This is to certify that the

dissertation entitled

DERIVATIVES OF MOLECULAR
ELECTROMAGNETIC PROPERTIES USING
NONLOCAL SUSCEPTIBILITY DENSITIES

presented by

EDMUND LEO TISKO

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemical Physics

Kath C Hunt
Major professor
Katharine C. Hunt

Date 30 July 1998

DERIVATIVES OF MOLECULAR ELECTROMAGNETIC PROPERTIES USING NONLOCAL SUSCEPTIBILITY DENSITIES

By

Edmund Leo Tisko

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1998

ABSTRACT

DERIVATIVES OF MOLECULAR ELECTROMAGNETIC PROPERTIES USING NONLOCAL SUSCEPTIBILITY DENSITIES

by

Edmund L. Tisko

This thesis presents three analytic derivative relationships. The underlying concept of these three relationships is connecting the change of a molecular property to other well-defined molecular properties. The foundation of this work lies in nonlocal polarizability density theory. The nonlocal polarizability density characterizes the polarization at one point in a molecule due to its reaction with an electric field at another point in the molecule.

In the first part, the derivative of the electronic hyperpolarizability with respect to a Cartesian nuclear coordinate is related to the nonlocal second hyperpolarizability density, the nuclear charge and the dipole propagator. The derivation uses the derivatives of the wavefunctions and operators that comprise the six-term hyperpolarizability. These derivatives, which are also derived, are substituted into the hyperpolarizability to yield a sixty-term expression. The initial result is manipulated algebraically in a nontrivial way to yield the equality. A brief review of hyper-Raman scattering theory is given. Recent applications of hyper-Raman scattering are considered.

In the second part, a new expression for the derivative of the polarization propagator with respect to an arbitrary coordinate is derived in terms of the quadratic polarization

propagator and a sum of polarization propagators. The derivation involves calculating the derivative of a creation and annihilation operator pair with respect to an arbitrary parameter. Then the propagator derivative is calculated via the derivatives of many-electron wavefunctions. Past work calculating the derivatives of molecular properties using polarization propagator techniques is briefly reviewed.

The third part concerns finding an expression for the derivative of the electronic magnetic moment with respect to nuclear momentum and its relationship to a nonlocal magnetizability density. The magnetizability density has a structure similar to the chemical shift. The relationship is found by considering the magnetic field produced by a moving nucleus as a perturbation on the electronic structure. The ground state wavefunctions are corrected to first order in perturbation theory using the nuclear magnetic field as the perturbation. The corrected wavefunctions are used to calculate the expectation value of the magnetic moment. When the derivative of this expectation value is taken with respect to nuclear momentum, its relationship with the nonlocal chemical shift density is uncovered. The result is correct when adiabatic wavefunctions that go beyond the Born-Oppenheimer approximation are used. The physical content of the equation is interpreted as a description of intramolecular magnetic response.

Other possible paths to a complete susceptibility theory are considered. One path involves substitution of 4-currents into the definition of the nonlocal polarizability density. Other paths arise from an initial consideration of the relativistic Dirac equation and subsequent analysis using the Gordon decomposition and the Foldy-Wouthuysen transformation.

The heavens declare the glory of God;

The sky proclaims its builder's craft.

One day to the next conveys that message;

One night to the next imparts that knowledge.

There is no word or sound,

No voice is heard;

Yet their report goes forth through all the earth,

Their message, to the ends of the earth.

The people who walked in darkness have seen a great light;

Upon those who dwelt in the land of gloom a light has shone.

You have brought them abundant joy and great rejoicing,

As they rejoice before you as at the harvest

For the yoke that burdened them, the pole on their shoulder,

And the rod of their taskmaster you have smashed.

For a child is born to us, a son is given us;

Upon his shoulder dominion rests.

ACKNOWLEDGMENTS

My profound thanks and gratitude to God who has given me the ability and opportunity to ponder His marvelous and awesome Creation.

I will always be appreciative of the great patience and generosity shown to me by my research mentor, Dr. Katharine L. C. Hunt. Her treatment of me gives me a goal for the treatment of my own students. Because of her confidence in me, another physical chemistry professor is on the loose.

My thanks to Dr. Richard H. Schwendeman who has served as my second reader with much attention to detail. Thanks to the other members of my research committee, Dr. Gary J. Blanchard, Dr. James F. Harrison and Dr. James E. "Ned" Jackson who have given me encouragement, often unknowingly, during periods of great trial.

My thanks to the members of the Hunt group who have helped me understand the incomprehensible: Dr. Xiaoping Li, Dr. Pao-Hua Liu, Dr. Olga Jenkins, Sandjaja Tjahajadiputra, Chetan Ahuja and Mark Champagne.

My gratitude to my father, Thomas F. Tisko, whose love of learning has been infectious. I am forever indebted to my mother, Marie Ellen Tisko, for her kind encouragement throughout my entire 26 year educational career. Thanks to my brother, Thomas F. Tisko, whose own quest for excellence has been an inspiration. Thanks to my sister, Therese M. Warner, for her good humor and her faith.

Finally I am grateful for my wife, Christina, who has had much to endure as I completed this research and thesis. I truly hope that its completion is a comfort to you. Note to Joey, Jamie, John and Mary(?): Daddy's finally coming home.

TABLE OF CONTENTS

KEY TO SYMBOLS AND NOTATION

Symbols

Greek

α	polarizability, polarizability density
$\alpha_{\alpha\beta}$	$\alpha\beta$ component of polarizability, polarizability density
α_1, α_2, α_3, β	noninvariant Dirac matrices
β	hyperpolarizability, hyperpolarizability density
γ	second hyperpolarizability, second hyperpolarizability density
γ	Lorentz factor
γ_0, γ_1, γ_2, γ_3	invariant Dirac matrices
δ_{mn}	Kronecker delta $\delta_{mn} = 1$ if $m = n$; $\delta_{mn} = 0$ if $m \neq n$
ε_0	permittivity of free space
η	arbitrary parameter
$\theta(t - t')$	Heaviside step function
μ_α	αth component of dipole, dipole density
μ_0	permeability of free space
$\bar{\mu}$	electronic magnetic moment
μ_B	Bohr magneton
μ_N	nuclear magneton
λ	arbitrary parameter
λ	gauge function

$\bar{\pi}$	canonical linear momentum, $\bar{\pi} = \bar{p} - e\bar{A}$
$\rho, \rho(\bar{r})$	charge density, charge density at point $\bar{r}$
$\rho(t)$	N-electron density operator
$\rho(\bar{r}, t)$	single-electron density operator
ρ_{κ}^{λ}	ground state expectation value of the replacement operator a_{κ}^{λ}
$\bar{\sigma}$	Pauli spin matrix
$\sigma_{\alpha\beta}^{HF}(\bar{r}, \bar{r}')$	nonlocal high-frequency chemical shift density
ϕ	basis function
ϕ	electrostatic potential
$\chi^{(3)}$	third order susceptibility
$\chi(t, t')$	density time correlation function
$\chi_{\rho\rho}(E)$	energy dependent density correlation function
$\chi_{\alpha}^{\rho m}$	αth component of the charge-current susceptibility density
ψ	basis function
ω	frequency
$\omega_1, \omega_2, \omega', \omega''$	distinct frequencies
ω_{σ}	sum of incident frequencies
ω_Q	vibrational frequency of normal mode coordinate
ω_{m0}	transition frequency $\omega_{mo} = \omega_m - \omega_0$
Γ_n	inverse of the excited state radiative lifetime
$\Pi_{kl}^{ij}(\omega), \Pi_{\kappa,\kappa'}^{\lambda,\lambda'}(\omega)$	polarization propagator

$\Pi^{\lambda,\lambda',\lambda''}_{\kappa,\kappa',\kappa''}(\omega)$	nonlinear (quadratic) polarization propagator
Σ'	summation where ground state eigenfunction is not included
$\sum\limits_{\{n_k\}}$	summation over the n_k set of occupation numbers
Ψ	wavefunction
Ω_{m0}	transition frequency with damping $\Omega_{m0} = \omega_{m0} - i\Gamma_m/2$

Roman

a	annihilation operator
$a^\dagger$	creation operator
a^λ_κ	replacement operator, $a^\lambda_\kappa = a^\dagger_\lambda a_\kappa$
c	speed of light
e	charge of an electron
g	magnetogyric ratio of the electron
g_α	magnetogyric ratio of the αth nucleus
h_0	single-electron Hamiltonian operator
$\hbar$	reduced Planck's constant $\hbar = h/2\pi$
j, j_e	current, electronic current
$\bar{l}$	electronic orbital angular momentum
m, m_e	electron mass
$\overline{m}_e$	electronic magnetic moment, electronic magnetization density
m_0	rest mass of a particle
n	unspecified multi-electron state

n_i	occupation number of ith state as in $n_{1s\alpha}$
$\bar{p}$	mechanical linear momentum
$\bar{p}^K$	mechanical linear momentum of nucleus K
$\bar{r},\bar{r}',\bar{r}'',\bar{r}'''$	distinct positions within molecular charge distribution
r_{ij}	distance between point $\bar{r}_i$ and $\bar{r}_j$
$\bar{s}_i$	spin of the ith electron
$\bar{v}$	velocity

A_ω	amplitude of sinusoidal wave
$\bar{A}$	vector potential
$\bar{B}$	magnetic field, magnetic induction
$B_n(\bar{r})$	magnetic field of nucleus at point $\bar{r}$
$C(\{\omega_i\}\rightarrow\{-\omega_i\})$	complex conjugation operator, see pg. 17
$\bar{D}$	electric displacement field
E, E_0, E_n	energy, ground state energy, energy of state n
$E_z(\omega_i)$	z-component of electric field with frequency ω_i
$\mathcal{E}$	energy
$\bar{F}^e(\bar{r},\omega)$	applied electric field with frequency ω at point $\bar{r}$
$\bar{F}^K$	electric field from the Kth nucleus
$F^{\mu\nu}, F_{\mu\nu}$	electromagnetic field tensor
$G(\omega)$	reduced resolvent

$\mathcal{H}$	Hamiltonian
$\bar{H}$	magnetic field
$\bar{I}_{\alpha}$	spin of the αth nucleus
I_{xz}	scattering intensity in z direction from incident light in x direction
$\mathrm{Im}(z)$	imaginary part of z
${}^{1}J(H, C)$	first-order spin-spin coupling constant
${}^{2}J(H, H)$	second-order spin-spin coupling constant
${}^{3}J(H, F)$	third-order spin-spin coupling constant
${}^{TS}J(P, P)$	through-space spin-spin coupling constant
$\mathcal{L}$	Lagrangian
M^{K}	mass of nucleus K
$\bar{M}$	magnetization
N	number of electrons
$\bar{P}(\bar{r},\omega)$	polarization with frequency ω at point $\bar{r}$
$P_{\alpha}^{0}(\bar{r})$	fluctuating polarization at point $\bar{r}$
P_{12}	permutation operator, see pg. 39
Q	normal-mode coordinate
$\bar{R}^{K}$	position of the Kth nucleus
$R(\omega)$	reduced resolvent
S_{λ}	summation of operator exchanges to state λ, see pg. 51
$\mathbf{T}_{\alpha\beta}\left(\bar{r},\bar{R}^{K}\right)$	component $\alpha\beta$ of the dipole propagator

V	potential energy
$\overline{V}$	vortex function, see pg. 71
Z	charge in multiples of e
Z^K	charge of nucleus K

Miscellaneous

$\partial^\mu, \partial_\mu$	four-dimensional differentiation operator, see pg. 80
∇, ∇_α	del operator, αth component of del operator
$\wp_0 = \lvert 0\rangle\langle 0\rvert$	ground-state projection operator
$\wp_{\beta\gamma}, \wp_{\beta\gamma\delta}$	permutator of components β and γ; permutator of β, γ and δ
0	ground state, DC electric field, time component in 4-vector
$\lvert\varnothing\rangle$	vacuum state

Notations

Subscripts on vectors or tensors indicate Cartesian components of the vector or tensor.

