function of the wave-function parameters. The remaining task is to elucidate how the Fourier components of the wave-function parameters vary in response to the external perturbation.

## Perturbation expansion of the time-averaged variational principle

In previous sections, we established that comprehending the variations in the dipole moment relative to external perturbations necessitates understanding the alterations in the wave function parameters in relation to the external field. This section is dedicated to formulating equations that detail the order corrections to the wave function parameters as influenced by the external field. The parameterization for the wave function was presented in Eq. (3.23), we will now look in more detail at the time-dependent parameter vector part ${ }^{39}$

$$
\begin{equation*}
\boldsymbol{\eta}(t)=\binom{\eta_{n}(t)}{\eta_{n}^{*}(t)} . \tag{3.51}
\end{equation*}
$$

Each wave function parameter can be expressed in terms of its Fourier components as follows

$$
\begin{equation*}
\eta_{n}(t)=\sum_{k>0}\left(\eta_{n}(\omega) e^{-i w_{k} t}+\eta_{n}(-\omega) e^{i w_{k} t}\right) \tag{3.52}
\end{equation*}
$$

$$
\begin{equation*}
\eta_{n}^{*}(t)=\sum_{k>0}\left(\eta_{n}^{*}(\omega) e^{i w_{k} t}+\eta_{n}^{*}(-\omega) e^{-i w_{k} t}\right) \tag{3.53}
\end{equation*}
$$

Given that $\eta(t)$ is a complex function, the positive and negative frequency Fourier components are generally independent. This necessitates determining both components, illustrated by the inequality $\eta_{n}(\omega) \neq \eta^{n}(-\omega)$. Consequently, the wave function parameter vector can be written as

$$
\begin{equation*}
\boldsymbol{\eta}(t)=\sum_{k>0}\left[\binom{\eta_{n}(\omega)}{\eta_{n}^{*}(-\omega)} e^{-i \omega_{k} t}+\binom{\eta_{n}(-\omega)}{\eta_{n}^{*}(\omega)} e^{i \omega_{k} t}\right] \tag{3.54}
\end{equation*}
$$

We shall refer to the two vectors in Eq. (3.54) as

$$
\begin{equation*}
\boldsymbol{\eta}^{\omega}=\binom{\eta_{n}(\omega)}{\eta_{n}^{*}(-\omega)}, \boldsymbol{\eta}^{-\omega}=\binom{\eta_{n}(-\omega)}{\eta_{n}^{*}(\omega)} \tag{3.55}
\end{equation*}
$$

In the presence of the perturbation, we assume that we can approximate the wave function parameters with a power series in terms of the Fourier amplitudes of the field, centered at the reference state.

$$
\begin{align*}
& \eta_{n}^{F}\left(\omega_{\sigma}\right)=\sum_{k>0} \sum_{\alpha}\left(\left.\frac{d \eta_{n}^{\omega_{\sigma}}}{d F_{\alpha}^{\omega_{k}}}\right|_{F=0} F_{\alpha}^{\omega_{k}}+\left.\frac{d \eta_{n}^{\omega_{\sigma}}}{d F_{\alpha}^{-\omega_{k}}}\right|_{F=0} F_{\alpha}^{-\omega_{k}}\right) \\
& +\frac{1}{2!} \sum_{k, l>0} \sum_{\alpha, \beta}\left(\left.\frac{d^{2} \eta_{n}^{\omega_{\sigma}}}{d F_{\alpha}^{\omega_{k}} \partial F_{\beta}^{\omega_{l}}}\right|_{F=0} F_{\alpha}^{\omega_{k}} F_{\beta}^{\omega_{k}}+\left.\frac{d^{2} \eta_{n}^{\omega_{\sigma}}}{d F_{\alpha}^{-\omega_{k}} \partial F_{\beta}^{-\omega_{l}}}\right|_{F=0} F_{\alpha}^{-\omega_{k}} F_{\beta}^{-\omega_{l}}\right)+\cdots \tag{3.56}
\end{align*}
$$

and the complex conjugate of the negative frequency component can be expressed as

$$
\begin{align*}
& \eta_{n}^{* F}\left(-\omega_{\sigma}\right)=\sum_{k>0} \sum_{\alpha}\left(\left.\frac{d \eta_{n}^{*-\omega_{\sigma}}}{d F_{\alpha}^{\omega_{k}}}\right|_{F=0} F_{\alpha}^{-\omega_{k}}+\left.\frac{d \eta_{n}^{*-\omega_{\sigma}}}{d F_{\alpha}^{-\omega_{k}}}\right|_{F=0} F_{\alpha}^{\omega_{k}}\right) \\
& +\frac{1}{2!} \sum_{k, l>0} \sum_{\alpha, \beta}\left(\left.\frac{d^{2} \eta_{n}^{*-\omega_{\sigma}}}{d F_{\alpha}^{\omega_{k}} \partial F_{\beta}^{\omega_{l}}}\right|_{F=0} F_{\alpha}^{-\omega_{k}} F_{\beta}^{-\omega_{k}}+\left.\frac{d^{2} \eta_{n}^{*-\omega_{\sigma}}}{d F_{\alpha}^{-\omega_{k}} \partial F_{\beta}^{-\omega_{l}}}\right|_{F=0} F_{\alpha}^{\omega_{k}} F_{\beta}^{\omega_{l}}\right)+\cdots \tag{3.57}
\end{align*}
$$

The corrections to the wave function parameters are grouped into vectors, which we refer to as response vectors. The elements within these vectors denote the state or orbital-rotation amplitudes, illustrating the magnitude of the contribution each potential transition or orbital rotation to the overall response of the wave function. To assess the behavior of the wave function parameter vector in the presence of the field, we utilize a vector field expansion

$$
\begin{align*}
\boldsymbol{\eta}^{\omega_{\sigma}}(F) & =\boldsymbol{\eta}^{\omega_{\sigma}}+\left.\sum_{k} \sum_{\alpha} \frac{d \boldsymbol{\eta}^{\omega_{\sigma}}}{d F_{\alpha}^{\omega_{k}}}\right|_{F=0} F_{\alpha}^{\omega_{k}} \\
& +\left.\frac{1}{2!} \sum_{k, l} \sum_{\alpha, \beta} \frac{d^{2} \boldsymbol{\eta}^{\omega_{\sigma}}}{d F_{\alpha}^{\omega_{k}} \partial F_{\beta}^{\omega_{l}}}\right|_{F=0} F_{\alpha}^{\omega_{k}} F_{\beta}^{\omega_{k}}+\cdots \tag{3.58}
\end{align*}
$$

Using Eqs. (3.56)-(3.57), we get that the upper and lower parts of the response vectors have the following structure

$$
\begin{equation*}
\left.\frac{d \boldsymbol{\eta}^{\omega_{\sigma}}}{d F_{\beta}^{\omega_{k}}}\right|_{F=0}=\left.\binom{\frac{d \eta_{n}^{\omega_{\sigma}}}{d F_{\beta}^{\omega_{k}}}}{\frac{d \eta_{n}^{*-\omega_{\sigma}}}{d F_{\beta}^{-\omega_{k}}}}\right|_{F=0} \tag{3.59}
\end{equation*}
$$

$$
\begin{equation*}
\left.\frac{d^{2} \eta^{\omega_{\sigma}}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{m}}}\right|_{F=0}=\left.\binom{\frac{d^{2} \eta_{n}^{\omega_{\sigma}}}{d F_{\beta}^{\omega_{k}} \partial F_{\gamma}^{\omega_{l}}}}{\frac{d^{2} \eta_{n}^{*}-\omega_{\sigma}}{d F_{\beta}^{-\omega_{k}} \partial F_{\gamma}^{-\omega_{l}}}}\right|_{F=0} \tag{3.60}
\end{equation*}
$$

In order to determine the corrections to the wave function parameters at each order in the perturbation strengths, we expand the variational principle of Eq. (3.21) in a power series of the field.

## The quasi-energy variational principle

$$
\begin{align*}
\left(\frac{\partial Q_{T}}{\partial \eta_{n}^{\omega_{\sigma}}}\right)(F) & =\left.\frac{d}{d F_{\beta}^{\omega_{k}}}\left(\frac{\partial Q_{T}}{\partial \eta_{n}^{\omega_{\sigma}}}\right)\right|_{F=0} F_{\beta}^{\omega_{k}} \\
& +\left.\frac{d^{2}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}}}\left(\frac{\partial Q_{T}}{\partial \eta_{n}^{\omega_{\sigma}}}\right)\right|_{F=0} F_{\beta}^{\omega_{k}} F_{\gamma}^{\omega_{l}} \\
& +\left.\frac{d^{3}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}\left(\frac{\partial Q_{T}}{\partial \eta_{n}^{\omega_{\sigma}}}\right)\right|_{F=0} F_{\beta}^{\omega_{k}} F_{\gamma}^{\omega_{l}} F_{\delta}^{\omega_{m}} \\
& +\ldots=0 \tag{3.61}
\end{align*}
$$

Since the electronic gradient of the quasi-energy must be zero for all field strengths, it follows that all coefficients of the power series must be zero. From the stationary condition of the quasi-energy for each order we obtain equations for the order corrections of the wave function parameters, which we will refer to as the response equations

$$
\begin{align*}
& \left.\frac{d}{d F_{\beta}^{\omega_{k}}}\left(\frac{\partial Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}}}\right)\right|_{F=0}=\boldsymbol{M}_{\beta}+\frac{\partial^{2} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}}} \frac{d \boldsymbol{\eta}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}}=0,  \tag{3.62}\\
& \left.\frac{d^{2}}{d F_{\gamma}^{\omega_{k}} d F_{\beta}^{\omega_{l}}}\left(\frac{\partial Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}}}\right)\right|_{F=0}=\boldsymbol{M}_{\beta \gamma}^{\omega_{k}, \omega_{l}}+\frac{\partial^{2} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}, \omega_{l}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{k}, \omega_{l}}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}}}=0, \\
& \left.\frac{d^{3}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}\left(\frac{\partial Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}}}\right)\right|_{F=0}=\boldsymbol{M}_{\beta \gamma \delta}^{\omega_{k}, \omega_{l}, \omega_{m}}  \tag{3.63}\\
& +\frac{\partial^{2} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}, \omega_{l}, \omega_{m}}} \frac{d^{3} \boldsymbol{\eta}^{\omega_{k}, \omega_{l}, \omega_{m}}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}=0, \tag{3.64}
\end{align*}
$$

Within the expressions for the response equations, we have introduced the one, two, and three-photon transition moment vectors, denoted as $\boldsymbol{M}, \boldsymbol{M}^{\omega_{k}, \omega_{l}}, \boldsymbol{M}^{\omega_{k}, \omega_{l}, \omega_{m}}$. These vectors characterize the interaction between the external electric field and the molecular dipole moment operator and the perturbations of the energy gradient

$$
\begin{equation*}
\boldsymbol{M}_{\beta}=\frac{\partial^{2} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial F_{\beta}^{\omega_{k}}} \tag{3.65}
\end{equation*}
$$

$$
\begin{align*}
& \boldsymbol{M}_{\beta \gamma}^{\omega_{k}, \omega_{l}}=\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{l}} \partial F_{\beta}^{\omega_{k}}} \frac{d \boldsymbol{\eta}^{\omega_{l}}}{d F_{\gamma}^{\omega_{l}}}+\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{l}} \partial F_{\gamma}^{\omega_{l}}} \frac{d \boldsymbol{\eta}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}}  \tag{3.66}\\
& +\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}} \partial \boldsymbol{\eta}^{\omega_{l}}} \frac{d \boldsymbol{\eta}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}} \frac{d \boldsymbol{\eta}^{\omega_{l}}}{d F_{\gamma}^{\omega_{l}}} \\
& \boldsymbol{M}_{\beta \gamma \delta}^{\omega_{k}, \omega_{l}, \omega_{m}}=\frac{\partial^{4} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{l}} \partial \boldsymbol{\eta}^{\omega_{m}} \partial F_{\beta}^{\omega_{k}}} \frac{d \boldsymbol{\eta}^{\omega_{l}}}{d F_{\gamma}^{\omega_{l}}} \frac{d \boldsymbol{\eta}^{\omega_{m}}}{d F_{\delta}^{\omega_{m}}} \\
& +\frac{\partial^{4} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}} \partial \boldsymbol{\eta}^{\omega_{m}} \partial F_{\gamma}^{\omega_{l}}} \frac{d \boldsymbol{\eta}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}} \frac{d \boldsymbol{\eta}^{\omega_{m}}}{d F_{\delta}^{\omega_{m}}} \\
& +\frac{\partial^{4} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}} \partial \boldsymbol{\eta}^{\omega_{l}} \partial F_{\delta}^{\omega_{m}}} \frac{d \boldsymbol{\eta}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}} \frac{d \boldsymbol{\eta}^{\omega_{l}}}{d F_{\gamma}^{\omega_{l}}} \\
& +\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}, \omega_{l}} \partial F_{\delta}^{\omega_{m}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{k}, \omega_{l}}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}}} \\
& +\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}, \omega_{m}} \partial F_{\gamma}^{\omega_{l}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{k}, \omega_{m}}}{d F_{\beta}^{\omega_{k}} d F_{\delta}^{\omega_{m}}} \\
& +\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{l}, \omega_{m}} \partial F_{\beta}^{\omega_{k}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{l}, \omega_{m}}}{d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}  \tag{3.67}\\
& +\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}} \partial \boldsymbol{\eta}^{\omega_{l}, \omega_{m}}} \frac{d \boldsymbol{\eta}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{l}, \omega_{m}}}{d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}} \\
& +\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{l}} \partial \boldsymbol{\eta}^{\omega_{k}, \omega_{m}}} \frac{d \boldsymbol{\eta}^{\omega_{l}}}{d F_{\gamma}^{\omega_{l}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{k}, \omega_{m}}}{d F_{\beta}^{\omega_{k}} d F_{\delta}^{\omega_{m}}} \\
& +\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{m}} \partial \boldsymbol{\eta}^{\omega_{k}, \omega_{l}}} \frac{d \boldsymbol{\eta}^{\omega_{m}}}{d F_{\delta}^{\omega_{m}}} \frac{d^{2} \boldsymbol{\eta}^{\omega_{k}, \omega_{l}}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}}} \\
& +\frac{\partial^{4} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}} \partial \boldsymbol{\eta}^{\omega_{l}} \partial \boldsymbol{\eta}^{\omega_{m}}} \frac{d \boldsymbol{\eta}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}} \frac{d \boldsymbol{\eta}^{\omega_{l}}}{d F_{\gamma}^{\omega_{l}}} \frac{d \boldsymbol{\eta}^{\omega_{m}}}{d F_{\delta}^{\omega_{m}}}
\end{align*}
$$

By solving the response equations presented in equations (3.62) to (3.64), we are able to derive expressions for the variations in the wave function parameters in the presence of the perturbations. Subsequently, these expressions can be used to calculate the alterations in the Fourier components of the dipole moment using equations (3.48) to (3.50). In the next section, we will focus on deriving explicit expressions for the derivatives of the Fourier components of the wave function parameters and the dipole moment.

## Response functions within Exact state theory

In this section we will establish the connection between the order corrections of the Fourier coefficients of the dipole moment and the quantum mechanical properties of the system.

By inspection of the response equations delineated in Eqs. (3.62)(3.64), it becomes apparent that the solutions to the response equations are encapsulated by expressions of the form

$$
\begin{equation*}
\frac{d^{n} \boldsymbol{\eta}}{d F^{\omega_{k}} \ldots d F^{\omega_{n}}}=\left(\frac{\partial^{2} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}, . . \omega_{n}}}\right)^{-1} \boldsymbol{M}^{(n)} \tag{3.68}
\end{equation*}
$$

Consequently, we are tasked with inverting the electronic Hessian of the quasi-energy. Adopting the state-rotation parametrization and expressing the wave-function expansion in terms of the exact eigenstates of the Hamiltonian $\hat{H}_{0}$, we get that the electronic Hessian of the timeaveraged quasi-energy can be written as

$$
\begin{align*}
& \left.\frac{\partial^{2} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}}, \cdots}\right|_{\eta=0} \\
& =\left(\left.\frac{\partial^{2} E}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}, \cdots}}\right|_{\eta=0}-\left.\left(\omega_{k}+. .\right) \frac{\partial^{2} S}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}, \cdots}}\right|_{\eta=0}\right) \delta\left(\omega_{k}+. .+\omega_{\sigma}\right) \tag{3.69}
\end{align*}
$$

The electronic Hessian is evaluated at the expansion point $\eta=0$, which is the ground-state stationary point. Given that the energy is scalar and we are taking its derivative with respect to two vectors, the electronic Hessian emerges as a rank-two tensor, encompassing four blocks that stem from the block structure of the response vectors, see Eq. (3.51). The explicit expression for the electronic Hessian is given by

$$
\left.\frac{\partial^{2} E}{\partial \boldsymbol{\eta} \partial \boldsymbol{\eta}}\right|_{\eta=0}=\left(\begin{array}{cc}
\frac{\partial^{2} E}{\partial \eta_{\hbar}^{*} \partial \eta_{m}} & \frac{\partial^{2} E}{\partial \eta_{⿳}^{*} \partial \eta_{m}^{*}}  \tag{3.70}\\
\frac{\partial^{2} E}{\partial \eta_{n} \partial \eta_{m}} & \frac{\partial^{2} E}{\partial \eta_{n} \partial \eta_{m}^{*}}
\end{array}\right)_{\eta=0}
$$

Since the electronic-Hessian is the second-order derivative of the energy and we are using the eigenstates of $\hat{H}_{0}$, the off-diagonal elements of the electronic-Hessian are zero and the diagonal elements are equal to the energy difference between the energy of the expansion point and the other eigenstates of the unperturbed Hamiltonian

$$
\begin{align*}
\left.\frac{\partial^{2} E}{\partial \eta_{n} \partial \eta_{m}^{*}}\right|_{\eta=0} & =-\frac{1}{2}\left\langle\Psi_{0}\right|\left[\hat{R}_{n}^{\dagger},\left[\hat{R}_{m}, \hat{H}_{0}\right]\right]\left|\Psi_{0}\right\rangle-\frac{1}{2}\left\langle\Psi_{0}\right|\left[\hat{R}_{m},\left[\hat{R}_{n}^{\dagger}, \hat{H}_{0}\right]\right]\left|\Psi_{0}\right\rangle \\
& =\left(\left\langle\Psi_{n}\right| \hat{H}_{0}\left|\Psi_{n}\right\rangle-\left\langle\Psi_{0}\right| \hat{H}_{0}\left|\Psi_{0}\right\rangle\right) \delta_{n m} \\
& =\left(E_{n}-E_{0}\right) \delta_{n m}=\lambda_{n} \delta_{n m} \tag{3.71}
\end{align*}
$$

The generalized overlap tensor exhibits a similar structure and is diagonal, noting that the upper and lower blocks have opposite signs

$$
\begin{gather*}
\left.\frac{\partial^{2} S}{\partial \eta_{n}^{*} \partial \eta_{m}}\right|_{\eta=0}=\left\langle\Psi_{0}\right|\left[\hat{R}_{n}, \hat{R}_{m}^{\dagger}\right]\left|\Psi_{0}\right\rangle=\delta_{n m}  \tag{3.72}\\
\left.\frac{\partial^{2} S}{\partial \eta_{n} \partial \eta_{m}^{*}}\right|_{\eta=0}=\left\langle\Psi_{0}\right|\left[\hat{R}_{n}^{\dagger}, \hat{R}_{m}\right]\left|\Psi_{0}\right\rangle=-\delta_{n m} \tag{3.73}
\end{gather*}
$$

Given the expressions above, the tensors can be succinctly represented as

$$
\left.\frac{\partial^{2} E}{\partial \boldsymbol{\eta} \partial \boldsymbol{\eta}}\right|_{\eta=0}=\left(\begin{array}{cc}
\lambda & 0  \tag{3.74}\\
0 & \lambda
\end{array}\right),\left.\frac{\partial^{2} S}{\partial \boldsymbol{\eta} \partial \boldsymbol{\eta}}\right|_{\eta=0}=\left(\begin{array}{cc}
1 & 0 \\
0 & -1
\end{array}\right)
$$

Here, $\lambda$ are the exact energy differences between the excited eigenstates and the ground state of the unperturbed Hamiltonian $\hat{H}_{0}$. Since


FIGURE 3.1: The dispersion of the polarizability, as derived using standard response theory
the electronic quasi-energy Hessian is diagonal, it can be straightforwardly inverted, yielding

$$
\left(\frac{\partial^{2} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{k}, . . \omega_{n}}}\right)^{-1}=\left(\begin{array}{cc}
\frac{1}{\lambda-\omega_{\sigma}} & 0  \tag{3.75}\\
0 & \frac{1}{\lambda+\omega_{\sigma}}
\end{array}\right)
$$

We therefore get that the derivatives of the wave-function parameters with respect to the field to all orders have the structure

$$
\frac{d^{n} \boldsymbol{\eta}}{d F^{\omega_{k}} \ldots d F^{\omega_{n}}}=\left(\begin{array}{cc}
\frac{1}{\lambda-\omega_{\sigma}} & 0  \tag{3.76}\\
0 & \frac{1}{\lambda+\omega_{\sigma}}
\end{array}\right)\binom{-M}{M^{*}}
$$

In exact-state theory, the one-photon transition moment vector possesses the structure

$$
\begin{equation*}
\boldsymbol{M}_{\beta}=\frac{\partial^{2} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial F_{\beta}^{\omega_{k}}}=\binom{\left\langle\Psi_{0}\right|\left[\hat{R}_{n}^{\dagger}, \hat{\mu}_{\beta}\right]\left|\Psi_{0}\right\rangle}{\left\langle\Psi_{0}\right|\left[\hat{R}_{n}, \hat{\mu}_{\beta}\right]\left|\Psi_{0}\right\rangle}=\binom{-\left\langle\Psi_{0}\right| \hat{\mu}_{\beta}\left|\Psi_{n}\right\rangle}{\left\langle\Psi_{n}\right| \hat{\mu}_{\beta}\left|\Psi_{0}\right\rangle} \tag{3.77}
\end{equation*}
$$

Combining these equations with Eq. (3.45), we get that the polarizability in exact-state theory is given by the expression

$$
\begin{align*}
& \alpha_{\alpha \beta}(-\omega ; \omega)=\left.\frac{d^{2} Q_{T}}{d F_{\alpha}^{\omega} d F_{\beta}^{\omega_{2}}}\right|_{F=0} \\
& =-\sum_{i \neq 0}\left(\frac{\left\langle\Psi_{0}\right| \hat{\mu}_{\alpha}\left|\Psi_{i}\right\rangle\left\langle\Psi_{i}\right| \hat{\mu}_{\beta}\left|\Psi_{0}\right\rangle}{\lambda_{i}-\omega}+\frac{\left\langle\Psi_{0}\right| \hat{\mu}_{\beta}\left|\Psi_{i}\right\rangle\left\langle\Psi_{i}\right| \hat{\mu}_{\alpha}\left|\Psi_{0}\right\rangle}{\lambda_{i}+\omega}\right) \tag{3.78}
\end{align*}
$$

The Fourier coefficients of the polarizability that we have derived thus far are invariably real, implying that the response of the system will only encompass an in-phase component. If we assume the medium is isotropic we have that

$$
\begin{equation*}
P_{i}(\omega)=\bar{\alpha}(-\omega ; \omega) E_{i}(\omega) \tag{3.79}
\end{equation*}
$$

where $\bar{\alpha}$ in this context is a real number, given by Eq. (2.37). In scenarios where only one field perturbation is present and it is monochromatic, we find that the polarization is described as

$$
\begin{align*}
P_{i}(t) & =\frac{1}{2}\left(P_{i}(\omega) e^{-i \omega t}+P_{i}(-\omega) e^{i \omega t}\right)  \tag{3.80}\\
& =|\bar{\alpha}(-\omega ; \omega)|\left|E_{i}(\omega)\right| \cos (\omega t)
\end{align*}
$$

We note that the Fourier coefficients we derive exhibit singularities when the optical frequencies coincide with an excitation energy, as depicted in Fig.3.1. This results in non-physical behavior in the predicted polarization of Eq.(3.80), as the amplitude of the polarization would approach infinity near resonance. This unrealistic behavior stems from the assumption that the excited states possess infinite lifetimes in the derivation of the standard molecular response functions. To yield a more accurate representation of molecular properties that mirrors the correct physical behaviors at resonance frequencies, we
need to incorporate finite lifetimes for the excited states. This integration, however, is not easily achieved using a standard quantum chemical description, necessitating the introduction of finite lifetimes through a phenomenological approach ${ }^{40}$. This topic will be explored further in the following section.

## Inclusion of finite lifetime and relaxation dynamics

As mentioned in the previous section, the assumption of infinite lifetimes in Shrödinger equation leads to unphyiscal singularities of the response functions at resonance frequencies. Norman approached the depiction of finite lifetime effects from a unique perspective ${ }^{41}$. He adapted the Ehrenfest theorem, which dictates the time evolution of the molecular system, by adding a damping term. This adjustment effectively attributes finite lifetimes to the excited states. By leveraging the modified Ehrenfest theorem to generate complex response vectors. In conventional response theory, transitions from the ground state to the excited states are characterized using oscillator strengths, which are derived from the residues of response functions ${ }^{42}$. This leads to an absorption spectrum with sharply peaked residues. However, experimental absorption spectra demonstrate that these peaks are broader, and the oscillator strength is determined by integrating over the absorption band, which signifies the electronic transition. Various physical phenomena contribute to the experimentally observed broadening: molecular collisions, Doppler effects, molecular vibrations, and the inherent lifetime of the excited states due to spontaneous emission. To accurately depict these physical events, modifications to the Hamiltonian $\hat{H}_{0}$ are necessary. However, given the challenges in making such alterations within quantum chemistry, a practical approach has been adopted. In order to introduce finite life times to the excited states we rewrite the electronic Hessian and its higher-order derivatives as ${ }^{40}$

$$
\left.\frac{\partial^{2} E}{\partial \boldsymbol{\eta} \partial \boldsymbol{\eta}}\right|_{\eta=0}=\left(\begin{array}{cc}
\lambda-i \gamma & 0  \tag{3.81}\\
0 & \lambda+i \gamma
\end{array}\right)
$$

Where $\gamma$ is the damping parameter, which is related to the effective lifetime $\tau$ of the excited states as $\tau=\frac{1}{2 \gamma}$. If we include damping, we observe that the real and imaginary components of the polarizability become ${ }^{34}$

$$
\begin{align*}
& \mathbb{I}_{\alpha \beta}(-\omega ; \omega)=\sum_{i \neq 0}\left(\frac{\gamma\left\langle\Psi_{0}\right| \hat{\mu}_{\alpha}\left|\Psi_{i}\right\rangle\left\langle\Psi_{0}\right| \hat{\mu}_{\beta}\left|\Psi_{i}\right\rangle}{\left(\lambda_{i}-\omega\right)^{2}+\gamma^{2}}-\frac{\gamma\left\langle\Psi_{0}\right| \hat{\mu}_{\beta}\left|\Psi_{i}\right\rangle\left\langle\Psi_{0}\right| \hat{\mu}_{\alpha}\left|\Psi_{i}\right\rangle}{\left(\lambda_{i}+\omega\right)^{2}+\gamma^{2}}\right) \\
& { }^{\mathbb{R}} \alpha_{\alpha \beta}(-\omega ; \omega)  \tag{3.82}\\
& =\sum_{i \neq 0}\left(\frac{\left(\lambda_{i}-\omega\right)\left\langle\Psi_{0}\right| \hat{\mu}_{\alpha}\left|\Psi_{i}\right\rangle\left\langle\Psi_{0}\right| \hat{\mu}_{\beta}\left|\Psi_{i}\right\rangle}{\left(\lambda_{i}-\omega\right)^{2}+\gamma^{2}}+\frac{\left(\lambda_{i}+\omega\right)\left\langle\Psi_{0}\right| \hat{\mu}_{\beta}\left|\Psi_{i}\right\rangle\left\langle\Psi_{0}\right| \hat{\mu}_{\alpha}\left|\Psi_{i}\right\rangle}{\left(\lambda_{i}+\omega\right)^{2}+\gamma^{2}}\right) \tag{3.83}
\end{align*}
$$

The imaginary or out-of-phase component of the polarizability then assumes a Lorentzian shape, as can be observed in Fig. 3.2


FIGURE 3.2: The dispersion of the real and imaginary components of the polarizability's Fourier components

Assuming an isotropic medium and a monochromatic perturbation at the frequency $\omega$, the Fourier components of the polarization with damping will generally be complex, and the in-phase and out-of-phase contributions to the time-dependent polarization are given by

$$
\begin{equation*}
P_{i}(t)={ }^{\mathbb{R}} \bar{\alpha}(-\omega ; \omega)\left|E_{i}(\omega)\right| \cos \left(\omega_{k} t\right)+{ }^{\mathbb{}} \bar{\alpha}(-\omega ; \omega)\left|E_{i}(\omega)\right| \sin \left(\omega_{k} t\right) \tag{3.84}
\end{equation*}
$$

The polarization will now remain finite even at resonance, since the Fourier components no longer posses singularities. When the frequency of the perturbation is far from the resonance frequencies, the imaginary component approaches zero, and at resonance, the real part reduces to zero. According to the Poynting theorem, the imaginary component of the polarizability dictates how energy can be exchanged between the electric field and the molecule. From Eq.(3.82), we notice that as the optical field approaches a frequency that matches the energy difference between the eigenstates of the unperturbed Hamiltonian, the imaginary component of the polarizability reaches a maximum, as illustrated in Fig.3.2. This outcome aligns precisely with our expectations: at light frequencies that are far from any resonance frequency of the molecule, we anticipate the light to be transmitted, scattered, or reflected. Conversely, when the photon energy approaches with a resonance frequency, we expect that the molecule will begin to absorb energy from the electromagnetic field. The mechanism behind this phenomenon is explained by combining the Poynting theorem with Eq. (3.82).

$$
\begin{equation*}
\nabla I^{(1)}(\omega) \propto-\frac{2 \omega}{c \epsilon_{0}} \sum_{i \neq 0}\left(\frac{\gamma\left\langle\Psi_{0}\right| \hat{\mu}_{\alpha}\left|\Psi_{i}\right\rangle\left\langle\Psi_{0}\right| \hat{\mu}_{\beta}\left|\Psi_{i}\right\rangle}{\left(\lambda_{i}-\omega\right)^{2}+\gamma^{2}}-\frac{\gamma\left\langle\Psi_{0}\right| \hat{\mu}_{\beta}\left|\Psi_{i}\right\rangle\left\langle\Psi_{0}\right| \hat{\mu}_{\alpha}\left|\Psi_{i}\right\rangle}{\left(\lambda_{i}+\omega\right)^{2}+\gamma^{2}}\right) \tag{3.85}
\end{equation*}
$$

Hence, what characterizes the response of a molecule to the external field are the eigenstates of the unperturbed system, its excitation energies and the transition strengths which are given by the transition dipole moments $\left\langle\Psi_{0}\right| \hat{\mu}_{\alpha}\left|\Psi_{i}\right\rangle$ which describe how the dipole moment couples the different eigenstates of the system. We see that in order for a transition to be dipole allowed it must have a non zero transition dipole moment coupling those state together. The expression for the polarizability in terms of the exact eigenstates of $H_{0}$ acts as guidance for us to understand the structure and meaning of the the response functions in approximate state theory. In practice we will not have access to the eigenstates of the Hamiltonian $\hat{H}_{0}$. In order to describe the energy transfer between the light and the molecule when we don't have access to the exact eigenstates and energies there are now two different approaches that one can take. Once the expression for the polarizability has been derived one approach would be to get explicit approximations for all the eigenstates of the unperturbed Hamiltonian and then evaluate the imaginary component of the polarizabilites by simply substituting in the approximate excitation energies and eigenstates into Eq. (3.85). Another central focus of this thesis is the use of a single-determinant as the reference state, coupled with an orbitalrotation parametrization. This will be the subject of the subsequent section, where we will derive the polarizabilities using approximate state theory. Further, we aim to identify the approximate transition dipole moments and excitation energies by contrasting them with the expressions derived from the exact state theory.