Indices used for specific components are x, y, and z.

Indices used for arbitrary components are α, β, γ, δ and ε.

In Chapter 5, μ, ν and σ refer to components in four-dimensional space, while i, j and k refer to components in three-dimensional space.

$\langle \psi \lvert O \rvert \phi \rangle$	The bra-ket notation is used where $\langle \psi \lvert O \rvert \phi \rangle = \int \psi^{*} \hat{O} \, \phi \, d\tau$ and $d\tau$ is the differential volume element that may include summation over spin indices and/or integration over time depending on the context.

Densities are expressed as a function of positions and frequencies, as in the example $\beta_{\beta\gamma\delta}(\bar{r},\bar{r}',\bar{r}'';-\omega_{\sigma};\omega_{1},0)$ where $\bar{r},\bar{r}'$ and $\bar{r}''$ are positions within the molecule, $-\omega_{\sigma}$ is the frequency of the molecular response to incident frequencies ω_{1} and 0 (0 indicating a DC electric field).

$\hat{A}$	The caret above A indicates A is quantum mechanical operator.
$\bar{r}$	The bar above r indicates r is three-dimensional vector.
T	Bold face indicates a tensor or in Chapter 5 may indicate a four-dimensional vector.

The following symbols are used to label basis functions:

i, j, k, l and m $\qquad$ $\lambda,\lambda',\lambda'',\kappa,\kappa'$ and κ''.

$[\hat{A},\hat{B}]$	Commutator between operators A and B, $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$.
$\{\hat{A},\hat{B}\}$	Anticommutator between operators A and B, $\{\hat{A},\hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$.
$G^{*}(\omega)$	The asterisk indicates the complex conjugate of $G(\omega)$.
$\langle A \rangle$	The brackets indicate an average of the quantity A.
$\overline{A} \cdot \overline{B}$	The dot product between vectors $\overline{A}$ and $\overline{B}$
$\overline{A} \times \overline{B}$	The cross product between vectors $\overline{A}$ and $\overline{B}$
$\nabla \cdot \overline{A}$	The divergence of vector $\overline{A}$
$\nabla \times \overline{A}$	The curl of $\overline{A}$

CHAPTER 1: INTRODUCTION

The Derivatives of Molecular Properties and Nonlocal Susceptibility Densities

This thesis is comprised of three parts. The underlying concept of these three parts is relating the change of a molecular property to other well defined molecular properties. In the first part, the derivative of the electronic hyperpolarizability with respect to a Cartesian nuclear coordinate is related to the nonlocal second hyperpolarizability density, the nuclear charge and the dipole propagator. In the second part, a new expression for the derivative of the polarization propagator with respect to an arbitrary coordinate is derived in terms of the quadratic polarization propagator and a sum of polarization propagators. The third part, contained in chapters four and five, concerns finding an expression for the derivative of the electronic magnetic moment with respect to nuclear momentum and its relationship to a nonlocal magnetizability density.

The foundation of this work lies in nonlocal polarizability density theory. The nonlocal polarizability density characterizes the polarization at one point in a molecule due to its reaction with an electric field at another point in the molecule. The densities may be described as the distribution of a molecule's polarizable matter. Nonlocal polarizability densities have been used to describe optical rotation,[1] dielectric properties of condensed matter,[2] and light scattering in dense fluids.[3] Hunt has further exploited the properties of nonlocal polarizability theory in the theory of intermolecular forces,[4,5] intermolecular electronic forces on nuclei,[6,7,8] nonadditive three-body intermolecular forces,[9] zero temperature homogeneous electron gases,[10] molecular softness,[11] and vibrational force constants and anharmonicities.[12] Nonlocal susceptibilities densities have also been used in the construction of a theory of vibrational circular dichroism.[13] Closer to the purposes of this work, nonlocal susceptibility densities have been used in expressions for the derivatives of molecular properties.[11,13,14,15]

Hyperpolarizability Derivative

The derivation of the nuclear coordinate derivative of the hyperpolarizability is found in Chapter 2.[16]

$$\partial\beta_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}',\mathbf{r}'';-\omega_\sigma;\omega_1,\omega_2)/\partial\mathbf{R}_\delta^K = \int d\mathbf{r}'''\gamma_{\alpha\beta\gamma\varepsilon}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';-\omega_\sigma;\omega_1,\omega_2,0)Z^K\mathbf{T}_{\varepsilon\delta}(\mathbf{r}''',\mathbf{R}^K)\,.\text{(1)}$$

The derivation starts with the Orr and Ward's expression for the hyperpolarizability.[17] Then derivatives of the wavefunctions and operators that comprise the six-term hyperpolarizability are substituted into one term of the hyperpolarizability to yield a ten- term expression. The derivatives used are derived in detail in Appendix A. The initial result is manipulated algebraically in a nontrivial way to yield the equality in Equation (1). The form of the second hyperpolarizability density in Equation (1) was adapted from the expression for the second hyperpolarizability in Orr and Ward.[17] The complete derivation involves a sixty-term expression which has been included in Appendix B.

The nuclear-coordinate derivative of the hyperpolarizability yields intensity information for nonresonant vibrational hyper-Raman scattering.[18] Hyper-Raman scattering is the nonlinear analog of Raman scattering. In a hyper-Raman scattering event, two quanta are absorbed in taking the scatterer from its initial state to a virtual electronic state. Then, as in Raman scattering, one quantum is emitted as the scatterer relaxes into an excited or deexcited vibrational state. A brief review of hyper-Raman scattering theory is given. Recent applications of hyper-Raman scattering are also considered.

Polarization Propagator Derivative

Chapter 3 contains the derivation of the derivative of the polarization propagator[19,20,21] that was found to be related to the quadratic polarization propagator[20,22] and a sum of polarization propagators.

$$
\begin{aligned}
\frac{\partial \Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)}{\partial \eta} &= \left[\frac{\partial h_0}{\partial \eta}\right]^{\kappa''}_{\lambda''} \Pi^{\lambda,\lambda',\lambda''}_{\kappa,\kappa',\kappa''}(\omega,0) \\
&+ \sum_{m\neq\lambda} C_{\lambda m}\Pi^{m,\lambda'}_{\kappa,\kappa'}(\omega) + \sum_{m\neq\lambda} C_{\lambda' m}\Pi^{\lambda,m}_{\kappa,\kappa'}(\omega) \qquad (2) \\
&+ \sum_{k\neq\kappa'} C^{*}_{\kappa' k}\Pi^{\lambda,\lambda'}_{\kappa,k}(\omega) + \sum_{k\neq\kappa} C^{*}_{\kappa k}\Pi^{\lambda,\lambda'}_{k,\kappa'}(\omega).
\end{aligned}
$$

The relationship between the polarization propagator derivative and the quadratic polarization propagator was prompted by a relationship found by Hunt *et al.*[15] between the nuclear coordinate derivative of the electronic molecular polarizability and the electronic molecular hyperpolarizability density. A general relationship between derivatives of linear response properties and quadratic response properties was suggested by this specific relationship between polarizabilities.

The polarization propagator is employed in the calculation of linear response properties.[21] Polarization propagators can be constructed in a conventional fashion as a sum-over-states or in a second quantized fashion using a sum over creation and annihilation operators and the techniques of "superoperator" algebra.[23] In the derivation of the derivative of the polarization propagator, the second quantized version is used. The advantage of second quantization comes from how the many-electron wavefunction is managed. The antisymmetrical nature of the many-electron wavefunction follows from the change of the wavefunction's sign when two electrons are interchanged. In second quantization, the antisymmetry of the wavefunction is ensured by the use of anticommutation relations between creation and annihilation operators. The relationships between the anticommutation relations and Slater determinants are discussed in this chapter.

The derivation involves techniques found in Appendices A and C. However, the novel portion of the derivation involves calculating the derivative of a creation and annihilation operator pair with respect to an arbitrary parameter. The derivative is calculated via the derivatives of many-electron wavefunctions. Throughout the derivation, the second quantization formalism is used; however, portions of the derivations are done in parallel with the Slater determinant formalism for pedagogical reasons.

The advantage of Equation (2) is proposed to be in the calculation of derivatives of molecular properties such as molecular gradients and Hessians.[24] The derivatives of many other molecular properties have been computed using analytical and numerical techniques. Past work calculating the derivatives of molecular properties using polarization propagator techniques is briefly reviewed in Chapter 3. Different possible applications of Equation (2) are discussed as well.

Magnetic Moment Derivative

In chapter 4, the derivative of the electronic magnetic moment with respect to nuclear momentum is found to be related to the molecular high-frequency ("paramagnetic") chemical shift density from the theory of nuclear magnetic resonance.[25,26]

$$\frac{\partial \overline{m}_{e\alpha}(\bar{r}')}{\partial p_z} = -\frac{\mu_0 Ze}{4\pi M} \times \int \sigma_{\alpha\beta}^{HF}(\bar{r},\bar{r}')\overline{V}_\beta \, d^3r \,. \tag{3}$$

The relationship is found by considering the magnetic field produced by a moving nucleus as a perturbation on the electronic structure. The ground state wavefunctions are corrected to first order in perturbation theory using the nuclear magnetic field as the perturbation. The corrected wavefunctions are used to calculate the expectation value of the magnetic moment. When the derivative of this expectation value is taken with respect to nuclear momentum, its relationship with the nonlocal chemical shift density is uncovered. The result is correct when wavefunctions that go beyond the Born-Oppenheimer approximation are used.[27] A brief review of research using nuclear momentum derivatives, especially with application to vibrational circular dichroism spectroscopy, is given.

Equation (3) demonstrates that within a molecule the electronic response to an internal magnetic field occurs via a molecular property that describes the response to an external magnetic field. The analogous equivalence has been shown by Hunt *et al.*[14,15] for intramolecular electronic response to internal electric fields.

Chapter 5 considers possible routes to a more complete theory of intramolecular electromagnetic response. The first consideration involves classical electromagnetic theory in the context of special relativity. In the relativistic formulation of classical electrodynamics, the electric and magnetic fields are not two different vector quantities, but, rather they are both components of a second-rank four-dimensional tensor. The relativistic current density is a four dimensional vector that includes as the "time" component, the charge density. Similarly, the electrostatic potential and the magnetic vector potential are integrated into a four-dimensional vector potential. Molecular polarization and magnetization fields are not distinct, but rather the components of a four dimensional second-rank tensor. All of the quantities and laws of electrodynamics can be formulated very compactly in a relativistic formulation. The four Maxwell equations that fundamentally describe all electromagnetic phenomena become two equations in the relativistic formulation.