## Response functions within Approximate state theory

This section delves deeper into the computational aspects of calculating the order-corrections to the order-corrections to the wavefunction parameters within the framework of approximate state theory. By employing an orbital rotation parameterization and a single Slater determinant approach, we can describe the overall response of the wave function through coupled single-particle excitations and de-excitations between occupied and unoccupied orbitals. The response equations govern the extent to which each type of singleparticle excitation contributes to the total response, with the elements of the response vector functioning as weights that describe the contribution from each individual single-particle excitation. Since Slaterdeterminants are not eigenstates of the Hamiltonian the electronic Hessian of the quasi-energy is not in general diagonal and all the elements of the response vectors are coupled, that is they don't change independently. The off-diagonal elements of the electronic Hessian of the quasi-energy describe the coupling between the single-particle excitation and how they interact and influence each other. Ultimately, they are all adjusting in a coupled manner so that the Dirac-Frenkel variation principle is satisfied to each order of the perturbation. Our starting point is an BCH expansion of the quasi-energy in terms of the
orbital rotation parameters

$$
\begin{align*}
& Q(t)=\langle 0| e^{\hat{\kappa}(t)}\left(\hat{H}(t)-i \frac{\partial}{\partial t}\right) e^{-\hat{\kappa}(t)}|0\rangle \\
& =\langle 0| \hat{Q}(\boldsymbol{r})|0\rangle+\sum_{n}\langle 0|\left[\kappa_{r}(t) \hat{q}_{n}^{\dagger}-\kappa_{n}^{*}(t) \hat{q}_{n},\left(\hat{H}(t)-i \frac{\partial}{\partial t}\right)\right]|0\rangle \\
& +\frac{1}{2!} \sum_{n, m}\langle 0|\left[\kappa_{r}(t) \hat{q}_{n}^{\dagger}-\kappa_{n}^{*}(t) \hat{q}_{n},\left[\kappa_{m}(t) \hat{q}_{m}^{\dagger}-\kappa_{m}^{*}(t) \hat{q}_{m},\left(\hat{H}(t)-i \frac{\partial}{\partial t}\right)\right]\right]|0\rangle \\
& +\ldots, \tag{3.86}
\end{align*}
$$

Since the gradient of the quasi-energy will contain the gradient of the energy, the overlap, and the perturbation we start by rewriting the electronic-gradient of the quasi-energy as

$$
\begin{equation*}
\left(\frac{\partial Q_{T}}{\partial \boldsymbol{\kappa}^{-\omega_{\sigma}}}\right)=\boldsymbol{f}(\boldsymbol{\kappa}(F))+\boldsymbol{s}(\boldsymbol{\kappa}(F))+\boldsymbol{v}(\boldsymbol{\kappa}(F), F)=0 \tag{3.87}
\end{equation*}
$$

In these equations $\boldsymbol{f}$ is a BCH expansion of the gradient of the energy and is hence an expansion of the occupied-virtual elements of the Fock matrix.

$$
\begin{equation*}
\boldsymbol{f}(\boldsymbol{\kappa}(F))=\boldsymbol{f}+\left.\frac{d \boldsymbol{f}}{d \boldsymbol{\kappa}}\right|_{\kappa=0} \boldsymbol{\kappa}+\left.\frac{1}{2} \frac{d^{2} \boldsymbol{f}}{d \boldsymbol{\kappa} d \boldsymbol{\kappa}}\right|_{\kappa=0} \boldsymbol{\kappa} \boldsymbol{\kappa}+\cdots \tag{3.88}
\end{equation*}
$$

The compound indices, $n, m, \ldots$, follow the same convention as introduced in section 3.3 and the terms in the energy-gradient expansion of Eq. (3.88) are given as

$$
\begin{align*}
& f_{n}=\left\langle\Theta_{0}\right|\left[\hat{q}_{n}, \hat{H}_{0}\right]\left|\Theta_{0}\right\rangle \\
& \left.\frac{d f_{n}}{d \kappa_{m}}\right|_{\kappa=0}=P_{n, m} \frac{1}{2}\left\langle\Theta_{0}\right|\left[\hat{q}_{n},\left[\hat{q}_{m}, \hat{H}_{0}\right]\right]\left|\Theta_{0}\right\rangle  \tag{3.89}\\
& \left.\frac{d^{2} f_{n}}{d \kappa_{m} d \kappa_{l}}\right|_{\kappa=0}=P_{n, m, l} \frac{1}{3}\left\langle\Theta_{0}\right|\left[\hat{q}_{n},\left[\hat{q}_{m},\left[\hat{q}_{l}, \hat{H}_{0}\right]\right]\right]\left|\Theta_{0}\right\rangle
\end{align*}
$$

In Eq. (3.87), $s$, corresponds to the BCH-expansion of the $\left[\hat{q}_{n}^{\dagger},-i \frac{\partial}{\partial t}\right]$ operator

$$
\begin{equation*}
\boldsymbol{s}(\boldsymbol{\kappa}(F))=\boldsymbol{s}-\left.\omega_{\sigma} \frac{d \boldsymbol{s}}{d \boldsymbol{\kappa}}\right|_{\kappa=0} \boldsymbol{\kappa}-\left.\omega_{\sigma} \frac{d^{2} \boldsymbol{s}}{d \boldsymbol{\kappa} d \boldsymbol{\kappa}}\right|_{\kappa=0} \boldsymbol{\kappa} \boldsymbol{\kappa}+\cdots \tag{3.90}
\end{equation*}
$$

where each each term in the expansion can be written explicitly as

$$
\begin{align*}
& s_{n}=\left\langle\Theta_{0}\right| \hat{q}_{n}\left|\Theta_{0}\right\rangle \\
& \left.\frac{d s_{n}}{d \kappa_{m}}\right|_{\kappa=0}=P_{n, m} \frac{1}{2}\left\langle\Theta_{0}\right|\left[\hat{q}_{n}, \hat{q}_{m}\right]\left|\Theta_{0}\right\rangle  \tag{3.91}\\
& \left.\frac{d^{2} s_{n}}{d \kappa_{m} d \kappa_{l}}\right|_{\kappa=0}=P_{n, m, l} \frac{1}{3}\left\langle\Theta_{0}\right|\left[\hat{q}_{n},\left[\hat{q}_{m}, \hat{q}_{l}\right]\right]\left|\Theta_{0}\right\rangle
\end{align*}
$$

Likewise, $v_{n}$ is the corresponding BCH-expansion of the electronicgradient of the perturbation operator. We can can then conveniently
express the time-averaged variational principle in approximate state theory as

$$
\begin{align*}
& \left.\frac{d}{d F_{\beta}^{\omega_{k}}}\left(\frac{\partial Q_{T}}{\partial \boldsymbol{\kappa}^{-\omega_{\sigma}}}\right)\right|_{F=0}=\frac{d \mathbf{v}}{d F_{\beta}^{\omega_{k}}}+\frac{d \mathbf{f}}{d F_{\beta}^{\omega_{k}}}+\frac{d \mathbf{s}}{d F_{\beta}^{\omega_{k}}}=0,  \tag{3.92}\\
& \left.\frac{d^{2}}{d F_{\gamma}^{\omega_{k}} d F_{\beta}^{\omega_{l}}}\left(\frac{\partial Q_{T}}{\partial \boldsymbol{\kappa}^{-\omega_{\sigma}}}\right)\right|_{F=0}=\frac{d^{2} \mathbf{v}}{d F_{\gamma}^{\omega_{k}} d F_{\beta}^{\omega_{l}}}+\frac{d^{2} \mathbf{f}}{d F_{\gamma}^{\omega_{k}} d F_{\beta}^{\omega_{l}}}+\frac{d^{2} \mathbf{s}}{d F_{\gamma}^{\omega_{k}} d F_{\beta}^{\omega_{l}}}=0, \\
& \left.\frac{d^{3}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}\left(\frac{\partial Q_{T}}{\partial \boldsymbol{\kappa}^{-\omega_{\sigma}}}\right)\right|_{F=0}=  \tag{3.93}\\
& \frac{d^{3} \mathbf{v}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}+\frac{d^{3} \mathbf{f}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}+\frac{d^{3} \mathbf{s}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}=0, \tag{3.94}
\end{align*}
$$

The most computationally demanding terms of these equations, as will be illustrated below, are found in the field derivatives of the energy gradient vector $f$, which encompasses the occupied-virtual elements of the Fock matrix. This can be understood since these terms necessitate the evaluation and contraction of the two-electron integral tensors. The energy-gradient vector field-derivatives that emerge in Eqs. (3.92)-(3.94) are more explicitly given by following tensor con-

$$
\begin{align*}
& \qquad\left.\frac{d \mathbf{f}}{d F_{\beta}^{\omega_{k}}}\right|_{F=0}=\frac{\partial \mathbf{f}}{\partial \boldsymbol{\kappa}} \frac{d \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{k}}} \\
& \qquad\left.\frac{d^{2} \mathbf{f}}{d F_{\gamma}^{\omega_{k}} d F_{\beta}^{\omega_{l}}}\right|_{F=0}=\frac{\partial \mathbf{f}}{\partial \boldsymbol{\kappa}} \frac{d^{2} \boldsymbol{\kappa}}{d F_{\gamma}^{\omega_{k}} d F_{\beta}^{\omega_{l}}}+\frac{\partial^{2} \mathbf{f}}{\partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}} \frac{d \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{k}}} \frac{d \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{l}}}  \tag{3.95}\\
& \left.\frac{d^{3} \mathbf{f}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}\right|_{F=0}=\frac{\partial \mathbf{f}}{\partial \boldsymbol{\kappa}} \frac{d^{3} \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{k}} d F_{\gamma}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}+\frac{\partial^{2} \mathbf{f}}{\partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}} \frac{d^{2} \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{k}} d F_{\delta}^{\omega_{m}}} \frac{d \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{l}}}  \tag{3.96}\\
& +\frac{\partial^{2} \mathbf{f}}{\partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}} \\
& d \boldsymbol{\kappa}  \tag{3.97}\\
& d F_{\beta}^{\omega_{k}}
\end{align*} \frac{d^{2} \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{l}} d F_{\delta}^{\omega_{m}}}+\frac{\partial^{3} \mathbf{f}}{\partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}} \frac{d \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{k}}} \frac{d \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{l}}} \frac{d \boldsymbol{\kappa}}{d F_{\delta}^{\omega_{m}}} . l .
$$

Each contraction of the energy gradient derivatives in these equations yields vectors representing the occupied-virtual elements of the transformed Fock matrices, denoted as $\bar{f}_{a i}, \overline{\bar{f}}_{a i}$, and $\overline{\bar{f}}_{a i}$.

$$
\begin{gather*}
\frac{\partial \mathbf{f}}{\partial \boldsymbol{\kappa}} \frac{d \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{k}}}=\left(\frac{\bar{f}_{a i}}{\bar{f}_{i a}}\right)  \tag{3.98}\\
\frac{\partial^{2} \mathbf{f}}{\partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}} \frac{d \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{k}}} \frac{d \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{l}}}=\binom{\overline{\bar{f}}_{a i}}{\bar{f}_{i a}}  \tag{3.99}\\
\frac{\partial^{3} \mathbf{f}}{\partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}} \frac{d \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{k}}} \frac{d \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{l}}} \frac{d \boldsymbol{\kappa}}{d F_{\delta}^{\omega_{m}}}=\binom{\overline{\bar{f}}_{a i}}{\overline{\bar{f}}_{i a}} \tag{3.100}
\end{gather*}
$$

Recalling that the compound index for the elements of a response vector refers to a pair of virtual (v) and occupied (o) molecular orbitals,
we scatter the elements of the response vectors into the ov- and voblocks of a matrix according to ${ }^{17,43,44}$

$$
\boldsymbol{\kappa}_{\alpha}^{\omega}=\left(\begin{array}{cc}
0 & \frac{d \kappa^{\omega}}{d F_{\alpha}^{\omega}}  \tag{3.101}\\
-\left(\frac{d \boldsymbol{\kappa}^{-\omega}}{d F_{\alpha}^{-\omega}}\right)^{*} & 0
\end{array}\right)
$$

The elements of field-derivatives of the the energy gradient vector of Eqs. (3.98)-(3.100) can then be written in terms of the auxillary Fock matrices $f_{a i}^{\omega_{k}}, f_{a i}^{\omega_{k}, \omega_{l}}, f_{a i}^{\omega_{k}, \omega_{l}, \omega_{m}}$ and the matrix representation of the response vectors of Eq. (3.101) as

$$
\begin{align*}
& \bar{f}_{a i}=\left[\boldsymbol{\kappa}^{\omega_{k}}, \boldsymbol{f}\right]_{a i}+f_{a i}^{\omega_{k}}  \tag{3.102}\\
& \overline{\bar{f}}_{a i}=\left[\boldsymbol{\kappa}^{\omega_{k}},\left[\boldsymbol{\kappa}^{\omega_{l}}, \boldsymbol{f}\right]+2 \boldsymbol{f}^{\omega_{l}}\right]_{a i}+\left[\boldsymbol{\kappa}^{\omega_{l}},\left[\boldsymbol{\kappa}^{\omega_{k}}, \boldsymbol{f}\right]+2 \boldsymbol{f}^{\omega_{k}}\right]_{a i}+f_{a i}^{\left(\omega_{k}, \omega_{l}\right)}  \tag{3.103}\\
& \overline{\bar{f}}_{a i}=\left[\boldsymbol{\kappa}^{\omega_{k}},\left[\boldsymbol{\kappa}^{\omega_{l}},\left[\boldsymbol{\kappa}^{\omega_{m}}, \boldsymbol{f}\right]+3 \boldsymbol{f}^{\omega_{m}}\right]+\left[\boldsymbol{\kappa}^{\omega_{m}},\left[\boldsymbol{\kappa}^{\omega_{l}}, \boldsymbol{f}\right]+3 \boldsymbol{f}^{\omega_{l}}\right]+3 \boldsymbol{f}^{\left(\omega_{l}, \omega_{m}\right)}\right]_{a i} \\
&+\left[\boldsymbol{\kappa}^{\omega_{k}},\left[\boldsymbol{\kappa}^{\omega_{l}},\left[\boldsymbol{\kappa}^{\omega_{m}}, \boldsymbol{f}\right]+3 \boldsymbol{f}^{\omega_{m}}\right]+\left[\boldsymbol{\kappa}^{\omega_{m}},\left[\boldsymbol{\kappa}^{\omega_{l}}, \boldsymbol{f}\right]+3 \boldsymbol{f}^{\omega_{l}}\right]+3 \boldsymbol{f}^{\left(\omega_{l}, \omega_{m}\right)}\right]_{a i} \\
&+\left[\boldsymbol{\kappa}^{\omega_{k}},\left[\boldsymbol{\kappa}^{\omega_{l}},\left[\boldsymbol{\kappa}^{\omega_{m}}, \boldsymbol{f}\right]+3 \boldsymbol{f}^{\omega_{m}}\right]+\left[\boldsymbol{\kappa}^{\omega_{m}},\left[\boldsymbol{\kappa}^{\omega_{l}}, \boldsymbol{f}\right]+3 \boldsymbol{f}^{\omega_{l}}\right]+3 \boldsymbol{f}^{\left(\omega_{l}, \omega_{m}\right)}\right]_{a i} \\
&+f_{a i}^{\left(\omega_{k}, \omega_{l}, \omega_{m}\right)} \tag{3.104}
\end{align*}
$$

where frequencies in parenthesis are permuted

$$
\begin{gather*}
f_{a i}^{\left(\omega_{k}, \omega_{l}\right)}=f_{a i}^{\omega_{k}, \omega_{l}}+f_{a i}^{\omega_{l}, \omega_{k}},  \tag{3.105}\\
f_{a i}^{\left(\omega_{k}, \omega_{l}, \omega_{m}\right)}=f_{a i}^{\omega_{k}, \omega_{l}, \omega_{m}}+f_{a i}^{\omega_{k}, \omega_{m}, \omega_{l}}+f_{a i}^{\omega_{l}, \omega_{k}, \omega_{m}}  \tag{3.106}\\
+f_{a i}^{\omega_{l}, \omega_{m}, \omega_{k}}+f_{a i}^{\omega_{m}, \omega, \omega_{k}}+f_{a i}^{\omega_{m}, \omega_{k}, \omega} .
\end{gather*}
$$