Maaskant and Oosterhoff[1] originally formulated the nonlocal polarizability density in terms of current densities. Hunt[4] reformulated polarizability density in terms of polarization operators. However Hunt's reformulation is derived with the assumption that the applied field is obtained from a scalar potential. It is suggested that a complete nonlocal electromagnetic susceptibility density theory could be found from the removal of this restriction and use of four-dimensional vector calculus.

A relativistically consistent four-dimensional quantum theory for electrons was constructed in the early days of quantum mechanics by Dirac.[28,29] In addition to increased accuracy in the calculation of atomic energies, the theory incorporated, in a fundamental way, the spin of the electron. However, a disadvantage of the theory was the appearance of energy states associated with the antimatter analog of the electron, the positron. In the description of electronic interactions with electric or magnetic fields, the positron states can not be neglected. Positrons in the description of low-energy interactions such as molecular interactions are difficult to conceptualize.

Fortunately, for low-energy interactions, techniques have been found that can remove the "positron" portion of energies in exchange for a series expansion of "electron" energies. The first and most commonly used expansion is the Foldy-Wouthuysen transformation.[30,31] In this nonrelativistic formulation of the Hamiltonian (nonrelativistic because it no longer involves positrons), several hyperfine terms are found that depend on the nuclear momentum and the nuclear magnetic moment. It is suggested that such terms be included in an application of perturbation theory to find new magnetic phenomena and novel explanations for discovered phenomena.

REFERENCES

[1] W. J. A. Maaskant and L. J. Oosterhoff, Molec. Phys. **8**, 319 (1964).

[2] L. M. Hafkensheid and J. Vlieger, Physica **75**, 57 (1974); **79**, 517 (1975).

[3] T. Keyes and B. M. Ladanyi, Molec. Phys. **33**, 1271 (1977).

[4] K. L. C. Hunt, J. Chem. Phys. **78**, 6149 (1983); **80**, 393 (1984).

[5] Y. Q. Liang and K. L. C. Hunt, J. Chem. Phys. **98**, 4626 (1993).

[6] K. L. C. Hunt, J. Chem. Phys. **92**, 1180 (1990).

[7] K. L. C. Hunt and Y. Q. Liang, J. Chem. Phys. **95**, 2549 (1991).

[8] P.-H. Liu and K. L. C. Hunt, J. Chem. Phys. **100**, 2800 (1994).

[9] X. Li and K. L. C. Hunt, J. Chem. Phys. **105**, 4076 (1996).

[10] R. Nimalakirthi and K. L. C. Hunt, J. Chem. Phys. J. Chem. Phys. **98**, 3066 (1993).

[11] P.-H. Liu and K. L. C. Hunt, J. Chem. Phys. **103**, 10597 (1995).

[12] K. L. C. Hunt, J. Chem. Phys. **103**, 3552 (1995).

[13] K. L. C. Hunt and R. A. Harris, J. Chem. Phys. **94**, 6995 (1991).

[14] K. L. C. Hunt, J. Chem. Phys. **90**, 4909 (1989).

[15] K. L. C. Hunt, Y. Q. Liang, R. Nimalakirthi and R. A. Harris, J. Chem. Phys. **91**, 5251 (1989).

[16] E. L. Tisko, X. Li and K. L. C. Hunt, J. Chem. Phys. **103**, 6873 (1995).

[17] B. J. Orr and J. F. Ward, Molec. Phys. **20**, 513 (1971).

[18] D. A. Long, in *Nonlinear Raman Spectroscopy and its Chemical Applications*, edited by W. Kiefer and D. A. Long, NATO ASI Ser. C **93** (Reidel, Dordrecht, 1982), pp. 99-130, 165-179.

[19] J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry* (Academic Press, New York, 1973).

[20] J. Olsen and P. Jørgensen, J. Chem. Phys. **82**, 3235 (1985).

[21] J. Oddershede, Adv. Quant. Chem. **11**, 275 (1978).

[22] H. Hettema, H. J. A. Jensen, P. Jørgensen and J. Olsen, J. Chem. Phys. **97**, 1174 (1992).

[23] P. Jørgensen and J. Simons, *Second Quantization-Based Methods in Quantum Chemistry* (Academic Press, New York, 1981).

[24] *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, P. Jørgensen and J. Simons, eds. NATO ASI Series C: Vol. **166** (D. Reidel Pub. Co., Dordrecht, 1985).

[25] N. F. Ramsey, *Molecular Beams* (Oxford University Press, Oxford, 1956).

[26] C. P. Slichter, *Principles of Magnetic Resonance* 2nd ed. (Springer-Verlag, Berlin, 1978).

[27] L. A. Nafie and T. B. Freedman, J. Chem. Phys. **78**, 7108 (1983).

[28] P. A. M. Dirac, Proc. Roy. Soc. Lon. **A117**, 610 (1928); **A126**, 360 (1930).

[29] R. H. Landau, *Quantum Mechanics II*, 2nd ed. (John Wiley and Sons, New York, 1996).

[30] L. L. Foldy and S. A. Wouthuysen, Phys. Rev. **78**, 29 (1950).

[31] R. E. Moss, *Advanced Molecular Quantum Mechanics* (Chapman and Hall, London, 1973).

CHAPTER 2: RELATION OF HYPERPOLARIZABILITY DERIVATIVES TO SECOND HYPERPOLARIZABILITY DENSITIES

Introduction

In this chapter, a new analytical result is derived for the nuclear coordinate dependence of the electronic hyperpolarizability $\beta(-\omega_\sigma;\omega_1,\omega_2)$, which gives rise to nonlinear optical processes such as frequency-sum and difference generation.[1,2,3,4,5,6] In earlier numerical work, derivatives of β with respect to nuclear coordinates have been estimated semiempirically[7] and calculated *ab initio*.[8,9,10,11] This chapter focuses on the interpretation of the β derivatives via their connection to a different molecular property. The derivative of $\beta(-\omega_\sigma;\omega_1,\omega_2)$ with respect to coordinate $\overline{R}^K$ of nucleus K is shown to depend on the second hyperpolarizability density $\gamma(\bar{r},\bar{r}',\bar{r}'',\bar{r}''';-\omega_\sigma;\omega_1,\omega_2,0)$ for the electronic state, on the nuclear charge, and on the dipole propagator $T(\bar{r}''',\overline{R}^K)$ from $\overline{R}^K$ to $\bar{r}'''$. This result holds because the electrons within a molecule respond to changes $\delta\overline{F}^K$ in the Coulomb field of the nucleus, due to an infinitesimal shift in the position of nucleus K, via the same nonlocal electrical susceptibilities that characterize their response to external electric fields.

Nonlocal Polarizability Densities, Polarization and Internal/External Electric Fields

Nonlocal polarizability densities $\alpha(\bar{r},\bar{r}';-\omega;\omega)$ [12,13,14,15] and nonlocal hyperpolarizability densities $\beta(\bar{r},\bar{r}',\bar{r}'';-\omega;\omega-\omega',\omega')$ and $\gamma(\bar{r},\bar{r}',\bar{r}'',\bar{r}''';-\omega;\omega-\omega'-\omega'',\omega',\omega'')$ [16] describe the distribution of polarizability within a molecule. When an external field $F^{e}(\bar{r},\omega)$ is applied, the electronic polarization $P(\bar{r},\omega)$ at point $\bar{r}$ is[16]

$$\begin{aligned}\mathbf{P}(\bar{r},\omega) = {} & \mathbf{P}_0(\bar{r},\omega)+\int d\bar{r}'\,\alpha(\bar{r};\bar{r}',\omega)\cdot\mathbf{F}(\bar{r}',\omega)\\ & +\frac{1}{2}\int_{-\infty}^{\infty} d\omega'\int d\bar{r}'d\bar{r}''\,\beta(\bar{r};\bar{r}',\omega-\omega',\bar{r}'',\omega'):\mathbf{F}(\bar{r}',\omega-\omega')\,\mathbf{F}(\bar{r}'',\omega')\\ & +\frac{1}{6}\int_{-\infty}^{\infty} d\omega'\int_{-\infty}^{\infty} d\omega''\int d\bar{r}'d\bar{r}''d\bar{r}'''\,\gamma(\bar{r};\bar{r}',\omega-\omega'-\omega'',\bar{r}'',\omega',\bar{r}''',\omega'')\,\vdots\,\mathbf{F}(\bar{r}',\omega-\omega'-\omega'')\\ & \times\mathbf{F}(\bar{r}'',\omega')\,\mathbf{F}(\bar{r}''',\omega'')+\cdots\quad .\end{aligned} \tag{1}$$

In equation (1), $P_0(\bar{r},\omega)$ denotes the polarization in the absence of the external field, and symbols such as $\cdot$, $:$, and $\vdots$ indicate tensor contractions. The convention used by Orr and Ward[17] and by Bishop[18] is followed in showing the frequency dependence of the susceptibilities. The polarization in equation (1) is related to the charge density by

$$\nabla\cdot\bar{P}(\bar{r},\omega) = -\rho(\bar{r},\omega) \tag{2}$$

and the same equation relates the polarization and charge density operators, $\hat{P}(\bar{r})$ and $\hat{\rho}(\bar{r})$. Thus the polarization contains the full information about the electronic charge redistribution of a molecule in the applied field, and not simply information about its dipole density.

The nonlocal polarizability density, $\alpha(\bar{r},\bar{r}';-\omega;\omega)$, is a tensor quantity which describes the linear response to the applied field, and it can be defined as[15,16]

$$\alpha_{\alpha\beta}(\bar{r},\bar{r}') = \langle 0|\hat{p}_{\alpha}(\bar{r})G(\omega)\hat{p}_{\beta}(\bar{r}')|0\rangle + \langle 0|\hat{p}_{\beta}(\bar{r}')G^{*}(-\omega)\hat{p}_{\alpha}(\bar{r})|0\rangle, \tag{3}$$

where $G(\omega)$ is the reduced resolvent operator

$$G(\omega) = (1-\wp_0)(\mathcal{H}-E_0-\hbar\omega)^{-1}(1-\wp_0). \tag{4}$$

$\mathcal{H}$ is the unperturbed molecular Hamiltonian, E_0 is the unperturbed ground-state energy, and $\wp_0$ is the ground-state projection operator $\wp_0 = |0\rangle\langle 0|$. Integration of $\alpha(\bar{r},\bar{r}';-\omega;\omega)$ over all space with respect to $\bar{r}$ and $\bar{r}'$ yields the molecular polarizability, $\alpha(-\omega;\omega)$. As in the work of Orr and Ward,[17] damping is treated approximately by allowing for complex eigenvalues of $\mathcal{H}$,

$$E_n = \hbar(\omega_n) - i\Gamma_n/2, \tag{5}$$

where Γ_n is the inverse of the excited state radiative lifetime for state $|n\rangle$ (and $\Gamma_0 = 0$).

The nonlocal hyperpolarizability density, $\beta(\bar{r},\bar{r}',\bar{r}'';-\omega;\omega-\omega',\omega')$, yields the lowest-order nonlinear term in the polarization, $\bar{P}(\bar{r},\omega)$, due to concerted action of fields $F^{e}(\bar{r}',\omega-\omega')$ and $F^{e}(\bar{r}'',\omega')$ at $\bar{r}'$ and $\bar{r}''$.[16] The second hyperpolarizability density describes nonlinear response at the next order. Integration of $\beta(\bar{r},\bar{r}',\bar{r}'';-\omega_{\sigma};\omega_1,\omega_2)$ over all space with respect to $\bar{r}$, $\bar{r}'$ and $\bar{r}''$ yields $\beta(-\omega_{\sigma};\omega_1,\omega_2)$ where $\omega_{\sigma} = \omega_1 + \omega_2$. For $\omega_1 = \omega_2$, the hyperpolarizability $\beta(-\omega_{\sigma};\omega_1,\omega_2)$ is the molecular tensor that generates second harmonics of the incident radiation. The intensities of hyper-Rayleigh scattering and second harmonic generation (SHG) depend on this tensor. When $\omega_2 = 0$,

β is the electro-optic tensor which is responsible for DC-induced birefringence. In general, the intensity of sum-frequency generation at $\omega_1 + \omega_2$ depends on $\beta(-\omega_\sigma;\omega_1,\omega_2)$.[1,2,3,4,5,6] Spatial integrals of second hyperpolarizability densities yield electronic properties such as the molecular tensor $\gamma(-3\omega;\omega,\omega,\omega)$ for third-harmonic generation.[19,20,21]

In earlier work, a chain of relations has been established linking permanent moments, linear response, and the lowest-order nonlinear response.[22,23] The change in the electronic dipole moment when nucleus K shifts is determined by $\alpha(\bar{r},\bar{r}';0;0)$, the charge on nucleus K and the dipole propagator from $\bar{R}^K$ to $\bar{r}'$, which gives the change in the Coulomb field of the nucleus, $\delta\bar{F}^K(\bar{r}')$, due to the shift $\delta\bar{R}^K$.[22] The change in the Coulomb field of the nucleus is related to the shift in the coordinate of the nucleus via

$$\partial F^K_\alpha(\bar{r}) = Z^K T_{\alpha\beta}\left(\bar{r},\bar{R}^K\right)\partial R^K_\beta \,. \tag{6}$$

After this equation is applied, the first relationship in the chain of relations is found as

$$\partial\mu_\beta(\bar{r}) / \partial R^K_\alpha = \int d\bar{r}'\alpha_{\beta\gamma}(\bar{r};\bar{r}',0) Z^K T_{\gamma\alpha}(\bar{r}',\bar{R}^K) \,. \tag{7}$$

The change in the electronic dipole moment of a molecule when a nucleus is moved from equilibrium depends on the response of the electrons to the change in the Coulomb field of the nucleus via the nonlocal polarizability density. Similarly, the chain of relations is extended to the change in the polarizability $\alpha(-\omega;\omega)$ since it is determined by $\beta(\bar{r},\bar{r}',\bar{r}'';-\omega;\omega,0)$, $\delta\bar{F}^K$ and equation (6)[22,23] which yields

$$\partial\alpha_{\beta\gamma}(\bar{r};\bar{r}',\omega) / \partial R^K_\alpha = \int d\bar{r}d\bar{r}'d\bar{r}''\beta_{\beta\gamma\delta}(\bar{r};\bar{r}',\omega,\bar{r}'',0) Z^K T_{\delta\alpha}(\bar{r}'',\bar{R}^K) \,, \tag{8}$$

where $\beta_{\beta\gamma\delta}(\bar{r};\bar{r}',\omega,\bar{r}'',0)$ is the nonlocal hyperpolarizability density tensor and the $\beta\gamma\delta$ subscripts indicate the Cartesian indices of a third-rank tensor.

In this chapter, the change in $\beta(-\omega_\sigma;\omega_1,\omega_2)$ due to a shift in the position of the nucleus K is proven to depend on the second hyperpolarizability density and $\delta\bar{F}^K$. This result is expected on physical grounds, as a continuation to higher order of the chain of relations between polarizabilities; however, an explicit derivation is considered useful, because the proof involves transformations of a 60-term perturbation expression. The Born-Oppenheimer approximation is used to determine the parametric dependence of the electronic hyperpolarizability on the nuclear coordinates. In this chapter, only specific terms will be considered. The full 60-term derivation is given in Appendix B of this volume.

Applications of the Hyperpolarizability Derivative

The derivatives in this work are taken with respect to the nuclear coordinates $\bar{R}^K$, while any applied fields $\bar{F}^e$ are held fixed (typically, at $\bar{F}^e = 0$). Hence the chain of relations that links permanent moments, α, β and γ densities differs from well-known relations that apply to derivatives of effective electrical properties taken with respect to the external field strength.[24] The derivative of the effective electrical property of order n, with respect to $\bar{F}^e$, yields the effective property of order n +1, where the following identifications are made: n = 0 for μ, n = 1 for α, n = 2 for β, n = 3 for γ, etc. However, there is an underlying physical connection between the two chains of relations, since changes in electrical properties due to a shift in $\delta\bar{R}^K$, the position of nucleus K within a molecule, are determined by the electronic response to $\delta\bar{F}^K$, the change in the Coulomb field from nucleus K. Relations among the μ, α, β and γ for linear polymethine dyes (push-pull polyenes)[25,26,27] have been suggested based on differentiation with respect to an effective electric field **F** assumed to account for donor-acceptor strength, molecular topology and solvent interactions, in analogy with the approach of Buckingham and Pople.[24] The result obtained in this chapter differs from that of Marder *et al.*[25] in terms of the differentiation variable (**R**^{K} vs. **F**) and in terms of the quantity to which the hyperpolarizability derivative is related (the second hyperpolarizability density vs. the spatially integrated value of the second hyperpolarizability). For an explicit physical connection between the two approaches, a specification of the effective electric field **F** appearing in Marder's work is needed.[25] Such a specification could be made via the change of the effective electric field with respect to a change in the nuclear coordinate $\partial F_\alpha / \partial R_\beta^K$.

The results derived here provide a physical picture of the origin of vibrational hyper-Raman scattering intensities on the *intramolecular* scale. For light of angular frequency ω_i incident on a sample of molecules having the vibrational frequency ω_Q for normal mode Q, the nonresonant hyper-Raman scattering intensity at the frequency $2\omega_i \pm \omega_Q$ depends on $\partial\beta_{\alpha\beta\gamma}(\bar{r},\bar{r}',\bar{r}'';-2\omega_i;\omega_i,\omega_i)/\partial Q$ the derivative of the β hyperpolarizability with respect to the normal-mode coordinate Q.[28,29,30] This derivative, $\partial\beta_{\alpha\beta\gamma}(\bar{r},\bar{r}',\bar{r}'';-2\omega_i;\omega_i,\omega_i)/\partial Q$, is a linear combination of derivatives with respect to Cartesian nuclear coordinates. Additionally, these derivatives of β appear in the *vibrational* contribution to the net molecular second hyperpolarizability,[11,26,27,31,32,33,34,35] reflecting the change in electronic energy induced by an applied field.

Hyper-Raman scattering was predicted theoretically by Güttinger,[28] Decius and Rauch,[36] Kielich,[37] and Li,[38] and first observed by Terhune, Maker and Savage.[39] Reviews of hyper-Raman spectroscopy have been written.[40,41,42,43] For molecules or crystal unit cells with centers of symmetry, hyper-Raman scattering is useful as a probe of molecular vibrations that are silent both in IR absorption and in Raman scattering at frequencies $\omega_i \pm \omega_Q$[29,30,44,45] such as the twisting modes of A_u symmetry in tetrachloroethylene[46] and in cyclohexane,[47] modes of B_{1u}, B_{2u} or E_{2u} symmetry in C_6H_6 and C_6D_6,[48] the F_1 librational mode in crystalline NH_4Cl,[49] and the F_{2u} modes of $SrTiO_3$,[50,51,52,53,54] $BaTiO_3$,[55,56] and $KTaO_3$,[53,57] the A_{2u} mode of $BaTiO_3$,[58,59,60] and the soft-optic mode of $K_{1-x}Li_xTaO_3$.[61] Charge transfer excitons which disrupt the centrosymmetry in semiconductors such as Cu_2O crystals,[62] germanium-doped silica fibres,[63,64] and other inorganic glasses[65] have been investigated with hyper-Raman scattering. The spectroscopy has been used to examine the lattice dynamics of silica polymorphs.[66] For helical polymers, optical phonon dispersion curves can be probed by hyper-Raman experiments at four frequencies, of which two are excluded by IR selection rules.[67]

Hyper-Raman scattering also offers a useful probe of very low-frequency modes of large molecules or crystals--even modes that are IR or Raman active--because interferences are generally reduced.[42,48,50] For example, low-frequency Raman scattering may be masked by intense Rayleigh scattering,[44,48] while the weaker hyper-Rayleigh peak does not overlap the hyper-Raman bands appreciably. For the perovskites near ferroelectric phase transitions,[50] IR measurements are limited in applicability because of unusually broad reflection bands with reflectivities near 1, as well as the shallow penetration of far-IR radiation, which leads to variation in the spectra with surface conditions. Thus, hyper-Raman spectroscopy has been used to determine the imaginary part of the dielectric permittivity $\varepsilon''(\omega)$ at low frequencies for these materials,[50,51,52,53,54,55,56,57] and then combined with IR reflectivity data at higher frequencies, in order to generate the real part $\varepsilon'(\omega)$.[50] Other experimental applications of hyper-Raman scattering have also been reported.[68,69,70,71,72,73]

Surface enhancement of hyper-Raman scattering has been observed for SO_3^{2-} adsorbed on silver powder,[74] dye molecules adsorbed on silver colloids[75,76,77,78,79] (e.g. oxa- and thia-carbocyanines,[76] basic fuchsin,[77] 3-hydroxykynurenine,[77] crystal violet[78,79] and malachite green[79]), and for pyridine[7] and trans-1,2-bis(4-pyridyl)ethylene[80] on silver electrode surfaces or for pyridine on aqueous silver citrate sols.[81]

The electronic property connected to the intensities of vibrational hyper-Raman scattering by this work is the density of the second hyperpolarizability, $\gamma(\bar{r},\bar{r}',\bar{r}'',\bar{r}''';-2\omega;\omega,\omega,0)$. An integration over all space with respect to the spatial variables yields the electronic contribution to the tensor $\gamma(-2\omega;\omega,\omega,0)$ that governs DC electric-field induced second harmonic generation (EFISH) by nondipolar species, and the electronic part (i. e., the nonorientational part) of EFISH intensities for dipolar molecules.[82,83,84,85] The conversion from molecular susceptibilities treated here to the macroscopic EFISH susceptibilities $\chi^{(3)}(-2\omega;\omega,\omega,0)$ depends on the densities and the local field factors at the frequencies 2ω, ω and 0.[84] This conversion is similar to the conversion of the molecular polarizability to the dielectric constant.[86] The susceptibility $\chi^{(3)}(-2\omega;\omega,\omega,0)$ also determines the applied-potential dependence of the optical second-harmonic response of polished surfaces in electrolyte solutions,[87] as shown in studies of the Ag(111) surface in aqueous electrolytes[88] and Si(111)/electrolyte or Si(111)/SiO_2/electrolyte interfaces.[89]

This chapter considers the electronic contributions to the hyperpolarizabilities β and γ, for specified values of the nuclear coordinates. The relative magnitudes of the nuclear contributions to the total molecular β and γ values[11,31,32,33,34,35] depend on the frequencies involved.[6] For example, among processes that depend on the macroscopic susceptibility $\chi^{(3)}$, the vibrational and rotational contributions tend to increase in the order:[6] third harmonic generation, EFISH, degenerate four-wave mixing, AC Kerr effect (optically induced birefringence), CARS (coherent anti-Stokes Raman scattering), and DC Kerr effect (static field induced birefringence). Third harmonic generation and EFISH are the preferred methods of investigating the electronic contribution to γ. These results apply to hyper-Raman intensities that can be described by the nonlinear analog of the Placzek theory. Resonant[90,91,92] and preresonant[93] hyper-Raman scattering are not treated.