The construction of the auxiliary Fock matrices in atomic orbital basis requires the evaluation of the rank four two-electron integral tensors, denoted as $(\mu \nu \mid \lambda \sigma)$

$$
\begin{equation*}
(\mu \nu \mid \lambda \sigma)=\iint \frac{\psi_{\mu}^{*}\left(\boldsymbol{r}_{1}\right) \psi_{\nu}\left(\boldsymbol{r}_{\mathbf{1}}\right) \psi_{\lambda}^{*}\left(\boldsymbol{r}_{\mathbf{2}}\right) \psi_{\sigma}\left(\boldsymbol{r}_{\mathbf{2}}\right)}{\boldsymbol{r}_{12}} d \boldsymbol{r}_{1} d \boldsymbol{r}_{2} \tag{3.107}
\end{equation*}
$$

In a basis of N atomic orbitals there would $N^{4}$ elements of which $\frac{N^{4}}{8}$ are unique. In order to construct an auxiliary Fock matrix one would then need to perform the following matrix tensor contraction

$$
\begin{align*}
f_{\mu \nu}^{\omega_{k}} & =\sum_{\lambda \sigma}^{N}\left[\boldsymbol{\kappa}^{\omega_{k}}, \boldsymbol{D}_{0}\right]_{\lambda \sigma}\left[(\mu \nu \mid \sigma \lambda)-\frac{1}{2}(\mu \lambda \mid \sigma \nu)\right] .  \tag{3.108}\\
f_{a i}^{\omega_{k}, \omega_{l}} & =\sum_{\lambda \sigma}^{N}\left[\boldsymbol{\kappa}^{\omega_{k}},\left[\boldsymbol{\kappa}^{\omega_{l}}, \boldsymbol{D}_{0}\right]_{\lambda \sigma}\left[(\mu \nu \mid \sigma \lambda)-\frac{1}{2}(\mu \lambda \mid \sigma \nu)\right] .\right.  \tag{3.109}\\
f_{a i}^{\omega_{k}, \omega_{l}, \omega_{m}} & =\sum_{\lambda \sigma}^{N}\left[\boldsymbol{\kappa}^{\omega_{k}},\left[\boldsymbol{\kappa}^{\omega_{l}},\left[\boldsymbol{\kappa}^{\omega_{m}}, \boldsymbol{D}_{0}\right]\right]\right]_{\lambda \sigma}\left[(\mu \nu \mid \sigma \lambda)-\frac{1}{2}(\mu \lambda \mid \sigma \nu)\right] . \tag{3.110}
\end{align*}
$$

Assuming we have N atomic basis functions the two-electron tensor contraction with the density matrix would require $2 N^{4}-2 N^{2}$ operations. The construction of the transformed Fock matrices in Eqs. (3.98)-(3.100) and the associated auxillary Fock matrices of Eqs. (3.108)-(3.110) which in essence describe the energy changes of the system are the core and most computationally demanding components required in order to evaluate the response of the system.

## SIMULTANEOUS DIAGONALIZATION

While the response equations for large scale systems in practice are solved using a Davidson subspace procedure, as detailed in ${ }^{45,46}$,our discussion here will predominantly concentrate on a qualitative understanding. Within approximate state theory with a single Slaterdeterminant approximation the response equations relate the derivatives of the occupied-virtual elements of the Fock, overlap and perturbation matrices. When the perturbation is switched on, the orbitalrotation parameters $\kappa^{\omega}$ are functions of the field strength and the allowed variations for these parameters are such that the sum of the field derivatives of the occupied-virtual elements of the these three matrices are zero to all orders in the perturbation. From Eq. (3.92), we get that the linear response equation takes the form

$$
\begin{equation*}
\left(\frac{\partial \boldsymbol{f}}{\partial \boldsymbol{\kappa}}-\omega \frac{\partial \boldsymbol{s}}{\partial \boldsymbol{\kappa}}\right) \frac{d \boldsymbol{\kappa}}{d F_{\beta}^{\omega}}=-\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{\kappa}} \tag{3.111}
\end{equation*}
$$

In order to diagonalize the response equation and get the equations in a similar form as in exact state theory, Eqs. (3.62)-(3.63), we need to transform Eq. (3.111) to a basis in which the the response parameters are independent. Changing basis does not of course change the problem, it just shifts our perspective of the problem. In a basis where the electronic Hessian of the quasi-energy is diagonal, all the elements of the response vectors are decoupled and represent orthogonal excitation path ways, these are essentially "composite" single-particle excitations which are a mix of the original single-particle excitations, tailored in such a way that now each element of the response vector is independent of the other. In order to achieve this simultaneous diagonalization of the electronic Hessian $\frac{\partial \boldsymbol{f}}{\partial \boldsymbol{\kappa}}$ and the generalized overlap matrix $\frac{\partial s}{\partial \kappa}$ we are looking for a similarity transform facilitated by a matrix $\boldsymbol{X}$ such that we simultaneously diagonalize both the electronic Hessian and the generalized overlap matrix. The properties of this transformation matrix must be such that it can be made to be orthogonal with respect to the inner product induced by the electronic Hessian and to satisfy the generalized normalization condition ${ }^{42,47}$

$$
\begin{gather*}
\boldsymbol{X}_{l}^{\dagger} \frac{\partial \boldsymbol{f}}{\partial \boldsymbol{\kappa}} \boldsymbol{X}_{k}=\lambda_{k} \delta_{k l}  \tag{3.112}\\
\boldsymbol{X}_{l}^{\dagger} \frac{\partial \boldsymbol{s}}{\partial \boldsymbol{\kappa}} \boldsymbol{X}_{k}=\operatorname{sgn}(k) \delta_{k l} \tag{3.113}
\end{gather*}
$$

The orthogonality of the vectors $\boldsymbol{X}_{f}$ with respect to the generalized overlap matrix $S$ ensures that the composite single-particle excitations described by the elements of $\boldsymbol{X}_{f}$ are orthogonal or independent with respect to each each other. This transformation matrix, denoted as $\boldsymbol{X}$, can then be identified by solving the generalized eigenvector equations

$$
\begin{align*}
& \frac{\partial \boldsymbol{f}}{\partial \boldsymbol{\kappa}} \boldsymbol{X}_{f}=\lambda_{f} \frac{\partial \boldsymbol{s}}{\partial \boldsymbol{\kappa}} \boldsymbol{X}_{f}  \tag{3.114}\\
& \frac{\partial \boldsymbol{f}}{\partial \boldsymbol{\kappa}} \boldsymbol{X}_{-f}=-\lambda_{f} \frac{\partial \boldsymbol{s}}{\partial \boldsymbol{\kappa}} \boldsymbol{X}_{-f}
\end{align*}
$$

where the structure of the eigenvectors are given by

$$
\begin{equation*}
\boldsymbol{X}_{f}=\binom{X_{a i}\left(\lambda_{f}\right)}{X_{a i}^{*}\left(-\lambda_{f}\right)}, \quad \boldsymbol{X}_{-f}=\binom{X_{a i}\left(-\lambda_{f}\right)}{X_{a i}^{*}\left(\lambda_{f}\right)} \tag{3.115}
\end{equation*}
$$

We then form the transformation matrix $\boldsymbol{X}$ in terms of the eigenvectors of the generalized eigenvector equations as ${ }^{42,45,46}$

$$
\begin{equation*}
\boldsymbol{X}=\left(\boldsymbol{X}_{f}, \cdots, \boldsymbol{X}_{-f}\right) \tag{3.116}
\end{equation*}
$$

The generalized eigenvector equation in itself is worthwhile to discuss. Since we are evaluating the response equations at zero field strength, we are evaluating the approximate electronic Hessian or the curvature of the energy at $\kappa=0$ which is a stationary point (the reference point for the expansion). When the electronic Hessian is written in diagonal form in exact state theory and evaluated at a stationary point, the eigenvalues of the electronic Hessian are the the energy difference between the reference state and all other eigenstates of the Hamiltonian from which the electronic Hessain is derived, as was seen in Eq. (3.71). In approximate state theory the diagonalized Hessian at a stationary point contains the approximations to the excitation energies. Hence once we have diagonalized the electronic Hessian and the generalized overlap simultaneously the approximate excitation energies will be the diagonal elements $\lambda$ of the electronic Hessian

$$
\boldsymbol{X}^{\dagger} \frac{\partial \boldsymbol{f}}{\partial \boldsymbol{\kappa}} \boldsymbol{X}=\left(\begin{array}{cc}
\lambda & 0  \tag{3.117}\\
0 & \lambda
\end{array}\right), \boldsymbol{X}^{\dagger} \frac{\partial \boldsymbol{s}}{\partial \boldsymbol{\kappa}} \boldsymbol{X}=\left(\begin{array}{cc}
1 & 0 \\
0 & -1
\end{array}\right)
$$

Having diagonalized the electronic Hessian of the quasi-energy, taking its inverse is straight forward. Using the similarity transform $\boldsymbol{X}$ we diagonalize and invert the electronic quasi-energy Hessian and transform back as

$$
\begin{align*}
& \left(\frac{\partial^{2} Q_{T}}{\partial \boldsymbol{\kappa}^{-\omega_{\sigma}} \partial \boldsymbol{\kappa}^{\omega_{k}}}\right)^{-1}=\boldsymbol{X}\left(\boldsymbol{X}^{\dagger} \frac{\partial^{2} Q_{T}}{\partial \boldsymbol{\kappa}^{-\omega_{\sigma}} \partial \boldsymbol{\kappa}^{\omega_{k}}} \boldsymbol{X}\right)^{-1} \boldsymbol{X}^{\dagger} \\
& =\boldsymbol{X}\left(\begin{array}{cc}
\frac{1}{\lambda-\omega} & 0 \\
0 & \frac{1}{\lambda+\omega}
\end{array}\right) \boldsymbol{X}^{\dagger}=\sum_{f}\left[\frac{1}{\lambda_{f}-\omega} \boldsymbol{X}_{f} \boldsymbol{X}_{f}^{\dagger}+\frac{1}{\lambda_{f}+\omega} \boldsymbol{X}_{-f} \boldsymbol{X}_{-f}^{\dagger}\right] \tag{3.118}
\end{align*}
$$

In the orbital rotation parametrization, the matrix $M$ represents the one-photon transition moment in the basis of the single-particle excitations

$$
\begin{equation*}
\boldsymbol{M}_{\beta}=\frac{\partial^{2} Q_{T}}{\partial \boldsymbol{\kappa}^{-\omega_{\sigma}} \partial F_{\beta}^{\omega_{k}}}=\binom{\left\langle\Theta_{0}\right|\left[\hat{q}_{n}^{\dagger}, \hat{\mu}_{\beta}\right]|0\rangle}{\left\langle\Theta_{0}\right|\left[\hat{q}_{n}, \hat{\mu}_{\beta}\right]|0\rangle}=\binom{-\left\langle\Theta_{0}\right| \hat{\mu}_{\beta}\left|\Theta_{i}^{a}\right\rangle}{\left\langle\Theta_{i}^{a}\right| \hat{\mu}_{\beta}\left|\Theta_{0}\right\rangle} \tag{3.119}
\end{equation*}
$$

With the use of Eqs. (3.118)-(3.119), we can write the solutions of the response equations in terms of the eigenvectors of the generalized eigenvector equation of Eq. (3.114) as

$$
\begin{align*}
\frac{d \boldsymbol{\kappa}^{\omega_{k}}}{d F_{\beta}^{\omega_{k}}} & =\sum_{f}\left(\frac{\boldsymbol{X}_{f} \boldsymbol{X}_{f}^{\dagger}}{\lambda_{f}-\omega_{k}}+\frac{\boldsymbol{X}_{-f} \boldsymbol{X}_{-f}^{\dagger}}{\lambda_{f}+\omega_{k}}\right) \boldsymbol{M}_{\beta}  \tag{3.120}\\
& =\sum_{f} \frac{\langle 0| \hat{\mu}_{\alpha}|f\rangle}{\lambda_{f}-\omega_{k}} \boldsymbol{X}_{f}+\frac{\langle f| \hat{\mu}_{\alpha}|0\rangle}{\lambda_{f}+\omega_{k}} \boldsymbol{X}_{-f}
\end{align*}
$$

Here, $\langle 0| \hat{\mu}_{\alpha}|f\rangle$ represents the projection of the transition dipole moment vector in the basis of excited Slater-determinants onto the eigenvector $\boldsymbol{X}_{f}$ that make up the transformation matrix $\boldsymbol{X}$. This projection serves as our approximation to the many-body transition dipole moment found in exact-state theory

$$
\begin{align*}
& \langle 0| \hat{\mu}_{\alpha}|f\rangle=\boldsymbol{M}_{\alpha}^{\dagger} \boldsymbol{X}_{f},\langle f| \hat{\mu}_{\beta}|0\rangle=\boldsymbol{X}_{f}^{\dagger} \boldsymbol{M}_{\beta}  \tag{3.121}\\
& \langle f| \hat{\mu}_{\alpha}|0\rangle=\boldsymbol{M}_{\alpha}^{\dagger} \boldsymbol{X}_{-f},\langle 0| \hat{\mu}_{\beta}|f\rangle=\boldsymbol{X}_{-f}^{\dagger} \boldsymbol{M}_{\beta}
\end{align*}
$$

Within the framework of response theory we do not work with explicit expressions for any of the excited states as linear combinations of excited Slater determinants as in configuration-interaction singles, the notation $|f\rangle$ serves as a placeholder. Instead of having explicit expressions for the excited states, we obtain the approximations of the transition moments as projections onto the eigenvectors $\boldsymbol{X}_{f}$. The approximate transition dipole moments become weighted sums of transition dipole moments between Slater determinants

$$
\begin{align*}
& \langle 0| \hat{\mu}_{\alpha}|f\rangle=\boldsymbol{M}_{\alpha}^{\dagger} \boldsymbol{X}_{f}=\sum_{i a}\left(\left\langle\Theta_{i}^{a}\right| \hat{\mu}_{\alpha}\left|\Theta_{0}\right\rangle X_{i a}\left(\lambda_{f}\right)-\left\langle\Theta_{0}\right| \hat{\mu}_{\alpha}\left|\Theta_{i}^{a}\right\rangle X_{i a}^{*}\left(-\lambda_{f}\right)\right)  \tag{3.122}\\
& \langle f| \hat{\mu}_{\alpha}|0\rangle=\boldsymbol{M}_{\alpha}^{\dagger} \boldsymbol{X}_{-f}=\sum_{i a}\left(\left\langle\Theta_{i}^{a}\right| \hat{\mu}_{\alpha}\left|\Theta_{0}\right\rangle X_{i a}\left(-\lambda_{f}\right)-\left\langle\Theta_{0}\right| \hat{\mu}_{\alpha}\left|\Theta_{i}^{a}\right\rangle X_{i a}^{*}\left(\lambda_{f}\right)\right) \tag{3.123}
\end{align*}
$$

Combining the expression for the response vector of Eq.(3.120) with the expression for the polarizability of Eq.(3.45), we find that the response function in approximate state theory becomes

$$
\begin{equation*}
\left.\frac{d^{2} Q_{T}}{d F_{\alpha}^{-\omega_{\sigma}} d F_{\beta}^{\omega}}\right|_{F=0}=-\sum_{f} \boldsymbol{M}_{\alpha}^{\dagger}\left(\frac{\boldsymbol{X}_{f} \boldsymbol{X}_{f}^{\dagger}}{\lambda_{f}-\omega-i \gamma}+\frac{\boldsymbol{X}_{-f} \boldsymbol{X}_{-f}^{\dagger}}{\lambda_{f}+\omega+i \gamma}\right) \boldsymbol{M}_{\beta} . \tag{3.124}
\end{equation*}
$$

Each vector $\boldsymbol{X}_{f}$ corresponds to the specific changes in the wavefunction parameters, representing approximations for the transitions from the reference state to the other stationary states of the unperturbed Hamiltonian. In the orbital rotation parametrization, each approximate transition consists of one or more single-particle excitations. To illustrate this clearly, Fig.3.3 depicts the predominant singleparticle excitation associated with a specific eigenvector $\boldsymbol{X}_{f}$, as defined in Eq.(3.114). In this case, the sole non-zero element of the eigenvector corresponds to the orbital rotation occurring between the HOMO and LUMO orbitals. Generally, there might be multiple nonzero elements, potentially leading to more complex excitations.