Derivation of the Dependence of the Hyperpolarizability on Nuclear Coordinates

The hyperpolarizability density $\beta(\bar{r},\bar{r}',\bar{r}'';-\omega_\sigma;\omega_1,\omega_2)$ satisfies[16]

$$\begin{aligned}\beta(\bar{r},\bar{r}',\bar{r}'';-\omega_\sigma;\omega_1,\omega_2) = \wp_{\beta\gamma}[&\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}^0_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\ &+\langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)\hat{p}^0_\beta(\bar{r}')G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{r})|0\rangle + \langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)\hat{p}^0_\alpha(\bar{r})G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle]\end{aligned} \quad (9)$$

where $\wp_{\beta\gamma}$ denotes the sum of the permutations of $\hat{p}_\beta(\bar{r}')$ and $\hat{p}_\gamma(\bar{r}'')$, simultaneously with their associated frequencies ω_1 and ω_2, respectively, in the expression that follows the operator; $\omega_\sigma = \omega_1 + \omega_2$, and

$$\hat{p}^0_\alpha(\bar{r}) = \hat{p}_\alpha(\bar{r}) - \langle 0|\hat{p}_\alpha(\bar{r})|0\rangle . \tag{10}$$

Full permutation symmetry of $\beta_{\alpha\beta\gamma}$ exists only if damping is neglected. Equation (9) is analogous to Equation (43b) for the spatially integrated hyperpolarizability $\beta_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2)$ given by Orr and Ward.[17]

To find the derivative of $\beta_{\alpha\beta\gamma}(\bar{r},\bar{r}',\bar{r}'';-\omega_\sigma;\omega_1,\omega_2)$ with respect to the nuclear Cartesian coordinate R^K_δ, the derivative of the ground state wavefunction with respect to an arbitrary parameter λ is used.[94]

$$\frac{\partial|0\rangle}{\partial\lambda} = -G(0)\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle . \tag{11}$$

For consistency with the approximate treatment of damping, as in the work of Orr and Ward,[17] the imaginary components of the eigenvalues in off-resonant denominators are neglected; then G*(0) can be replaced by G(0), and the derivative of G(ω) with respect to λ satisfies[23,94]

$$\frac{\partial G(\omega)}{\partial\lambda} = -G(\omega)\frac{\partial(\mathcal{H}-E_0)}{\partial\lambda}G(\omega) + \wp_0\frac{\partial\mathcal{H}}{\partial\lambda}G(0)\,G(\omega) + G(\omega)\,G(0)\frac{\partial\mathcal{H}}{\partial\lambda}\wp_0 . \tag{12}$$

Also[94]

$$\frac{\partial\hat{p}^0_\alpha(\bar{r})}{\partial\lambda} = \langle 0|\frac{\partial\mathcal{H}}{\partial\lambda}G(0)\,\hat{p}_\alpha(\bar{r})|0\rangle + \langle 0|\hat{p}_\alpha(\bar{r})G(0)\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle . \tag{13}$$

If $\lambda = R^K_\delta$, the δ Cartesian coordinate of nucleus K, then[22,23,94]

$$\frac{\partial \mathcal{H}}{\partial R_\delta^K} = -\int d\bar{r}'''\, Z^K p_\varepsilon(\bar{r}''')\mathbf{T}_{\varepsilon\delta}\left(\bar{r}''', \bar{R}^K\right). \tag{14}$$

The change in the inverse lifetimes of the excited states due to an infinitesimal shift in R_δ^K has been neglected. In Equation (14), $\mathbf{T}_{\varepsilon\delta}\left(\bar{r}''', \bar{R}^K\right)$ is the dipole propagator, which determines the field at $\bar{r}'''$ due to the polarization at $\bar{R}^K$; in general,

$$\mathbf{T}_{\alpha\beta}(\bar{r}, \bar{r}') = \nabla_\alpha \nabla_\beta \left(\frac{1}{|\bar{r} - \bar{r}'|}\right). \tag{15}$$

The Einstein convention of summation over repeated Greek subscripts is followed in Equation (14) and below. From Equations (9) through (13), each of the six terms in Equation (9) for $\beta_{\alpha\beta\gamma}\left(\bar{r}, \bar{r}', \bar{r}''; -\omega_\sigma; \omega_1, \omega_2\right)$ generates ten terms when differentiated with respect to R_δ^K. The contribution to the hyperpolarizability derivative from the first term (taken as representative) is

$$\begin{aligned}
&\frac{\partial}{\partial R_\delta^K}\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\gamma^0(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle = \int d\bar{r}'''\, Z^K \mathbf{T}_{\varepsilon\delta}\left(\bar{r}''', \bar{R}^K\right) \\
&\times\left\{\begin{array}{l}
\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\gamma^0(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
+\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\varepsilon^0(\bar{r}''')G(\omega_\sigma)\hat{p}_\gamma^0(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
-\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\langle 0|\hat{p}_\alpha(\bar{r})|0\rangle G(\omega_\sigma)\hat{p}_\gamma^0(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
-\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{P}_\gamma^0(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
-\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\hat{p}_\gamma(\bar{r}'')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
-\langle 0|\hat{p}_\gamma(\bar{r}'')G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
+\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\gamma^0(\bar{r}'')G(\omega_1)\hat{p}_\varepsilon^0(\bar{r}''')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
-\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\gamma^0(\bar{r}'')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
-\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\gamma^0(\bar{r}'')G(\omega_1)\langle 0|\hat{p}_\beta(\bar{r}')|0\rangle G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle \\
+\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\gamma^0(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle
\end{array}\right\}
\end{aligned} \tag{16}$$

The fourth term of this expression contains the fluctuating polarization operator $\hat{p}^0_\gamma(\bar{r}'')$ which can be changed to a total polarization operator $\hat{p}_\gamma(\bar{r}'')$ through the identity[95]

$$\begin{aligned}&\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}^0_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\\ &\quad=\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle.\end{aligned} \tag{17}$$

Similarly, the eighth term has a fluctuating polarization operator, which can be converted to a total fluctuation operator. Also with the definition of the fluctuating polarization operator, the first and third terms within the brackets in Equation (16) combine to yield

$$\begin{aligned}&\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}^0_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\\ &\quad-\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\langle 0|\hat{p}_\alpha(\bar{r})|0\rangle G(\omega_\sigma)\hat{p}^0_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\\ &\quad=\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\hat{p}^0_\alpha(\bar{r})G(\omega_\sigma)\hat{p}^0_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle.\end{aligned} \tag{18}$$

Similarly, the ninth and tenth terms within the brackets of Equation (16) combine to give the matrix element

$$\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}^0_\gamma(\bar{r}'')G(\omega_1)\hat{p}^0_\beta(\bar{r}')G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle. \tag{19}$$

From Equations (16), (17), (18) and the expressions generated by differentiating the remaining terms in Equation (9) with respect to $\bar{R}^K_\delta$, we obtain

$$\begin{aligned}&\frac{\partial\beta_{\alpha\beta\gamma}(\bar{r},\bar{r}',\bar{r}'';-\omega_\sigma;\omega_1,\omega_2)}{\partial R^K_\delta}=\int d\bar{r}'''\,Z^K\mathbf{T}_{\varepsilon\delta}(\bar{r}''',\bar{R}^K)\times\left[1+C(\{\omega_i\}\to\{-\omega_i\})\right]\\ &\times\left\{\begin{aligned}&\wp_{\beta\gamma\varepsilon}\left[\begin{aligned}&\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}^0_\varepsilon(\bar{r}''')G(\omega_\sigma)\hat{p}^0_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\\ &+\langle 0|\hat{p}_\beta(\bar{r}')G^*(-\omega_1)\hat{p}^0_\gamma(\bar{r}'')G^*(-\omega_\sigma)\hat{p}^0_\alpha(\bar{r})G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\end{aligned}\right]\\ &-\wp_{\beta\gamma}\left[\begin{aligned}&\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\\ &+\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\hat{p}_\gamma(\bar{r}'')|0\rangle\\ &+\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\\ &+\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(\omega_2)G(0)\hat{p}_\gamma(\bar{r}'')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\beta(\bar{r}')|0\rangle\\ &+\langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\\ &+\langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\hat{p}_\alpha(\bar{r})|0\rangle\end{aligned}\right]\end{aligned}\right\}\end{aligned} \tag{20}$$

where $\wp_{\beta\gamma\varepsilon}$ denotes the sum of all permutations of $\hat{p}_\beta(\bar{r}')$, $\hat{p}_\gamma(\bar{r}'')$, and $\hat{p}_\varepsilon(\bar{r}''')$, simultaneously with ω_1, ω_2 and 0 (respectively) in the expression that follows. The operator $C(\{\omega_i\} \to \{-\omega_i\})$ takes the complex conjugate and replaces each ω_i by $-\omega_i$; the operation applies to ω_1, ω_2 and ω_σ. Again damping has been neglected in off-resonant terms; it is reiterated that G(0) and G*(0) are interchangeable at this level of approximation.

In order to connect the hyperpolarizability derivative to the second hyperpolarizability, the following identity is used,[95]

$$\begin{aligned}
&\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\hat{p}_\gamma(\bar{r}'')|0\rangle \\
&\quad+\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)G(\omega_2)\hat{p}_\gamma(\bar{r}'')|0\rangle \\
&=\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(\omega_2)\hat{p}_\gamma(\bar{r}'')|0\rangle \\
&\quad+\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)G(\omega_2)\hat{p}_\gamma(\bar{r}'')|0\rangle,
\end{aligned} \tag{21}$$

which is proven by converting both sides S_1 and S_2 in Equation (21) to the explicit sum over states form

$$S_1 = S_2 = \hbar^{-2}\sum_m{}'\sum_j{}'\frac{\langle 0|\hat{p}_\alpha(\bar{r})|m\rangle\langle m|\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')|j\rangle\langle j|\hat{p}_\beta(\bar{r}'')|0\rangle(\Omega_{m0}+\Omega_{j0}-\omega_1-\omega_2)}{(\Omega_{m0}-\omega_\sigma)(\Omega_{m0}-\omega_1)\Omega_{j0}(\Omega_{j0}-\omega_2)} \tag{22}$$

where $\Omega_{m0} = \omega_{m0} - i\Gamma_m/2$ and the primes on the summations over m and j imply that the ground state is excluded from the sum. We also use the complex conjugate of the identity in Equation (21). Then Equation (20) can be simplified using the permutation operator $\wp_{\beta\gamma\varepsilon}$.

$$\begin{aligned}
&\left[1+C\left(\{\omega_i\}\to\{-\omega_i\}\right)\right] \\
&\times\wp_{\beta\gamma}\begin{bmatrix}
\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
+\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\hat{p}_\gamma(\bar{r}'')|0\rangle \\
+\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle \\
+\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(\omega_2)G(0)\hat{p}_\gamma(\bar{r}'')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\beta(\bar{r}')|0\rangle \\
+\langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
+\langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\hat{p}_\alpha(\bar{r})|0\rangle
\end{bmatrix} \\
&=\left[1+C\left(\{\omega_i\}\to\{-\omega_i\}\right)\right] \\
&\times\wp_{\beta\gamma\varepsilon}\begin{bmatrix}
\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
+\langle 0|\hat{p}_\alpha(\bar{r})G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle
\end{bmatrix}.
\end{aligned}\tag{23}$$

Therefore

$$\begin{aligned}
&\frac{\partial\beta_{\alpha\beta\gamma}(\bar{r},\bar{r}',\bar{r}'';-\omega_\sigma;\omega_1,\omega_2)}{\partial R^K_\delta}=\int d\bar{r}'''\,Z^K T_{\varepsilon\delta}(\bar{r}''',\bar{R}^K)\times\left[1+C\left(\{\omega_i\}\to\{-\omega_i\}\right)\right] \\
&\times\wp_{\beta\gamma\varepsilon}\begin{bmatrix}
\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}^0_\varepsilon(\bar{r}''')G(\omega_\sigma)\hat{p}^0_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
+\langle 0|\hat{p}_\beta(\bar{r}')G^*(-\omega_1)\hat{p}^0_\gamma(\bar{r}'')G^*(-\omega_\sigma)\hat{p}^0_\alpha(\bar{r})G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle \\
-\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
-\langle 0|\hat{p}_\alpha(\bar{r})G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle
\end{bmatrix}.
\end{aligned}\tag{24}$$

The quantity in the brackets of Equation (24) can be compared to the second hyperpolarizability density. The equation used for the second hyperpolarizability is taken from Orr and Ward's article on nonlinear optical polarization.[17] The equation is directly quoted.

$$
\begin{gathered}
P^{\omega_\sigma} = K\left(-\omega_\sigma;\omega_1,\omega_2,\omega_3\right)\hbar^{-3} I_{1,2,3} \\
\times\left\{
\begin{aligned}
&\sum_{lmn}{}' \left[
\begin{aligned}
&\frac{\left\langle P\right\rangle_{gl}\left\langle \overline{H}'^{\omega 3}\right\rangle_{lm}\left\langle \overline{H}'^{\omega 2}\right\rangle_{mn}\left\langle H'^{\omega 1}\right\rangle_{ng}}{\left(\Omega_{lg}-\omega_\sigma\right)\left(\Omega_{mg}-\omega_1-\omega_2\right)\left(\Omega_{ng}-\omega_1\right)}
+\frac{\left\langle H'^{\omega 3}\right\rangle_{gl}\left\langle \overline{P}\right\rangle_{lm}\left\langle \overline{H}'^{\omega 2}\right\rangle_{mn}\left\langle H'^{\omega 1}\right\rangle_{ng}}{\left(\Omega_{lg}^{\bullet}+\omega_3\right)\left(\Omega_{mg}-\omega_1-\omega_2\right)\left(\Omega_{ng}-\omega_1\right)} \\
&+\frac{\left\langle H'^{\omega 1}\right\rangle_{gl}\left\langle \overline{H}'^{\omega 2}\right\rangle_{lm}\left\langle \overline{P}\right\rangle_{mn}\left\langle H'^{\omega 3}\right\rangle_{ng}}{\left(\Omega_{lg}^{\bullet}+\omega_1\right)\left(\Omega_{mg}^{\bullet}+\omega_1+\omega_2\right)\left(\Omega_{ng}-\omega_3\right)}
+\frac{\left\langle H'^{\omega 1}\right\rangle_{gl}\left\langle \overline{H}'^{\omega 2}\right\rangle_{lm}\left\langle \overline{H}'^{\omega 3}\right\rangle_{mn}\left\langle P\right\rangle_{ng}}{\left(\Omega_{lg}^{\bullet}+\omega_1\right)\left(\Omega_{mg}^{\bullet}+\omega_1+\omega_2\right)\left(\Omega_{ng}^{\bullet}+\omega_\sigma\right)}
\end{aligned}
\right] \\
&-\sum_{mn}{}' \left[
\begin{aligned}
&\frac{\left\langle P\right\rangle_{gm}\left\langle H'^{\omega 3}\right\rangle_{mg}\left\langle H'^{\omega 2}\right\rangle_{gn}\left\langle H'^{\omega 1}\right\rangle_{ng}}{\left(\Omega_{mg}-\omega_\sigma\right)\left(\Omega_{mg}-\omega_3\right)\left(\Omega_{ng}-\omega_1\right)}
+\frac{\left\langle P\right\rangle_{gm}\left\langle H'^{\omega 3}\right\rangle_{mg}\left\langle H'^{\omega 2}\right\rangle_{gn}\left\langle H'^{\omega 1}\right\rangle_{ng}}{\left(\Omega_{mg}-\omega_3\right)\left(\Omega_{ng}^{\bullet}+\omega_2\right)\left(\Omega_{ng}-\omega_1\right)} \\
&+\frac{\left\langle H'^{\omega 3}\right\rangle_{gm}\left\langle \overline{P}\right\rangle_{mg}\left\langle H'^{\omega 1}\right\rangle_{gn}\left\langle H'^{\omega 2}\right\rangle_{ng}}{\left(\Omega_{mg}^{\bullet}+\omega_\sigma\right)\left(\Omega_{mg}^{\bullet}+\omega_3\right)\left(\Omega_{ng}^{\bullet}+\omega_1\right)}
+\frac{\left\langle H'^{\omega 1}\right\rangle_{gm}\left\langle H'^{\omega 2}\right\rangle_{mg}\left\langle H'^{\omega 3}\right\rangle_{gn}\left\langle P\right\rangle_{ng}}{\left(\Omega_{mg}^{\bullet}+\omega_3\right)\left(\Omega_{ng}-\omega_2\right)\left(\Omega_{ng}^{\bullet}+\omega_1\right)}
\end{aligned}
\right]
\end{aligned}
\right\}. \quad (25)
\end{gathered}
$$

Orr and Ward's equation for the second hyperpolarizability is identical to the expression in the brackets of Equation (24), though explanation is needed to relate the two equations to each other. First the frequencies are compared; the ω_3 in the second hyperpolarizability corresponds to 0 in the hyperpolarizability derivative. The matrix element notation translates as

$$
\begin{aligned}
\left\langle \overline{H}'^{\omega 3}\right\rangle_{lm} &= \left\langle l\right| -\int \overline{H}'^{\omega_3}(\bar{r})E^{\omega_3}(\bar{r})d\bar{r}\left| m\right\rangle \rightarrow \left\langle l\right|\hat{p}_\varepsilon^0(\bar{r}''')\left| m\right\rangle \\
\left\langle H'^{\omega 3}\right\rangle_{lm} &= \left\langle l\right| -\int H'^{\omega_3}(\bar{r})E^{\omega_3}(\bar{r})d\bar{r}\left| m\right\rangle \rightarrow \left\langle l\right|\hat{p}_\varepsilon(\bar{r}''')\left| m\right\rangle.
\end{aligned}
\qquad (26)
$$

Note that the expression from Orr and Ward includes the incident electric field to obtain the net polarization whereas in this formulation, flexibility is maintained to multiply by the electric field subsequently. The correlation is complete when it is remembered that summation on the index of the polarization operator over all the Cartesian coordinates in Equation (24) is necessary. The $I_{1,2,3}$ operator is the same permutation operator as $\wp_{\beta\gamma\varepsilon}$ and the $\hbar$ in the denominator of the equation of the second hyperpolarizability can be distributed through the frequency expressions to yield the energy expressions of the equation for the hyperpolarizability.

One can use the definition of the reduced resolvent to simplify the sum-over-states in the equation for the second hyperpolarizability. Then the frequency conjugation operator $C(\{\omega_i\} \rightarrow \{-\omega_i\})$ can be factored from the second hyperpolarizability equation to simplify further. The first and fourth, second and third, fifth and seventh, and sixth and eighth terms of the second hyperpolarizability equation are frequency conjugates of each other. Finally, the coefficient $K(-\omega_\sigma;\omega_1,-\omega_2,-\omega_3)$ depends on the number of zero frequencies and the number of repeated frequencies in the set ω_1, ω_2, ω_3 and ω_σ. The value of K becomes clear for specific frequencies when integrations over the frequency values are taken. Integration over a single ω will yield a different number than three integrations over three distinct frequencies.

Thus being aware of all of these equivalencies, the equation for the second hyperpolarizability can be written as

$$\gamma_{\alpha\beta\gamma\varepsilon}(\bar{r},\bar{r}',\bar{r}'',\bar{r}''';-\omega_\sigma;\omega_1,\omega_2,\omega_3)$$
$$=\left[1+C(\{\omega_i\} \rightarrow \{-\omega_i\})\right] \times \wp_{\beta\gamma\varepsilon} \begin{bmatrix} \langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}^0_\varepsilon(\bar{r}''')G(\omega_\sigma)\hat{p}^0_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\ +\langle 0|\hat{p}_\beta(\bar{r}')G^*(-\omega_1)\hat{p}^0_\gamma(\bar{r}'')G^*(-\omega_\sigma)\hat{p}^0_\alpha(\bar{r})G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle \\ -\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\ -\langle 0|\hat{p}_\alpha(\bar{r})G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \end{bmatrix} \quad (27)$$

Relating Equation (27) to Equation (24) yields the goal of the derivation.

$$\partial\beta_{\alpha\beta\gamma}(\bar{r},\bar{r}',\bar{r}'';-\omega_\sigma;\omega_1,\omega_2)/\partial R^K_\delta = \int d\bar{r}'''\gamma_{\alpha\beta\gamma\varepsilon}(\bar{r},\bar{r}',\bar{r}'',\bar{r}''';-\omega_\sigma;\omega_1,\omega_2,0)Z^K\mathbf{T}_{\varepsilon\delta}(\bar{r}''',\bar{R}^K).(28)$$