FIGURE 3.3: An illustrative single-particle excitation corresponding to a HOMO to LUMO transition

Assuming real one-photon transition moment vectors, we can express the real and imaginary components of the polarizabilities in approximate state theory as

$$
\begin{align*}
{ }^{\mathbb{I}} \alpha_{\alpha \beta}(-\omega ; \omega)= & \sum_{f}\left(\frac{\gamma\langle 0| \hat{\mu}_{\alpha}|f\rangle\langle f| \hat{\mu}_{\beta}|0\rangle}{\left(\lambda_{f}-\omega\right)^{2}+\gamma^{2}}-\frac{\gamma\langle 0| \hat{\mu}_{\beta}|f\rangle\langle f| \hat{\mu}_{\alpha}|0\rangle}{\left(\lambda_{f}+\omega\right)^{2}+\gamma^{2}}\right) \\
{ }^{\mathbb{R}} \alpha_{\alpha \beta}(-\omega ; \omega) & =\sum_{f}\left(\frac{\left(\lambda_{f}-\omega\right)\langle 0| \hat{\mu}_{\alpha}|f\rangle\langle f| \hat{\mu}_{\beta}|0\rangle}{\left(\lambda_{f}-\omega\right)^{2}+\gamma^{2}}\right.  \tag{3.125}\\
& \left.+\frac{\left(\lambda_{f}+\omega\right)\langle 0| \hat{\mu}_{\beta}|f\rangle\langle f| \hat{\mu}_{\alpha}|0\rangle}{\left(\lambda_{f}+\omega\right)^{2}+\gamma^{2}}\right) \tag{3.126}
\end{align*}
$$

This formulation is reminiscent of the exact-state theory expressions detailed in Eqs. (3.82)-(3.83), but now incorporates our approximate transition dipole moments and approximate excitation energies.


FIGURE 3.4: An illustration of the imaginary component of the polarizability (blue curve) and the one-photon transition strengths (black bars).

From Fig.3.4, we can observe that for each eigenvector and eigenvalue pair, $\boldsymbol{X}_{f}$ and $\lambda_{f}$, from equation Eq.(3.114), there corresponds a peak indicative of an excitation $0 \rightarrow f$. The strength of each transition depends on the magnitude of $M_{\alpha}^{\dagger} X_{f} X_{f}^{\dagger} M_{\beta}$, representing the coupling between the reference state and the excited state f mediated by the dipole moment operator. By summing over all states $f$ and applying the Lorentzian broadening implied by Eq.(3.125), we obtain the absorption spectrum, as depicted in Fig.3.4.

## Non-linear response and multiple-photon interactions

When an intense field interacts with a material, multiple simultaneous field interactions can occur, causing the material's response to become nonlinear. This means that the response is no longer merely the sum of the individual responses. Our goal is to describe how multiple photons can interact with the material simultaneously and explore phenomena such as two-photon absorption ${ }^{48-61}$ or second harmonic generation ${ }^{62-69}$. To model this, we need to examine how the initial response from the first field interaction is influenced by the presence of other concurrent field interactions. This aspect is encapsulated by the nonlinear response, which captures the cooperative effects that would not be apparent when considering multiple, separate first-order responses. We can gain insights into this process by considering the second- and third-order corrections to the Fourier coefficients of the dipole moments, which were given by Eqs. (3.49)-(3.50). We have observed that the dispersion behavior of these Fourier coefficients is primarily determined by the behavior and characteristics of the order
corrections to the wave-function parameters. In particular the imaginary component of the first-order corrections take the form ${ }^{70}$

$$
\begin{equation*}
\mathbb{I} \frac{d \boldsymbol{\eta}^{\omega}}{d F_{\beta}^{\omega}}=\sum_{f}\left(\frac{\gamma \boldsymbol{X}_{f} \boldsymbol{X}_{f}^{\dagger}}{\left(\lambda_{f}-\omega\right)^{2}+\gamma^{2}}+\frac{\gamma \boldsymbol{X}_{-f} \boldsymbol{X}_{-f}^{\dagger}}{\left(\lambda_{f}+\omega\right)^{2}+\gamma^{2}}\right) \boldsymbol{M}_{\beta} \tag{3.127}
\end{equation*}
$$

These are non-zero only near resonance frequencies. The secondorder derivatives, representing the rate of change of linear response, take the form
$\mathbb{I} \frac{d^{2} \boldsymbol{\eta}^{\omega_{k}, \omega_{k}}}{d F_{\beta}^{\omega_{k}} F_{\delta}^{\omega_{l}}}=\sum_{f}\left(\frac{\gamma \boldsymbol{X}_{f} \boldsymbol{X}_{f}^{\dagger}}{\left(\lambda_{f}-\left(\omega_{k}+\omega_{l}\right)\right)^{2}+\gamma^{2}}+\frac{\gamma \boldsymbol{X}_{-f} \boldsymbol{X}_{-f}^{\dagger}}{\left(\lambda_{f}+\left(\omega_{k}+\omega_{l}\right)\right)^{2}+\gamma^{2}}\right) \boldsymbol{M}_{\beta \delta}^{\omega, \omega}$
The rate of change of the linear response with respect to a second field interaction introduces new non-zero contributions at frequencies corresponding to combinations of the perturbation frequencies


FIGURE 3.5: An illustration of the dispersion of one component of the firstorder and second-order corrections to the Fourier components of the wavefuncton parameters

As illustrated in Fig. 3.5, incorporating the non-linear response vectors into our model suddenly enables the material to exchange energy with the field at spectral frequencies that would not have been possible if the perturbations were treated as completely separate events. The cooperative effect of two photons, for instance, can be observed in two-photon absorption transitions that are forbidden in onephoton absorption. These processes could not occur if one considered the effect of each photon separately. Information regarding simultaneous two-photon absorption can be obtained from the cubic response function as was shown by the Poynting theorem. The quadratic response function however also contains information regarding twophoton absorption as will be discussed in the section concerning the residue of the quadratic response function. Drawing from the Poynting theorem, we have determined that the second-order correction to
the intensity gradient is directly given by the imaginary component of the isotropic second-nonlinear hyperpolarizability

$$
\begin{equation*}
\nabla I^{(2)}(\omega)=\frac{4 \omega}{c^{2} \epsilon_{0}^{2}} \mathbb{I} \bar{\gamma}(-\omega ; \omega,-\omega, \omega) I^{2}(\omega) \tag{3.129}
\end{equation*}
$$

The second-order nonlinear hyperpolarizability of Eq. (3.50) can be rewritten in terms of the only the first and second-order corrections to the wave-function parameters and the explicit expression of a single tensor component is given by the following expression ${ }^{71-75}$

$$
\begin{align*}
& \gamma_{\alpha \beta \gamma \delta}(-\omega ; \omega,-\omega, \omega)= \\
& \frac{d \boldsymbol{\kappa}^{-\omega}}{d F_{\alpha}^{-\omega}} \frac{\partial^{4} Q_{T}}{\partial F \partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}}\left[\frac{d \boldsymbol{\kappa}^{-\omega}}{d F_{\gamma}^{-\omega}} \frac{d \boldsymbol{\kappa}^{\omega}}{d F_{\delta}^{\omega}}+\frac{d \boldsymbol{\kappa}^{\omega}}{d F_{\beta}^{\omega}} \frac{d \boldsymbol{\kappa}^{\omega}}{d F_{\delta}^{\omega}}+\frac{d \boldsymbol{\kappa}_{k}^{\omega}}{d F_{\beta}^{\omega}} \frac{d \boldsymbol{\kappa}_{l}^{-\omega}}{d F_{\gamma}^{-\omega}}\right] \\
& +\frac{d \boldsymbol{\kappa}^{-\omega}}{d F_{\alpha}^{-\omega}} \frac{\partial^{3} Q_{T}}{\partial F \partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}}\left[\frac{d^{2} \boldsymbol{\kappa}^{-\omega, \omega}}{d F_{\gamma}^{-\omega} F_{\delta}^{\omega}}+\frac{d^{2} \boldsymbol{\kappa}^{\omega, \omega}}{d F_{\beta}^{\omega} F_{\delta}^{\omega}}+\frac{d^{2} \boldsymbol{\kappa}^{\omega,-\omega}}{d F_{\beta}^{\omega} F_{\gamma}^{-\omega}}\right] \\
& +\frac{d \boldsymbol{\kappa}^{-\omega}}{d F_{\alpha}^{-\omega}} \frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}}\left[\frac{d \boldsymbol{\kappa}^{\omega}}{d F_{\beta}^{\omega}} \frac{d^{2} \boldsymbol{\kappa}^{-\omega, \omega}}{d F_{\gamma}^{-\omega} d F_{\delta}^{\omega}}+\frac{d \boldsymbol{\kappa}^{-\omega}}{d F_{\gamma}^{-\omega}} \frac{d^{2} \boldsymbol{\kappa}^{\omega, \omega}}{d F_{\beta}^{\omega} F_{\delta}^{\omega}}+\frac{d \boldsymbol{\kappa}^{\omega}}{d F_{\delta}^{\omega}} \frac{d^{2} \boldsymbol{\kappa}_{l}^{\omega,-\omega}}{d F_{\beta}^{\omega} d F_{\gamma}^{-\omega}}\right] \\
& +\frac{d \boldsymbol{\kappa}^{-\omega}}{d F_{\alpha}^{-\omega}} \frac{\partial^{4} Q_{T}}{\partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}} \frac{d \boldsymbol{\kappa}^{\omega}}{d F_{\beta}^{\omega}} \frac{d \boldsymbol{\kappa}^{-\omega}}{d F_{\gamma}^{-\omega}} \frac{d \boldsymbol{\kappa}^{\omega}}{d F_{\delta}^{\omega}} \\
& +\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{\omega} \partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}}\left[\frac{d \boldsymbol{\kappa}^{\omega}}{d F_{\beta}^{\omega}} \frac{d^{2} \boldsymbol{\kappa}^{-\omega, \omega}}{d F_{\gamma}^{-\omega} F_{\delta}^{\omega}}+\frac{d \boldsymbol{\kappa}^{-\omega}}{d F_{\gamma}^{-\omega}} \frac{d^{2} \boldsymbol{\kappa}^{\omega, \omega}}{d F_{\beta}^{\omega} F_{\delta}^{\omega}}+\frac{d \boldsymbol{\kappa}^{\omega}}{d F_{\delta}^{\omega}} \frac{d^{2} \boldsymbol{\kappa}^{\omega,-\omega}}{d F_{\beta}^{\omega} F_{\gamma}^{-\omega}}\right] \\
& +\frac{\partial^{4} Q_{T}}{\partial F \partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}} \frac{d \boldsymbol{\kappa}^{\omega}}{d F_{\beta}^{\omega}} \frac{d \boldsymbol{\kappa}^{-\omega}}{d F_{\gamma}^{-\omega}} \frac{d \boldsymbol{\kappa}^{\omega}}{d F_{\delta}^{\omega}}, \tag{3.130}
\end{align*}
$$

Looking at Eq.(3.130), it is seen that evaluating a single tensor element necessitates the resolution of both linear and quadratic response equations, along with several contractions of Fock-matrix derivatives up to the third order.

## THE REDUCED EXPRESSION FOR TWO-PHOTON ABSORPTION CROSS SECTIONS

In this section, we will discuss a reduced expression for the secondorder nonlinear hyperpolarizability pertinent to the articles II and IV included in this thesis. Looking at Fig.3.5, it is seen that in regions far removed from any one-photon resonance, the imaginary components of all the first-order response vectors are approximately zero. Consequently, all the first-order response vectors are predominantly real in such spectral regions. This suggests that the two-photon absorption transition moment vectors of Eq.(3.66) are also real. However, the second-order nonlinear hyperpolarizability encompasses quadratic response vectors as described in Eq.(3.128). These quadratic response vectors might possess non-zero imaginary components if combinations of frequencies align closely with resonance energies, as depicted in Fig.3.5. Thus, we infer that within the imaginary component of the
second-order nonlinear hyperpolarizability, many terms are equal to zero far from any one-photon resonance. By isolating only the nonzero contributions from the imaginary component of Eq. (3.130), we obtain a substantially simplified expression ${ }^{76}$.

$$
\begin{align*}
& { }^{\mathbb{I}} \gamma_{\alpha \beta \gamma \gamma \delta}^{\mathrm{red}}(-\omega ; \omega,-\omega, \omega) \\
& \approx\left[\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}} \frac{d \boldsymbol{\kappa}^{-\omega}}{d F_{\alpha}^{-\omega}} \frac{d \boldsymbol{\kappa}^{-\omega}}{d F_{\gamma}^{-\omega}}+P_{\alpha, \gamma} \frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{-\omega} \partial \boldsymbol{\kappa} \partial \boldsymbol{\kappa}} \frac{d \boldsymbol{\kappa}^{-\omega}}{d F_{\gamma}^{-\omega}}\right] \frac{d^{2} \boldsymbol{\kappa}^{\omega, \omega}}{d F_{\beta}^{\omega} F_{\delta}^{\omega}} \\
& =\left(\boldsymbol{M}_{\alpha \gamma}^{-\omega,-\omega}\right)^{\dagger} \sum_{f}\left(\frac{\gamma \boldsymbol{X}_{f} \boldsymbol{X}_{f}^{\dagger}}{\left(\lambda_{f}-2 \omega\right)^{2}+\gamma^{2}}+\frac{\gamma \boldsymbol{X}_{-f} \boldsymbol{X}_{-f}^{\dagger}}{\left(\lambda_{f}+2 \omega\right)^{2}+\gamma^{2}}\right) \boldsymbol{M}_{\beta \delta}^{\omega, \omega} \tag{3.131}
\end{align*}
$$

This derived expression for the hyperpolarizability, denoted as $\gamma^{\text {red }}$, which is valid only in one-photon off-resonance regions, is referred to as the reduced expression. In contrast, in the one-photon resonance regions, we utilize the imaginary component of Eq. (3.130), termed the full expression. In analogy to the first-order case, see Eq. (3.121), we get expressions for the approximate two-photon transition moments as the projections:

$$
\begin{equation*}
{ }^{0 \rightarrow f} S_{\alpha \beta}^{\omega_{l}, \omega_{m}}=\left(\boldsymbol{M}_{\alpha \beta}^{\omega_{l}, \omega_{m}}\right)^{\dagger} \boldsymbol{X}_{f},\left({ }^{0 \rightarrow f} S_{\alpha \beta}^{\omega_{l}, \omega_{m}}\right)^{\dagger}=\boldsymbol{X}_{f}^{\dagger} \boldsymbol{M}_{\alpha \beta}^{\omega_{l}, \omega_{m}} \tag{3.132}
\end{equation*}
$$

Therefore, in one-photon off-resonance regions, the second-order correction to the intensity gradient is proportional to the following expression ${ }^{40}$

$$
\begin{align*}
& \nabla I^{(2)}(\omega) \propto \\
& -\omega \sum_{f}\left(\frac{\gamma^{0 \rightarrow f} S_{\alpha \gamma}^{-\omega,-\omega}\left({ }^{0 \rightarrow f} S_{\beta \delta}^{\omega, \omega}\right)^{\dagger}}{\left(\lambda_{f}-2 \omega\right)^{2}+\gamma^{2}}+\frac{\gamma\left({ }^{0 \rightarrow f} S_{\alpha \gamma}^{-\omega,-\omega}\right)^{\dagger}{ }^{0 \rightarrow f} S_{\beta \delta}^{\omega, \omega}}{\left(\lambda_{f}+2 \omega\right)^{2}+\gamma^{2}}\right) I^{2}(\omega) \tag{3.133}
\end{align*}
$$

In Fig. 3.6, both the imaginary component of the polarizability $\alpha(-\omega, \omega)$, corresponding to one-photon absorption, and the second hyperpolarizability $\gamma(-\omega, \omega,-\omega, \omega)$ have been plotted. Due to the incorporation of the second-order response vector, the hyperpolarizability exhibits resonance in one-photon off-resonance regions.


FIGURE 3.6: Dispersion of the real and imaginary component of the Fourier components of the polarizability and the second hyperpolarizability

To conclude, when $\omega=0.5 \lambda_{f}$ in one-photon off-resonance regions the energy transfer from the field to the molecule is proportional to the complex magnitude squared of the two-photon transition moments corresponding to that excitation.

## THE RESIDUE APPROACH

The two-photon transition moments can also be discerned using the quadratic response function ${ }^{42}$. In this section, we will delve deeper into the nuances of two-photon transition moments and explore an alternative method for their calculation and the residue approach, employed in paper V, will be discussed in more detail. Within nondamped response theory, the residue approach is used where the response functions exhibit singularities at spectral frequencies at the excitation energies. In this method, the quantities of interest are computed as follows

$$
\begin{equation*}
R_{f}=\lim _{\omega \rightarrow \lambda_{f}}\left(\omega-\lambda_{f}\right) R(\omega) \tag{3.134}
\end{equation*}
$$

Here, R denotes the response function and $R_{f}$ represents the terms within the response function that persist post-division by $\left(\omega-\lambda_{f}\right)$ as $\omega$ approaches $\lambda_{f}$. Looking at Eq. (3.78), it is evident that such a residue can isolate the product of transition moments corresponding to $\lambda_{f}$. Likewise, the two-photon transition moments can be extracted from the quadratic response function, a process detailed in the subsequent discussion. Once the two-photon transition strengths are obtained, the two-photon absorption spectrum can be constructed by aggregating all transitions strengths and incorporating a broadening function. Performing a rotational average of the two-photon transition
strengths yields the effective two-photon transition strength as ${ }^{75,77}$.

$$
\begin{align*}
& \delta_{f}^{T P A}=\frac{1}{15} \sum_{\alpha \beta}[0 \rightarrow f \\
& S_{\alpha \alpha}^{-}-\frac{\lambda_{f}}{2},-\frac{\lambda_{f}}{2}(0 \rightarrow f  \tag{3.135}\\
&\left.S_{\beta \beta}^{-\frac{\lambda_{f}}{2},-\frac{\lambda_{f}}{2}}\right)^{\dagger} \\
&+{ }^{0 \rightarrow f} S_{\alpha \beta}^{-\frac{\lambda_{f}}{2},-\frac{\lambda_{f}}{2}}\left({ }^{0 \rightarrow f} S_{\alpha \beta}^{-\frac{\lambda_{f}}{2},-\frac{\lambda_{f}}{2}}\right)^{\dagger} \\
&+{ }^{0 \rightarrow f} S_{\beta \alpha}^{-\frac{\lambda_{f}}{2},-\frac{\lambda_{f}}{2}}(0 \rightarrow f \\
&\left.\left.S_{\beta \alpha}^{-\frac{\lambda_{f}}{2},-\frac{\lambda_{f}}{2}}\right)^{\dagger}\right]
\end{align*}
$$

The two-photon absorption cross section as a function of the optical frequency is then given by the expression

$$
\begin{equation*}
\sigma^{(2)}(\omega)=\frac{N \pi^{2} \alpha^{2} \hbar^{4}}{e^{4}} \omega^{2} \sum_{f} \delta_{f}^{T P A} \mathcal{L}(\omega) \tag{3.136}
\end{equation*}
$$

where the Lorentzian broadening function is given by the expression

$$
\begin{equation*}
\mathcal{L}(\omega)=\frac{\gamma}{\left(\lambda_{f}-\omega\right)^{2}+\gamma^{2}} \tag{3.137}
\end{equation*}
$$

The starting point for this approach is as mentioned the quadratic response function. After some algebraic manipulation we arrive at the working expression for the quadratic response function in terms of first-order response vectors as

$$
\begin{align*}
& \left.\frac{d^{3} Q_{T}}{d F_{\alpha}^{-\omega_{\sigma}} d F_{\beta}^{\omega_{2}} d F_{\gamma}^{\omega_{3}}}\right|_{F=0}=\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{2}} \partial \boldsymbol{\eta}^{\omega_{3}}} \frac{d \boldsymbol{\eta}^{\omega_{2}}}{d F_{\beta}^{\omega_{2}}} \frac{d \boldsymbol{\eta}^{\omega_{3}}}{d F_{\gamma}^{\omega_{3}}} \\
& +\frac{d \boldsymbol{\eta}^{-\omega_{\sigma}}}{d F_{\alpha}^{-\omega_{\sigma}}}\left[\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{3}} \partial F_{\beta}^{\omega_{2}}} \frac{d \boldsymbol{\eta}^{\omega_{3}}}{d F_{\gamma}^{\omega_{3}}}+\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{2}} \partial F_{\gamma}^{\omega_{3}}} \frac{d \boldsymbol{\eta}^{\omega_{2}}}{d F_{\beta}^{\omega_{2}}}\right] \\
& +\frac{d \boldsymbol{\eta}^{-\omega_{\sigma}}}{d F_{\alpha}^{-\omega_{\sigma}}} \frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{2}} \partial \boldsymbol{\eta}^{\omega_{3}}} \frac{d \boldsymbol{\eta}^{\omega_{2}}}{d F_{\beta}^{\omega_{2}}} \frac{d \boldsymbol{\eta}^{\omega_{3}}}{d F_{\gamma}^{\omega_{3}}} \tag{3.138}
\end{align*}
$$

where the response equations in standard response theory are given by Eq. (3.120). Taking the residue as $\omega_{3} \rightarrow \lambda_{f}$ of the quadratic response function for $\omega_{2}=-\frac{\lambda_{f}}{2}$ we get that all the terms in the quadratic response function that do not contain the factor $\left(\lambda_{f}-\omega_{3}\right)$ are eliminated and we get an expression for the two-photon transition
moment ${ }^{42}$

$$
\begin{align*}
& \left.\lim _{\omega_{3} \rightarrow-\lambda_{f}}\left(\lambda_{f}+\omega_{3}\right) \frac{d^{3} Q_{T}}{d F_{\alpha}^{-\omega_{\sigma}} d F_{\beta}^{\frac{\lambda_{f}}{2}} d F_{\gamma}^{\omega_{3}}}\right|_{F=0} \\
& =\left[\left(\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\frac{-\lambda_{f}}{2}} \partial \boldsymbol{\eta}^{\lambda_{f}}}+\frac{d \boldsymbol{\eta}^{-\omega_{\sigma}}}{d F_{\alpha}^{-\omega_{\sigma}}} \frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{-\frac{\lambda_{f}}{2}} \partial \boldsymbol{\eta}^{\lambda_{f}}}\right) \frac{d \boldsymbol{\eta}^{-\frac{\lambda_{f}}{2}}}{d F_{\beta}^{-\frac{\lambda_{f}}{2}}} \boldsymbol{X}_{f}\right. \\
& \left.+\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\lambda_{f}} \partial F_{\beta}^{-\frac{\lambda_{f}}{2}}} \frac{d \boldsymbol{\eta}^{-\omega_{\sigma}}}{d F_{\alpha}^{-\omega_{\sigma}}} \boldsymbol{X}_{f}\right] \boldsymbol{X}_{f}^{\dagger} \boldsymbol{M}_{\gamma} \\
& =0 \rightarrow f S_{\alpha \beta}^{-\frac{\lambda_{f}}{2},-\frac{\lambda_{f}}{2}}\langle f| \hat{\mu}_{\gamma}|0\rangle \tag{3.139}
\end{align*}
$$

The term to the right of the square bracket in Eq. (3.139) corresponds to $\langle f| \hat{\mu}_{\gamma}|0\rangle$ and the term in the bracket corresponds to the two-photon transition moment. In exact state theory we have that the cubic Hessian of the quasi-energy is zero so we get that the two-photon transition moment is given by the expression

$$
\begin{align*}
& 0 \rightarrow f S_{\alpha \beta}^{-\frac{\lambda_{f}}{2},-\frac{\lambda_{f}}{2}}= \\
& {\left[\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\frac{\lambda_{f}}{2}} \partial \boldsymbol{\eta}^{\lambda_{f}} \partial F_{\beta}^{-\frac{\lambda_{f}}{2}}} \frac{d \boldsymbol{\eta}^{-\frac{\lambda_{f}}{2}}}{d F_{\alpha}^{-\frac{\lambda_{f}}{2}}}+\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{-\frac{\lambda_{f}}{2}} \partial \boldsymbol{\eta}^{-\frac{\lambda_{f}}{2}} \partial \boldsymbol{\eta}^{\lambda_{f}}} \frac{d \boldsymbol{\eta}^{-\frac{\lambda_{f}}{2}}}{d F_{\beta}^{-\frac{\lambda_{f}}{2}}}\right] \boldsymbol{X}_{f}} \tag{3.140}
\end{align*}
$$

The the generalized dipole tensors in Eq. (3.139) can be written explicitly as

$$
\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{\omega_{2}} \partial \boldsymbol{\eta}^{\omega_{3}}}=\left(\begin{array}{cc}
\frac{\partial^{2} \mu_{\alpha}^{-\omega_{\sigma}}}{\partial \eta_{m}^{*} \eta_{n}} & \frac{\partial^{2} \mu_{\alpha}^{-\omega_{\sigma}}}{\partial \eta_{m}^{*} \eta_{n}^{*}}  \tag{3.141}\\
\frac{\partial^{2} \mu_{\alpha}^{-\omega_{\sigma}}}{\partial \eta_{m} \eta_{n}} & \frac{\partial^{2} \mu_{\alpha}^{-} \omega_{\sigma}}{\partial \eta_{m} \eta_{n}^{*}}
\end{array}\right)
$$

Only the diagonal blocks are non-zero in exact state theory and using the BCH expansion of Eq. (3.86) we have that the upper left block and the lower right block can be written as

$$
\begin{align*}
\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{-\omega_{\sigma}} \partial \eta_{m}^{*} \partial \eta_{n}} & =-\frac{1}{2}\left\langle\Psi_{0}\right|\left[\hat{R}_{n}^{\dagger},\left[\hat{R}_{m}, \hat{\mu}_{\alpha}\right]\right]\left|\Psi_{0}\right\rangle-\frac{1}{2}\left\langle\Psi_{0}\right|\left[\hat{R}_{m},\left[\hat{R}_{n}^{\dagger}, \hat{\mu}_{\alpha}\right]\right]\left|\Psi_{0}\right\rangle \\
& =\left(\left\langle\Psi_{m}\right| \hat{\mu}_{\alpha}\left|\Psi_{n}\right\rangle-\left\langle\Psi_{0}\right| \hat{\mu}_{\alpha}\left|\Psi_{0}\right\rangle \delta_{n m}\right) \\
\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{-\omega_{\sigma}} \partial \eta_{m} \partial \eta_{n}^{*}} & =-\frac{1}{2}\left\langle\Psi_{0}\right|\left[\hat{R}_{n},\left[\hat{R}_{m}^{\dagger}, \hat{\mu}_{\alpha}\right]\right]\left|\Psi_{0}\right\rangle-\frac{1}{2}\left\langle\Psi_{0}\right|\left[\hat{R}_{m}^{\dagger},\left[\hat{R}_{n}, \hat{\mu}_{\alpha}\right]\right]\left|\Psi_{0}\right\rangle  \tag{3.142}\\
& =\left(\left\langle\Psi_{n}\right| \hat{\mu}_{\alpha}\left|\Psi_{m}\right\rangle-\left\langle\Psi_{0}\right| \hat{\mu}_{\alpha}\left|\Psi_{0}\right\rangle \delta_{n m}\right) . \tag{3.143}
\end{align*}
$$

Furthermore, in exact state theory, the eigenvectors have the structure

$$
\begin{equation*}
\boldsymbol{X}_{f}=\binom{\delta_{m f}}{0}, \boldsymbol{X}_{-f}=\binom{0}{\delta_{m f}} \tag{3.144}
\end{equation*}
$$

such that after contracting the tensors we get the expressions

$$
\begin{align*}
& \frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{-\frac{\lambda_{f}}{2}} \partial \boldsymbol{\eta}^{-\frac{\lambda_{f}}{2}} \partial \boldsymbol{\eta}^{\lambda_{f}}} \frac{d \boldsymbol{\eta}^{-\frac{\lambda_{f}}{2}}}{d F_{\beta}^{-\frac{\lambda_{f}}{2}}} \boldsymbol{X}_{f}=\sum_{n, m} \frac{\left\langle\Psi_{0}\right| \mu_{\beta}\left|\Psi_{n}\right\rangle}{\lambda_{n}-\frac{\lambda_{f}}{2}} \frac{\partial^{2} \mu_{\alpha}^{-\frac{\lambda_{f}}{2}}}{\partial \eta_{m}^{*} \eta_{n}} \delta_{m f} \\
& \frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\frac{\lambda_{f}}{2}} \partial \boldsymbol{\eta}^{\lambda_{f}} \partial F_{\beta}^{-\frac{\lambda_{f}}{2}}} \frac{d \boldsymbol{\eta}^{-\frac{\lambda_{f}}{2}}}{d F_{\alpha}^{-\frac{\lambda_{f}}{2}}} \boldsymbol{X}_{f}=\sum_{n, m} \frac{\left\langle\Psi_{0}\right| \mu_{\alpha}\left|\Psi_{n}\right\rangle}{\lambda_{n}-\frac{\lambda_{f}}{2}} \frac{\partial^{2} \mu_{\beta}^{-\frac{\lambda_{f}}{2}}}{\partial \eta_{m}^{*} \eta_{n}} \delta_{m f} \tag{3.145}
\end{align*}
$$