If damping is completely negligible, Equation (24) can be cast into the more compact form

$$\begin{aligned}\frac{\partial\beta_{\alpha\beta\gamma}\left(\bar{r},\bar{r}',\bar{r}'';-\omega_\sigma;\omega_1,\omega_2\right)}{\partial\bar{R}_\delta^K} &= \int d\bar{r}'''\, Z^K \mathbf{T}_{\varepsilon\delta}\left(\bar{r}''',\bar{R}^K\right) \\ &\times \wp_{\alpha\beta\gamma\varepsilon}\begin{bmatrix}\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\varepsilon^0(\bar{r}''')G(\omega_\sigma)\hat{p}_\gamma^0(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\ -\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(-\omega_2)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\end{bmatrix}.\end{aligned} \tag{29}$$

which again yields Equation (28) on comparison with Equation (44c) in Orr and Ward's paper.[17] In Equation (29), $\wp_{\alpha\beta\gamma\varepsilon}$ denotes the sum of all permutations of the pairs $\{\hat{p}_\alpha(\bar{r}),-\omega_\sigma\}$, $\{\hat{p}_\beta(\bar{r}'),\omega_1\}$, $\{\hat{p}_\gamma(\bar{r}''),\omega_2\}$ and $\{\hat{p}_\varepsilon(\bar{r}'''),0\}$ in the expression that follows; here the frequency associated with $\hat{p}_\alpha(\bar{r})$ is $-\omega_\sigma$ rather than ω_σ. In deriving Equation (29), we have used Equation (21), the equation obtained from Equation (21) by interchanging the roles of $\{\hat{p}_\beta(\bar{r}'),\omega_1\}$ and $\{\hat{p}_\gamma(\bar{r}''),\omega_2\}$, the result

$$\begin{aligned}&\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{r}')G(-\omega_1)G(\omega_2)\hat{p}_\gamma(\bar{r}'')|0\rangle \\ &\quad+\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{r}')G(-\omega_1)\hat{p}_\gamma(\bar{r}'')|0\rangle \\ &=\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{r}')G(\omega_2)\hat{p}_\gamma(\bar{r}'')|0\rangle \\ &\quad+\langle 0|\hat{p}_\alpha(\bar{r})G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{r}')G(-\omega_1)G(\omega_2)\hat{p}_\gamma(\bar{r}'')|0\rangle \\ &=\hbar^{-2}\sum_m{}'\sum_j{}'\frac{\langle 0|\hat{p}_\alpha(\bar{r})|m\rangle\langle m|\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{r}')|j\rangle\langle j|\hat{p}_\gamma(\bar{r}'')|0\rangle(\Omega_{m0}+\Omega_{j0}-\omega_2)}{(\Omega_{m0}-\omega_\sigma)\Omega_{m0}(\Omega_{j0}+\omega_1)(\Omega_{j0}-\omega_2)}\end{aligned} \tag{30}$$

and the analog of Equation (30) with the roles of $\{\hat{p}_\beta(\bar{r}'),\omega_1\}$ and $\{\hat{p}_\gamma(\bar{r}''),\omega_2\}$ interchanged. Equation (30) corresponds to Equation (21) with $\hat{p}_\beta(\bar{r}')$ and $\hat{p}_\varepsilon(\bar{r}''')$ interchanged, $G(0)$ replaced by $G(-\omega_1)$, $G(\omega_1)$ replaced by $G(0)$, and damping neglected.

Further Applications of the Hyperpolarizability Derivative

The analytic result given in Equation (28) is needed to relate quartic anharmonicities of potential energy surfaces to electronic hyperpolarization energies,[96] and to relate nonadditive three-body forces to the three-body polarization.[97] Equation (28) is potentially useful for analyzing the origins of hyper-Raman scattering on the intramolecular scale, and for making qualitative predictions about hyper-Raman intensities. In *ab initio* calculations with a given basis set and method, a direct evaluation of the left-hand side of Equation (28) is expected to be more efficient computationally. However, use of the form on the right may assist in basis-set optimization by indicating which regions of the molecule contribute most to the hyperpolarizability derivative.

The Hyperpolarizability Derivative and Hyper-Raman Intensities

The derivative of the net molecular hyperpolarizability $\beta_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2)$ with respect to the vibrational normal-mode coordinate Q is

$$\begin{aligned}&\partial\beta_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2)/\partial Q\\ &\quad=\sum_{K,\delta}\int d\bar{r}\,d\bar{r}'d\bar{r}''d\bar{r}'''\gamma_{\alpha\beta\gamma\varepsilon}(\bar{r},\bar{r}',\bar{r}'',\bar{r}''';-\omega_\sigma;\omega_1,\omega_2,0)Z^K\mathbf{T}_{\varepsilon\delta}(\bar{r}''',\bar{R}^K)\frac{\partial R_\delta^K}{\partial Q}.\end{aligned}\tag{31}$$

Intensities for vibrational hyper-Raman scattering depend upon the derivative given by Equation (31), with ω_1 and ω_2 both equal to the frequency of the incident radiation ω_i, and $\omega_\sigma = 2\omega_i$.[28,29,30] This connection[10,29,30,40,45] for hyper-Raman scattering of incident light plane-polarized along the space-fixed Z axis, initially propagating in the -X direction toward a scatterer at the origin in the space-fixed axis system (X, Y, Z) is reviewed.

Scattered radiation of frequency ω_s is detected along the Y axis. The intensity (per unit solid angle) $I_{ZZ}(\omega_s)$ of the scattered radiation plane-polarized along Z, due to an isolated molecule that undergoes a transition from vibrational state m to n is given by[40]

$$I_{ZZ}(\omega_s) = \frac{\omega_s^4}{32\pi^2 \varepsilon_0 c^3} \left|\langle m|\mu_Z|n\rangle\right|^2 . \tag{32}$$

The intensity $I_{XZ}(\omega_s)$ of scattered radiation plane-polarized along X satisfies Equation (32) with μ_Z replaced by μ_X. At the level of the Placzek theory as applied to hyper-Raman scattering, μ_Z and μ_X are identified as the electronic dipoles induced by nonlinear response to the electric field of the incident light, so

$$\mu_X = 1/2\, \beta_{XZZ}(-2\omega_i;\omega_i,\omega_i)\, E_Z(\omega_i)\, E_Z(\omega_i), \tag{33}$$

where $E_Z(\omega_i)$ is the electric field of the incident light (and similarly for μ_Z). Below, $\beta_{XZZ}(-2\omega_i;\omega_i,\omega_i)$ and $\beta_{ZZZ}(-2\omega_i;\omega_i,\omega_i)$ are abbreviated as β_{XZZ} and β_{ZZZ}, respectively. The hyperpolarizability components β_{IJK} (IJK = XZZ or ZZZ) are expanded as series in the normal mode coordinates Q_v, about the equilibrium nuclear configuration (denoted by the subscript eq),

$$\beta_{IJK} = \beta_{IJK}\big|_{eq} + \sum_v \frac{\partial \beta_{IJK}}{\partial Q_v}\bigg|_{eq} Q_v + \cdots . \tag{34}$$

Hyper-Raman scattering occurs at frequencies ω_s shifted from $2\omega_i$ by $(E_m - E_n)/\hbar$, with intensity $I_{XZ}(\omega_s)$ given by[40]

$$I_{XZ}(\omega_s) = \frac{\omega_s^4}{128\pi^2 \varepsilon_0 c^3} \left|\langle m|Q_v|n\rangle\right|^2 \left(\frac{\partial \beta_{XZZ}}{\partial Q_v}\bigg|_{eq} \right)^2 E_Z(\omega_i)^4 \tag{35}$$

and similarly for $I_{ZZ}(\omega_s)$ with $\beta_{XZZ} \rightarrow \beta_{ZZZ}$. For transitions between the ground vibrational state and the state with one quantum of excitation in the mode Q_v, in the harmonic approximation, the strength of the transition is

$$|\langle m|Q_v|n\rangle|^2 = \hbar/2\omega_v, \tag{36}$$

where ω_v is the frequency of the normal mode Q_v. For a sample of N freely rotating molecules, with probability P_m to occupy the initial state $|m\rangle$, the intensity $I_{XZ}(\omega_s)$ of hyper-Raman scattering is related to the isotopic average of the hyperpolarizability derivative, $\left\langle \left(\partial\beta_{XZZ}/\partial Q_v |_{eq}\right)^2 \right\rangle$ by[40]

$$I_{XZ}(\omega_s) = \frac{\omega_s^4}{32\pi^2\varepsilon_0^3 c^5} N P_m I_0^2 |\langle m|Q_v|n\rangle|^2 \left\langle \left(\frac{\partial\beta_{XZZ}}{\partial Q_v}\Big|_{eq} \right)^2 \right\rangle, \tag{37}$$

and similarly for $I_{ZZ}(\omega_s)$. In Equation (37), I_0 is the irradiance,[40] defined by

$$I_0 = 1/2\, c\varepsilon_0 g E_Z(\omega_i)^2, \tag{38}$$

and g is a coherence factor.[98] The space-fixed tensor components $\partial\beta_{IJK}/\partial Q_v |_{eq}$ are related to the molecule-fixed components $\partial\beta_{ijk}/\partial Q_v |_{eq}$ by

$$\frac{\partial\beta_{IJK}}{\partial Q_v}\Big|_{eq} = \sum_{i,j,k} a_{Ii} a_{Jj} a_{Kk} \frac{\partial\beta_{ijk}}{\partial Q_v}\Big|_{eq} \tag{39}$$

where a_{Ii} is the direction cosine between the molecular axis i and the space-fixed axis I.

Since Equation (37) relates observed hyper-Raman intensities to the derivatives of the hyperpolarizability, by Equation (31) the hyper-Raman intensities are also related to the second hyperpolarizability density $\gamma(\bar{r},\bar{r}',\bar{r}'',\bar{r}''';-2\omega_i;\omega_i,\omega_i,0)$.

Conclusion

The principal result of this work is contained in Equation (28), which establishes a link between the derivative of the lowest-order nonlinear response tensor $\beta_{\alpha\beta\gamma}\left(-\omega_{\sigma};\omega_{1},\omega_{2}\right)$, taken with respect to the position of nucleus K, and the nonlinear susceptibility density $\gamma_{\alpha\beta\gamma\varepsilon}\left(\bar{r},\bar{r}',\bar{r}'',\bar{r}''';-2\omega_{i};\omega_{i},\omega_{i},0\right)$ of the next order. The second hyperpolarizability density determines the change in the effective value of the hyperpolarizability when a static external field is applied to a molecule (cf. References 24, 25 and 31 for cases with uniform applied fields and spatially integrated values of γ and β). When nucleus K shifts infinitesimally within a molecule, the electrons respond to the change in the nuclear Coulomb field via the *same* nonlocal susceptibilities that characterize their response to applied electric fields. This result is illustrated in Equation (28), since the change $\delta F_{\varepsilon}^{K}$ in the Coulomb field resulting from the shift in the position of nucleus K is given by $Z^{K}\mathbf{T}_{\varepsilon\delta}(\bar{r}''',\bar{R}^{K})\,\partial R_{\delta}^{K}$. Thus the second hyperpolarizability density determines the change in the hyperpolarizability due to small distortions of the molecular geometry. Based on Equations (31) and (37), the second hyperpolarizability density also determines band intensities for vibrational hyper-Raman scattering.

Acknowledgments

I wish to acknowledge the support of the National Science Foundation through Grant Numbers CHE-9309005 and CHE-9320633. I also wish thank Professor Hunt for her permission to adapt our article in the Journal of Chemical Physics for this chapter. Also, many thanks to Dr. Xiaoping Li of the K. Hunt group for many helpful discussions.

REFERENCES

[1] Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).

[2] *Molecular Nonlinear Optics: Materials, Physics, and Devices*, edited by J. Zyss (Academic, New York, 1993).

[3] *Materials for Nonlinear Optics: Chemical Perspectives*, edited by S. R. Marder, J. E. Sohn, and G. D. Stucky, ACS Symp. Ser. **455** (ACS, Washington, DC, 1991).

[4] P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers* (Wiley, New York, 1991).

[5] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford U. P., Oxford, 1995).

[6] D. P. Shelton and J. E. Rice, Chem. Rev. **94**, 3 (1994).

[7] J. T. Golab, J. R. Sprague, K. T. Carron, G. C. Schatz and R. P. Van Duyne, J. Chem. Phys. **88**, 7942 (1988).

[8] P. W. Fowler, Ann. Rep. Prog. Chem. C **84**, 3 (1987).

[9] R. D. Amos, Adv. Chem. Phys. **67**, 99 (1987).