Combining Eqs. (3.144)-(3.146) with Eq. (3.140) we get that the twophoton transition moment for two degenerate photons of half the excitation energy $\lambda_{f}$ between the states $\left|\Psi_{0}\right\rangle$ and $\left|\Psi_{f}\right\rangle$ is given by the expression

$$
\begin{align*}
{ }^{0 \rightarrow f} S_{\alpha \beta}^{--\frac{\lambda_{f}}{2}},-\frac{\lambda_{f}}{2} & =\sum_{n}\left[\frac{\left(\left\langle\Psi_{n}\right| \hat{\mu}_{\alpha}\left|\Psi_{f}\right\rangle-\left\langle\Psi_{0}\right| \hat{\mu}_{\alpha}\left|\Psi_{0}\right\rangle \delta_{n f}\right)\left\langle\Psi_{0}\right| \mu_{\beta}\left|\Psi_{n}\right\rangle}{\lambda_{n}-\frac{\lambda_{f}}{2}}\right] \\
& \left.+\frac{\left(\left\langle\Psi_{n}\right| \hat{\mu}_{\beta}\left|\Psi_{f}\right\rangle-\left\langle\Psi_{0}\right| \hat{\mu}_{\beta}\left|\Psi_{0}\right\rangle \delta_{n f}\right)\left\langle\Psi_{0}\right| \mu_{\alpha}\left|\Psi_{n}\right\rangle}{\lambda_{n}-\frac{\lambda_{f}}{2}}\right] \tag{3.147}
\end{align*}
$$

In approximate state theory, the cubic Hessian is non-zero and we get that the explicit expression for the two-photon transition moments in approximate state theory from the residue of the quadratic response function is given by the expression

$$
\begin{align*}
& { }^{0 \rightarrow f} S_{\alpha \beta}^{-\frac{\lambda_{f}}{2},-\frac{\lambda_{f}}{2}}=\frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\kappa}^{-\frac{\lambda_{f}}{2}} \partial \boldsymbol{\kappa}^{\lambda_{f}} \partial F_{\beta}^{-\frac{\lambda_{f}}{2}}} \frac{d \boldsymbol{\kappa}^{-\frac{\lambda_{f}}{2}}}{d F_{\alpha}^{-\frac{\lambda_{f}}{2}}} \boldsymbol{X}_{f} \\
& +\left(\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{-\frac{\lambda_{f}}{2} a} \partial \boldsymbol{\kappa}^{-\frac{\lambda_{f}}{2}} \partial \boldsymbol{\kappa}^{\lambda_{f}}}+\frac{d \boldsymbol{\kappa}^{-\frac{\lambda_{f}}{2}}}{d F_{\alpha}^{-\omega_{\sigma}}} \frac{\partial^{2} \boldsymbol{f}^{-\frac{\lambda_{f}}{2}}}{\partial \boldsymbol{\kappa}^{-\frac{\lambda_{f}}{2}} \partial \boldsymbol{\kappa}^{\lambda_{f}}}\right) \frac{d \boldsymbol{\kappa}^{-\frac{\lambda_{f}}{2}}}{d F_{\beta}^{-\frac{\lambda_{f}}{2}}} \boldsymbol{X}_{f} \tag{3.148}
\end{align*}
$$

Consequently, determining the two-photon transition moment from the residue of the quadratic response function necessitates solving the linear response equation and the generalized eigenvector equation, delineated in Eq.(3.114), as well as executing the Fock matrix contraction as per Eq.(3.99) and Eq. (3.103). This approach stands in stark contrast to the method detailed in the preceding section, where the two-photon transition moments are derived from the second hyperpolarizability within the theory of damped response; in that approach, eigenvectors are not utilized. Furthermore, the two-photon transition moments obtained from the residue of the quadratic response function manifest distinct singularities when the optical frequency matches an excitation energy. While calculating the twophoton transition moments as indicated in equation (3.131), these transition moments are computed employing damped response vectors, which remain finite at and in proximity to resonance. This implies that these two-photon transition moments obtained from the
residue of the quadratic response function are ill-suited for circumstances where the intermediate state in the TPA process represents a real eigenstate ${ }^{40}$.

## THE SUM-OVER STATES APPROACH

A final approach for obtaining two-photon absorption strengths is with the use of the two-state model, which will be presented in this section. While the sum-over-states expression has been somewhat supplanted by the method presented in the previous sections for practical calculations, it retains its value for theoretical analyses ${ }^{78,79}$. In this approach, we will truncate the expression for the two-photon transition moment of Eq. (3.147) to include only two states. We then get an approximation for the two-photon transition moment, which takes the form ${ }^{34}$

$$
\begin{align*}
{ }^{0 \rightarrow f} S_{\alpha \beta}^{\frac{\lambda_{f}}{2}, \frac{\lambda_{f}}{2}} & \approx \sum_{n} P_{\alpha \beta}\left[\frac{\left(\left\langle\Psi_{f}\right| \hat{\mu}_{\alpha}\left|\Psi_{n}\right\rangle-\left\langle\Psi_{0}\right| \hat{\mu}_{\alpha}\left|\Psi_{0}\right\rangle \delta_{n f}\right)\left\langle\Psi_{n}\right| \mu_{\beta}\left|\Psi_{0}\right\rangle}{\lambda_{n}-\frac{\lambda_{f}}{2}}\right] \delta_{n f} \\
& =\frac{2}{\lambda_{f}}\left[\Delta \mu_{\alpha}^{f}\left\langle\Psi_{n}\right| \mu_{\beta}\left|\Psi_{0}\right\rangle+\Delta \mu_{\beta}^{f}\left\langle\Psi_{n}\right| \mu_{\alpha}\left|\Psi_{0}\right\rangle\right] \tag{3.149}
\end{align*}
$$

In this expression, we have defined $\Delta \mu_{\alpha}^{f}$, which represents the difference between the dipole moment of the excited state f and the ground state. Taking the isotropic average of these two-state model two-photon transition moments, we find that the isotropic averaged two-photon absorption strength is defined by ${ }^{80}$

$$
\begin{align*}
\delta_{f}^{2 S M} & =\frac{4}{15} \frac{\langle 0| \hat{\mu}|0\rangle\langle 0| \hat{\mu}|0\rangle\langle 0| \hat{\mu}|f\rangle\langle f| \hat{\mu}|0\rangle}{0.25 \lambda_{f}^{2}}\left(1+2 \cos ^{2} \theta_{0 f}^{00}\right) \\
& -\frac{8}{15} \frac{\langle 0| \hat{\mu}|0\rangle\langle 0| \hat{\mu}|f\rangle\langle f| \hat{\mu}|0\rangle\langle f| \hat{\mu}|f\rangle}{0.25 \lambda_{f}^{2}}\left(2 \cos \theta_{00}^{0 f} \cos \theta_{0 f}^{f f}+\cos \theta_{00}^{f f}\right) \\
& +\frac{4}{15} \frac{\langle 0| \hat{\mu}|f\rangle\langle f| \hat{\mu}|0\rangle\langle f| \hat{\mu}|f\rangle\langle f| \hat{\mu}|f\rangle}{0.25 \lambda_{f}^{2}}\left(1+2 \cos ^{2} \theta_{f f}^{0 f}\right) \tag{3.150}
\end{align*}
$$

To assess the two-photon transition momenta within the context of the two-state model, it is necessary to calculate the dipole moment of the excited state. In approximate state theory, we lack explicit access to the excited state wave functions of $\hat{H}_{0}$, but we can derive the excited state dipole moment from the quadratic response function. This dipole moment can be obtained by taking the double residue of the quadratic response function ${ }^{42}$ for $\omega_{2} \rightarrow-\lambda_{f}$ and $\omega_{3} \rightarrow \lambda_{f}$.
$\lim _{\omega_{2} \rightarrow-\lambda_{f}}\left(\lambda_{f}+\omega_{2}\right)\left[\left.\lim _{\omega_{3} \rightarrow \lambda_{f}}\left(\lambda_{f}-\omega_{3}\right) \frac{d^{3} Q_{T}}{d F_{\alpha}^{-\omega_{\sigma}} d F_{\beta}^{\omega_{2}} d F_{\gamma}^{\omega_{3}}}\right|_{F=0}\right]=$
$\left[\left(\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{-\lambda_{f}} \partial \boldsymbol{\eta}^{\lambda_{f}}}+\frac{d \boldsymbol{\eta}^{-\omega_{\sigma}}}{d F_{\alpha}^{-\omega_{\sigma}}} \frac{\partial^{3} Q_{T}}{\partial \boldsymbol{\eta}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{-\lambda_{f}} \partial \boldsymbol{\eta}^{\lambda_{f}}}\right) \boldsymbol{X}_{f} \boldsymbol{X}_{-f}\right] \boldsymbol{X}_{f}^{\dagger} \boldsymbol{M}_{\beta} \boldsymbol{X}_{-f}^{\dagger} \boldsymbol{M}_{\gamma}$
In exact state theory, where the electronic cubic-Hessian is zero, the double residue transforms into a product involving the Hessian of the
generalized dipole moment tensor. As anticipated, this Hessian, when assessed at the stationary point, contains the difference between the dipole moments of the reference state and the other excited states of $\hat{H}_{0}$. Explicitly, the double residue is given as ${ }^{42,81}$

$$
\begin{align*}
& \lim _{\omega_{2} \rightarrow-\lambda_{f}}\left(\lambda_{f}+\omega_{2}\right)\left[\left.\lim _{\omega_{3} \rightarrow \lambda_{f}}\left(\lambda_{f}-\omega_{3}\right) \frac{d^{3} Q_{T}}{d F_{\alpha}^{-\omega_{\sigma}} d F_{\beta}^{\omega_{2}} d F_{\gamma}^{\omega_{3}}}\right|_{F=0}\right] \\
& =\left[\left(\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{-\omega_{\sigma}} \partial \boldsymbol{\eta}^{-\lambda_{f}} \partial \boldsymbol{\eta}^{\lambda_{f}}}\right) \boldsymbol{X}_{f} \boldsymbol{X}_{-f}\right] \boldsymbol{X}_{f}^{\dagger} \boldsymbol{M}_{\beta} \boldsymbol{X}_{-f}^{\dagger} \boldsymbol{M}_{\gamma}  \tag{3.152}\\
& =\left[\left\langle\Psi_{f}\right| \hat{\mu}_{\alpha}\left|\Psi_{f}\right\rangle-\left\langle\Psi_{0}\right| \hat{\mu}_{\alpha}\left|\Psi_{0}\right\rangle\right]\left\langle\Psi_{f}\right| \hat{\mu}_{\beta}\left|\Psi_{0}\right\rangle\left\langle\Psi_{0}\right| \hat{\mu}_{\gamma}\left|\Psi_{f}\right\rangle
\end{align*}
$$

Meanwhile, in approximate state theory, the corresponding residue of the quadratic response function incorporates a non-zero cubic Hessian tensor. Hence, the approximation for the excited state dipole moment will be given by the following expression

$$
\begin{align*}
& \langle f| \hat{\mu}_{\alpha}|f\rangle \\
& =\langle 0| \hat{\mu}_{\alpha}|0\rangle+\left[\left(\frac{\partial^{3} Q_{T}}{\partial F_{\alpha}^{-\omega_{\sigma}} \partial \boldsymbol{\kappa}^{-\lambda_{f}} \partial \boldsymbol{\kappa}^{\lambda_{f}}}+\frac{d \boldsymbol{\kappa}^{-\omega_{\sigma}}}{d F_{\alpha}^{-\omega_{\sigma}}} \frac{\partial^{2} \boldsymbol{f}^{-\omega_{\sigma}}}{\partial \boldsymbol{\kappa}^{-\lambda_{f}} \partial \boldsymbol{\kappa}^{\lambda_{f}}}\right) \boldsymbol{X}_{f} \boldsymbol{X}_{-f}\right] \tag{3.153}
\end{align*}
$$

Conclusively, the determination of the excited-state dipole moment necessitates the resolution of the generalized eigenvector equation, given in Eq.(3.114), along with the contraction of the energy-gradient derivatives as shown in Eq.(3.99) and Eq. (3.103)

# SUMMARY AND OUTLOOK 

## VeloxChem: A Python-driven density-functional theory program for spectroscopy simulations (Summary of paper I)

VeloxChem is an open-source program designed to calculate electronic response functions using Hartree-Fock and Kohn-Sham density functional theories. It employs an object-oriented structure written in a layered Python/C++ approach. This design promotes timeefficient prototyping of innovative methodologies within electronic structure theory without compromising computational efficiency. As described in previous sections, the response properties necessitated order corrections to the Fourier components of the wave-function parameters. VeloxChem addresses this by tackling multiple frequencies and transition dipole moment vectors concurrently within a single shared subspace. This shared subspace technique notably enhances convergence speeds compared to traditional serial computations ${ }^{82}$. A hallmark of VeloxChem is its integral code, based on a modified Obara-Saika scheme. A primary advantage of mentioned integral code is its low memory footprint, allowing the majority of the memory to be dedicated to storing auxiliary density and Fock matrices. This is important since, solving the response equations necessitates the creation of several auxiliary Fock matrices, a point underscored in earlier sections. This allows for many auxiliary Fock matrices to be constructed in parallel each time the two-electron tensor is constructed. The integral code and the response solver coalesce to position VeloxChem as an efficient platform for computing response properties.

## The tensor-average and subspace extraction technique

(Summary of paper II)
The key quantities of interest for simulating spectroscopic observables related to one- and two-photon absorption, as mentioned in previous sections, are the isotropic averages of polarizability Eq. (2.37) and second-order nonlinear hyperpolarizability Eq. (2.38). The calculation of the second-order nonlinear hyperpolarizability necessitates the formation of two- and three-photon transition moment vectors Eqs. (3.66)-(3.67), which in turn require the contraction of the cubic and quartic-Hessian as shown in Eqs.(3.99)-(3.100).

$$
\gamma \rightarrow\left\{\binom{\overline{\bar{f}}_{i i}}{\overline{\bar{f}}_{i a}},\binom{\overline{\bar{f}}_{a i}}{\overline{\bar{f}}_{i a}}\right\}
$$

The number of auxiliary Fock matrices per frequency required for the analytic form of this contraction follow a systematic and predictable number. The number of unique auxiliary Fock matrices needed for
computing all the distinct second-hyperpolarizability tensors, which are required for determining the isotropic average, are represented by the blue bar in Fig. 4.1, the details are discussed in paper II.

Given that the isotropic average is the quantity of interest, optimizations can be made since the auxiliary Fock matrices are constructed through a linear transformation with respect to the density matrix, as depicted in Eqs. (3.108)-(3.110). This implies that the auxillary Fock matrix construction preserves both matrix addition (additivity) and scalar multiplication (homogeneity), wherein the transformation of the sum of multiple densities equates to the sum of the individual densities, as described by the equation

$$
\begin{equation*}
F\left(D_{1}\right)+\ldots+F\left(D_{n}\right)=F\left(D_{1}+\ldots+D_{n}\right) \tag{4.1}
\end{equation*}
$$

Given that the auxiliary Fock matrices represent linear transformations of the perturbed densities, a new computational scheme is presented which is called the tensor-average approach. This scheme aims to leverage the inherent linearity to reduce the computational cost associated with determining the isotropic average directly, as opposed to evaluating the tensor components individually which we refer to as the tensor-component approach, all without sacrificing numerical accuracy. The aim of the tensor-average approach is hence to derive the analytic form of the orientiationally averaged cubic and quarticHessian tensor contractions which utilise the minimum amount of auxiliary Fock matrix constructions:

$$
\bar{\gamma} \rightarrow\left\{\left\langle\binom{\overline{\bar{f}}_{a i}}{\overline{\bar{f}}_{i a}}\right\rangle,\left\langle\binom{\overline{\bar{f}}_{a i}}{\overline{\bar{f}}_{i a}}\right\rangle\right\}
$$

The auxillary Fock matrices that can be added using Eq. (4.1) then define a set of compounded Fock matrices and the working equations are rewritten in terms of compounded auxillary Fock matrices. In the tensor-average approach, each time two-electron integrals are evaluated, applicable perturbed densities are cumulatively added, followed by a single linear transformation, thereby significantly reducing the number of necessary Fock matrix constructions need to be managed in parallel. Furhtermore, the response equations, in Eqs.(3.62)-(3.64), adopt the form:

$$
\begin{equation*}
\boldsymbol{A x}=\boldsymbol{m} \tag{4.2}
\end{equation*}
$$

These equations are addressed using an iterative subspace method. The actual subspace method used in VeloxChem is detailed in ${ }^{45}$, here a simplified but conceptual presentation is made to show the underlying logic for the subspace extraction technique developed in paper II. After n iterations, we accumulate n trial vectors $\boldsymbol{b}$, forming a trial space $\boldsymbol{b}^{n}$

$$
\begin{equation*}
\boldsymbol{b}^{n}=\left\{\boldsymbol{b}_{1}, \ldots, \boldsymbol{b}_{n}\right\} \tag{4.3}
\end{equation*}
$$

Our objective is to estimate the solution to the linear system in Eq.(4.2) using a combination of vectors that define the space in Eq. (4.3). A
critical step involves the transformation of these trial vectors using the matrix $\boldsymbol{A}$, resulting in a transformed space.

$$
\begin{equation*}
(\boldsymbol{A} \boldsymbol{b})^{n}=\left\{\boldsymbol{A} \boldsymbol{b}_{1}, \ldots, \boldsymbol{A} \boldsymbol{b}_{n}\right\} \tag{4.4}
\end{equation*}
$$

Subsequently, Eq. (4.2) is solved in the subspace spanned by Eq. (4.3) using the transformed space of Eq. (4.4) by inverting the reduced matrix in the following equation

$$
\left(\begin{array}{cccc}
\boldsymbol{b}_{1}^{\dagger} \boldsymbol{A} \boldsymbol{b}_{1} & \boldsymbol{b}_{1}^{\dagger} \boldsymbol{A} \boldsymbol{b}_{2} & \cdots & \boldsymbol{b}_{1}^{\dagger} \boldsymbol{A} \boldsymbol{b}_{n}  \tag{4.5}\\
\boldsymbol{b}_{2}^{\dagger} \boldsymbol{A} \boldsymbol{b}_{1} & \boldsymbol{b}_{2}^{\dagger} \boldsymbol{A} \boldsymbol{b}_{2} & \cdots & \boldsymbol{b}_{2}^{\dagger} \boldsymbol{A} \boldsymbol{b}_{n} \\
\vdots & \vdots & \ddots & \vdots \\
\boldsymbol{b}_{n}^{\dagger} \boldsymbol{A} \boldsymbol{b}_{1} & \boldsymbol{b}_{n}^{\dagger} \boldsymbol{A} \boldsymbol{b}_{2} & \cdots & \boldsymbol{b}_{n}^{\dagger} \boldsymbol{A} \boldsymbol{b}_{n}
\end{array}\right)\left(\begin{array}{c}
c_{1} \\
c_{2} \\
\vdots \\
c_{n}
\end{array}\right)=\left(\begin{array}{c}
\boldsymbol{b}_{1}^{\dagger} \boldsymbol{m} \\
\boldsymbol{b}_{2}^{\dagger} \boldsymbol{m} \\
\vdots \\
\boldsymbol{b}_{n}^{\dagger} \boldsymbol{m}
\end{array}\right)
$$

After convergence, the optimal solution in the space spanned by Eq. (4.3) is written as a linear combination of the trial space vectors and the coefficents obtained from Eq. (4.5) as

$$
\begin{equation*}
\frac{d \boldsymbol{\kappa}}{d F}=\sum_{p}^{n} c_{p} \boldsymbol{b}_{p} \tag{4.6}
\end{equation*}
$$

In order to construct the reduced space matrix in Eq. (4.5) we required the transformed space of Eq. (4.4) and since the matrix $\boldsymbol{A}$ contains the electronic Hessian we would have contracted all the trial vectors with the electronic Hessian using Eq. (3.98)

$$
\begin{equation*}
\left(\frac{\partial \mathbf{f}}{\partial \boldsymbol{\kappa}} \boldsymbol{b}\right)^{n}=\left\{\frac{\partial \mathbf{f}}{\partial \boldsymbol{\kappa}} \boldsymbol{b}_{1}, \ldots, \frac{\partial \mathbf{f}}{\partial \boldsymbol{\kappa}} \boldsymbol{b}_{n}\right\}=\left\{\binom{\bar{f}_{a i}\left(\boldsymbol{b}_{1}\right)}{\bar{f}_{i a}\left(\boldsymbol{b}_{1}\right)}, \ldots,\binom{\bar{f}_{a i}\left(\boldsymbol{b}_{n}\right)}{\bar{f}_{i a}\left(\boldsymbol{b}_{n}\right)}\right\} \tag{4.7}
\end{equation*}
$$

When calculating the second-order nonlinear hyperpolarizability, we would need to contract the cubic and quartic Hessians using Eqs.(3.103)-(3.104). Since, in the subspace procedure, certain contractions are already made as per Eq.(4.7), some auxiliary Fock matrices can be retrieved from the subspace, thus avoiding redundant Fock matrix constructions. This observation becomes evident when combining Eqs. (4.6), (3.98), and (3.102) to arrive at the following equality

$$
\begin{equation*}
\frac{\partial \mathbf{f}}{\partial \boldsymbol{\kappa}} \frac{d \boldsymbol{\kappa}}{d F_{\beta}^{\omega_{k}}}=\sum_{p}^{n} c_{p} \frac{\partial \mathbf{f}}{\partial \boldsymbol{\kappa}} \boldsymbol{b}_{p}=\binom{\left[\boldsymbol{\kappa}^{\omega_{k}}, \boldsymbol{f}\right]_{a i}+f_{a i}^{\omega_{k}}}{\left[\boldsymbol{\kappa}^{\omega_{k}}, \boldsymbol{f}\right]_{i a}+f_{i a}^{\omega_{k}}} \tag{4.8}
\end{equation*}
$$

This equation can in turn be written in terms of the vectors spanning Eq. (4.7) and solved for a vector containing the auxiliary Fock matrices $\boldsymbol{f}^{\omega_{k}}$ found in Eq. (3.103)-(3.104) as

$$
\begin{equation*}
\binom{f_{a i}^{\omega_{k}}}{f_{i a}^{\omega_{k}}}=\sum_{p}^{n} c_{p}\binom{\bar{f}_{a i}\left(\boldsymbol{b}_{p}\right)}{\bar{f}_{i a}\left(\boldsymbol{b}_{p}\right)}-\binom{\left[\boldsymbol{\kappa}^{\omega_{k}}, \boldsymbol{f}\right]_{a i}}{\left[\boldsymbol{\kappa}^{\omega_{k}}, \boldsymbol{f}\right]_{i a}} \tag{4.9}
\end{equation*}
$$

THE PERFORMANCE OF THE TENSOR-AVERAGE AND SUBSPACE EXTRACTION TEHCNIQUES

The reduction in the total number of auxiliary Fock matrix constructions required when utilizing the proposed tensor average approach with the subspace extraction technique using the full expression for the second-order nonlinear hyperpolarizability amounts to $90 \%$ as illustrated in the black bars in Fig. 4.1.


FIGURE 4.1: The number of response vectors and auxiliary Fock matrices required per frequency for the evaluation of the full isotropic hyperpolarizability (Eq. (2.38) \& Eq. (3.130)) using the tensor-component and the new tensor-average algorithm. The blue bar in the figure represents the tensor component approach where each individual tensor component is calculated without exploiting the linearity of the Fock matrix construction or subspace extraction, serving as a reference. In contrast, the black bar represents the number of Fock matrix constructions based on the proposed tensor-average algorithm with subspace extraction.

In one-photon off-resonance regions the expression for the secondorder non-linear hyperpolarizability reduces to the simplified expression in Eq. (3.131). When the tensor average is applied with the subspace extraction technique, see Fig.4.2 one gets an $86 \%$ reduction in the number of auxiliary Fock matrix constructions per frequency when compared to a tensor component method without the use no subspace extraction.


FIGURE 4.2: The number of response vectors and auxiliary Fock matrices required per frequency for the evaluation of the isotropic hyperpolarizability (Eq. (2.38) \& Eq. (3.131)) using the tensor-component and the new tensoraverage algorithm in one-photon off-resonance regions. The blue bar in the figure represents the tensor-component approach where each individual tensor component is calculated without exploiting the linearity of the Fock matrix construction or using the subspace extraction technique, serving as a reference. In contrast, the black bar represents the number of Fock matrix constructions based on the proposed tensor average algorithm with use of the subspace extraction technique.

## Extensions to density functional theory (Summary of papers III and IV)

The tensor average method, elaborated in detail in paper II, was primarily designed for the Hartree-Fock approximation. In paper III, a proof of principle is provided for the application of the tensor average method in density functional theory. This paper demonstrates that, within the adiabatic approximation, the non-linear kernel integrations required for the construction of the auxiliary Fock matrices at the DFT level of theory can be construed as linear transformations with respect to the perturbed densities. This is demonstrated for the functionals belonging to the generalized gradient approximation and the second-order property of second-harmonic generation.

In paper IV, working equations for the calculation of two-photon absorption cross-sections using the tensor average method at the DFT level of theory are presented and extended to include functionals belonging to the meta-generalized gradient approximation (meta-GGA). This marks the first implementation of non-linear response for this class of functionals, in particular enabling the calculation of two-
photon absorption strengths with meta-GGA functionals for the first time.

## Benchmarking meta-GGA functionals for the calculation of two-photon absorption strengths (Summary of paper $V$ )

In paper $V$, the meta-GGA implementation of paper IV is used to benchmark the performance of meta-GGA functionals for the calculation of nonlinear response properties. A comprehensive benchmark study was carried out on 48 charge-transfer systems (see Fig. 4.3) primarily focused on pure, hybrid, and range-separated GGA and metaGGA functionals.


FIGURE 4.3: Structures of compounds included in the benchmark study.
Consistent with previous studies on this benchmark set ${ }^{80}$, the density functional approximations (DFAs) consistently underestimate the TPA strengths as can be seen in Fig. 4.4, where the TPA strengths calculated using Eqs. (3.135) and Eq. (3.148) are plotted against the corresponding TPA strengths using RI-CC2.


FIGURE 4.4: Two-photon absorption strengths computed using RI-CC2 and density functional approximations for the entire data set.

The TPA strengths in molecules 35-46 are dominated by a single transition as can be seen in Fig. 4.5 where the two-state model TPA strengths calculated using Eq. (3.150) are compared with the TPA strenghts calculating using the residue of the quadratic response function using Eq. (3.135) and Eq. (3.148).


FIGURE 4.5: Comparison of the two-state model (a) and RSP (b) TPA strengths for selected global meta-GGA functionals and a long-range corrected GGA functional, with the RI-CC2 level serving as a reference, for molecules numbered 35-46.

The main reason for the underestimation of TPA strengths has previously been attributed to the underestimation of the difference between the dipole moments of the ground and the excited state ${ }^{80}$. Using the fact that the TPA strengths are dominated by one transition, the excited state dipole moments for the dominant state are calculated using Eq. (3.153) and the dipole moment difference is plotted in Fig. 4.6


FIGURE 4.6: The difference between the excited- state and ground-state dipole moments for the dominant transition in molecules 35-46.

The results for the best global-hybrid meta-GGAs also follow this trend, as illustrated in Fig.4.6. We note that MN15 and M06-2X, which rank among the best DFAs in terms of correlation coefficients (see Fig.4.7) and mean relative errors (see Fig. 4.8 \& Table. 4.1), still underestimate the difference in the dipole moment between the ground and excited states, althought to a lesser extent compared to the best long-range corrected DFA, CAM-B3LYP.


FIGURE 4.7: Pearson-Correlation $\left(r^{2}\right)$ and Spearman-Correlation for the calculation of TPA strengths from the residue of the quadratic response function at the DFT level of theory for molecules 1-48 with RI-CC2 as reference.


FIGURE 4.8: Distribution of relative errors for the calculation of TPA strengths from the residue of quadratic response for molecules 1-48 with CC2 as reference.

| Functional | Mean Relative Error | Mean Signed Relative Error |
| :--- | :--- | :--- |
| MPW1B95 | 32.30 | -0.58 |
| R2SCAN-30 | 34.32 | -6.87 |
| R2SCAN-35 | 35.18 | -19.60 |
| MN15 | 35.33 | -32.48 |
| BB1K | 36.04 | -30.06 |
| B86B95 | 36.22 | 8.22 |
| PW6B95 | 37.47 | 9.34 |
| MPWB1K | 38.52 | -33.97 |
| R2SCAN-40 | 38.75 | -30.70 |
| PBE0 | 39.11 | 12.03 |
| SCAN0 | 39.14 | 0.14 |
| M05 | 39.90 | 1.44 |
| TPSS0 | 40.24 | 12.00 |
| M06 | 41.53 | 4.79 |
| PWB6K | 41.66 | -38.07 |
| R2SCAN-45 | 44.88 | -40.30 |
| M06-2X | 47.29 | -47.29 |
| M05-2X | 48.81 | -48.81 |
| CAM-B3LYP | 53.07 | -53.05 |

TABLE 4.1: Mean relative error, mean signed relavtie error, min and max relative errors for the calculation of two-photon absorption strengths with the residue of the quadaratic response function. Reference: RI-CC2

In regards to the performance on the prediction of excited state dipole moments, the meta-GGA functionals did exceptioanlly well as can be seen in Fig. 4.9


FIGURE 4.9: Pearson-Correlation $\left(r^{2}\right)$ and Spearman-Correlation for the calculation of excited-state dipole moments for molecules 35-46 at the DFT level of theory with RI-CC2 as reference.

The functionals MN15, BB1K and MPWB1K displayed the best performance both in terms of correlation coefficients and mean relative errors as can be seen in Fig.4.10


FIGURE 4.10: Distribution of relative errors for the calculation of excitedstate dipole moments at the DFT and RI-CC2 level of theory for molecules 35-46.

In conclusion, the assessed meta-GGA functionals show promising performance in linear correlation and mean relative errors when compared to RI-CC2 for two-photon absorption strength calculations. Additionally, they exhibit significant improvements in accuracy and linear correlation against RI-CC2 in determining excited state dipole moments.

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Papers

Paper I VeloxChem: A Python-driven density-functional theory program for spectroscopy simulations in high-performance computing environments.
Zilvinas Rinkevicius, Xin Li, Olav Vahtras , Karan Ahmadzadeh Manuel Brand, Magnus Ringholm, Nanna Holmgaard List, Maximilian Scheurer, Mikael Scott, Andreas Dreuw, Patrick Norman.
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Paper II Efficient implementation of isotropic cubic response functions for two-photon absorption cross sections within the self- consistent field approximation.
Karan Ahmadzadeh, Mikael Scott, Manuel Brand, Olav Vahtras, Xin Li, Zilvinas Rinkevicius, and Patrick Norman.
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Paper III Efficient Kohn-Sham density-functional theory implementation of isotropic spectroscopic observables associated with quadratic response functions.
Karan Ahmadzadeh, Xin Li, Zilvinas Rinkevicius, and Patrick Norman
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Paper IV Efficient Kohn-Sham density-functional theory implementation of isotropic spectroscopic observables associated with cubic response functions going beyond the generalized gradient approximation.
Karan Ahmadzadeh, Xin Li, Zilvinas Rinkevicius, and Patrick Norman
(Manuscript)
Paper V Benchmarking Two-Photon Absorption Cross Sections: A Comparative study going beyond the generalized gradient approximation.
Karan Ahmadzadeh, Xin Li, Zilvinas Rinkevicius, and Patrick Norman
(Manuscript)

## AUTHOR'S CONTRIBUTIONS

In Paper I, I contributed to the software. In Paper II, I performed all the calculations, derived and implemented the tensor-average method, conceptualized the subspace extraction technique, and wrote the manuscript. In Paper III, I handled all calculations, derived all equations, conceptualized the proof establishing the generalizability of the tensor-average method in the context of density functional theory, and authored the manuscript. For Paper IV, I derived all equations, implemented the methods, and wrote the manuscript. In Paper $\mathbf{V}$, I conducted all the calculations and wrote the manuscript.