[10] W.-H. Yang and G. C. Schatz, J. Chem. Phys. **97**, 3831 (1992).

[11] D. M. Bishop and B. Kirtman, J. Chem. Phys. **95**, 2646 (1991); **97**, 5255 (1992); D. M. Bishop, B. Kirtman, H. A. Kurtz and J. E. Rice, J. Chem. Phys. **98**, 8024 (1993); D. M. Bishop, J. Pipin and B. Kirtman, J. Chem. Phys. **102**, 6778 (1995).

[12] W. J. A. Maaskant and L. J. Oosterhoff, Molec. Phys. **8**, 319 (1964).

[13] L. M. Hafkensheid and J. Vlieger, Physica **75**, 57 (1974).

[14] T. Keyes and B. M. Ladanyi, Molec. Phys. **33**, 1271 (1977).

[15] K. L. C. Hunt, J. Chem. Phys. **78**, 6149 (1983).

[16] K. L. C. Hunt, J. Chem. Phys. **80**, 393 (1984).

[17] B. J. Orr and J. F. Ward, Molec. Phys. **20**, 513 (1971).

[18] D. M. Bishop, J. Chem. Phys. **100**, 6535 (1994).

[19] J. A. Armstrong, N. Bloembergen, J. Ducuing and P. S. Pershan, Phys. Rev. **127**, 1918 (1962).

[20] P. D. Maker and R. W. Terhune, Phys. Rev. **137**, A801 (1965).

[21] G. H. C. New and J. F. Ward, Phys. Rev. Lett. **19**, 556 (1967).

[22] K. L. C. Hunt, J. Chem. Phys. **90**, 4909 (1989).

[23] K. L. C. Hunt, Y. Q. Liang, R. Nimalakirthi and R. A. Harris, J. Chem. Phys. **91**, 5251 (1989).

[24] A. D. Buckingham and J. A. Pople, Proc. Phys. Soc. A **68**, 905 (1955); Trans. Faraday Soc. **52**, 747 (1956); A. D. Buckingham, Adv. Chem. Phys. **12**, 107 (1967); Quart. Rev. Chem. Soc. (London) **21**, 195 (1967).

[25] S. R. Marder, C. B. Gorman, F. Meyers, J. W. Perry, G. Bourhill, J.-L. Brédas, and B. M. Pierce, Science **265**, 632 (1994).

[26] H.-S. Kim, M. Cho and S.-J. Jeon, J. Chem. Phys. **107**, 1936 (1997).

[27] M. DelZoppo, C. Castiglioni, V. Gerola, P. Zuliani and G. Zerbi, J. Opt. Soc. Am. B **15**, 308 (1998).

[28] P. Gütterger, Helv. Phys. Acta **5**, 237 (1932).

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

[30] D. A. Long and L. Stanton, Proc. R. Soc. London, Ser. A **318**, 441 (1970).

[31] D. M. Bishop, J. Chem. Phys. **86,** 5613 (1987).

[32] D. S. Elliott and J. F. Ward, Molec. Phys. **51,** 45 (1984).

[33] Z. Lu and D. P. Shelton, J. Chem. Phys. **87**, 1967 (1987); D. P. Shelton and L. Ulivi, J. Chem. Phys. **89**, 149 (1988).

[34] C. E. Dykstra, S.-Y. Liu and D. J. Malik, Adv. Chem. Phys. **75**, 37 (1990).

[35] M. Del Zoppo, C. Castiglioni, G. Zerbi, M. Rui and M. Gussoni, Synth. Met. **51**, 135 (1992).

[36] J. C. Decius and J. E. Rauch, *Ohio State Symposium on Molecular Structure and Spectroscopy* (1958), Paper 48.

[37] S. Kielich, Acta Phys. Polon. **26**, 135 (1964).

[38] Y.-Y. Li, Acta Phys. Sin. Abstr. **20**, 164 (1964).

[39] R. W. Terhune, P. D. Maker and C. M. Savage, Phys. Rev. Lett. **14**, 681 (1965).

[40] D. A. Long, in *Nonlinear Raman Spectroscopy and its Chemical Applications*, edited by W. Kiefer and D. A. Long, NATO ASI Ser. C **93** (Reidel, Dordrecht, 1982), pp. 99-130, 165-179.

[41] K. Altmann and G. Strey, J. Raman Spectrosc. **12**, 1 (1982).

[42] L. Ziegler, J. Raman Spectrosc. **21**, 769 (1990).

[43] S. Kielich and T. Bancewicz, J. Raman Spectrosc. **21**, 791 (1990).

[44] J. H. Christie and D. J. Lockwood, J. Chem. Phys. **54**, 1141 (1971).

[45] L. Stanton, Mol. Phys. **23**, 601 (1972); L. Stanton, J. Raman Spectrosc. **1**, 53 (1973).

[46] W. J. Schmid and H. W. Schrötter, Chem. Phys. Lett. **45**, 502 (1977).

[47] A. Hiraya, Y. Udagawa and M. Ito, Chem. Lett. **4**, 433 (1979).

[48] W. P. Acker, D. H. Leach and R. K. Chang, Chem. Phys. Lett. **155**, 491 (1989).

[49] C. M. Savage and P. D. Maker, Appl. Opt. **10**, 965 (1971).

[50] H. Vogt and G. Rossbroich, Phys. Rev. B **24**, 3086 (1981).

[51] K. Inoue, N. Asai and T. Sameshima, J. Phys. Soc. Japan **50**, 1291 (1981).

[52] V. N. Denisov, B. N. Mavrin, V. B. Podobedov and J. F. Scott, J. Raman Spectrosc. **14**, 276 (1983).

[53] H. Vogt, Phys. Rev. B **36**, 5001 (1987).

[54] Y. Inaba, A. Yamanaka, K. Inoue and E. Courtens, J. Korean Phys. Soc. **29**, S725 (1996).

[55] H. Vogt, J. A. Sanjurjo and G. Rossbroich, Phys. Rev. B **26**, 5904 (1982).

[56] K. Inoue and S. Akimoto, Solid State Commun. **46**, 441 (1983).

[57] H. Vogt and H. Uwe, Phys. Rev. B **29**, 1030 (1984).

[58] K. Inoue, M. Wada and A. Yamanaka, J. Korean Phys. Soc. **29**, S721 (1996).

[59] K. Inoue and A. Yamanaka, J. Phys. Soc. Japan **66**, 3277 (1997).

[60] E. Buixaderas, S. Kamba, J. Petzelt, M. Wada, A. Yamanaka and K. Inoue, J. Korean Phys. Soc. **32**, S578 (1998).

[61] H. Vogt, J. Phys - Condens. Matter **29**, 5913 (1995); Ferroelectrics **202**, 157 (1997).

[62] S. Kono, N. Naka, M. Hasuo, S. Saito, T. Suemoto and N. Nagasawa, Solid State Commun. **97**, 455 (1996).

[63] B. P. Antonyuk, V. B. Antonyuk, S. F. Musichenko and V. B. Podobedov, Phys. Lett. A **213**, 297 (1996).

[64] B. P. Antonyuk and V. B. Antonyuk, J. Mod. Optic. **45**, 257 (1998).

[65] V. B. Podobedov, J. Raman Spectrosc. **27**, 731 (1996).

[66] G. Dolino and M. Vallade, Rev. Mineral. **29**, 403 (1994).

[67] B. Fanconi and W. L. Peticolas, J. Chem. Phys. **50**, 2244 (1969).

[68] J. R. Verdieck, S. H. Peterson, C. M. Savage and P. D. Maker, Chem. Phys. Lett. **7**, 219 (1970).

[69] M. J. French and D. A. Long, J. Raman Spectrosc. **3**, 391 (1975); T. J. Dines, M. J. French, R. J. B. Hall and D. A. Long, J. Raman Spectrosc. **14**, 225 (1983).

[70] V. N. Denisov, B. N. Mavrin, V. B. Podobelov and J. F. Scott, J. Raman Spectrosc. **16**, 71 (1985).

[71] Y. Murioka and I. Nakagawa, Chem. Phys. Lett. **122**, 150 (1985).

[72] H. Vogt and H. Presting, Phys. Rev. B 31, **6731** (1985).

[73] J. P. Neddersen, S. A. Mounter, J. M. Bostick and C. K. Johnson, J. Chem. Phys. **90**, 4719 (1989).

[74] D. V. Murphy, K. U. von Raben, R. K. Chang and P. B. Dorian, Chem. Phys. Lett. **85**, 43 (1982).

[75] A. V. Baranov and Y. S. Bobovich, JETP Lett. **36**, 339 (1982); A. V. Baranov, Y. S. Bobovich and N. P. Vasilenko, Opt. Spectrosc. **61**, 490 (1986).

[76] N.-T. Yu, S. Nie and L. A. Lipscomb, J. Raman Spectrosc. **21**, 797 (1990).

[77] S. Nie, L. A. Lipscomb, S. Feng and N.-T. Yu, Chem. Phys. Lett. **167**, 35 (1990).

[78] K. Kneipp, H. Kneipp and F. Seifert, Chem. Phys. Lett. **233**, 519 (1995).

[79] S. Schneider, G. Brehm and P. Freunscht, Phys. Status Solidi B - Basic Res. **189**, 37 (1995).

[80] W. H. Yang, J. Hulteen, G. C. Schatz and R. P. VanDuyne, J. Chem. Phys. **104,** 4313 (1996).

[81] C. K. Johnson and S. A. Soper, J. Phys. Chem. **93,** 7281 (1989).

[82] G. Mayer, C. R. Acad. Sci. B **267,** 54 (1968); F. Hauchecorne, R. Kerherve and G. Mayer, J. Phys. (Paris) **32,** 47 (1971).

[83] R. S. Finn and J. F. Ward, J. Chem. Phys. **60,** 454 (1974); J. F. Ward and I. J. Bigio, Phys. Rev. A **11,** 60 (1975).

[84] M. Stähelin, C. R. Moylan, D. M. Burland, A. Willetts, J. E. Rice, D. P. Shelton and E. A. Donley, J. Chem. Phys.**98,** 5595 (1993); E. A. Donley and D. P. Shelton, Chem. Phys. Lett. **215,** 156 (1993).

[85] R. W. Terhune, P. D. Maker and C. M. Savage, Phys. Rev. Lett. **8,** 404 (1962).

[86] J. D. Jackson, *Classical Electrodynamics* 2nd ed. (John Wiley & Sons, New York, 1975).

[87] C. H. Lee, R. K. Chang and N. Bloembergen, Phys. Rev. Lett. **18,** 167 (1967).

[88] R. A. Bradley, R. Georgiadis, S. D. Kevan and G. L. Richmond, J. Chem. Phys. **99,** 5535 (1993).

[89] P. R. Fischer, J. L. Daschbach and G. L. Richmond, Chem. Phys. Lett. **218,** 200 (1994).

[90] J. S. Horowitz, B. E. Kohler and T. A. Spiglanin, J. Phys. Chem. **89,** 1574 (1985).

[91] L. D. Ziegler and J. L. Roebber, Chem. Phys. Lett. **136,** 377 (1987); Y. C. Chung and L. D. Ziegler, J. Chem. Phys. **88,** 7287 (1988).

[92] C. C. Bonang and S. M. Cameron, Chem. Phys. Lett. **187,** 619 (1991); **192,** 303 (1992).

[93] C. C. Bonang, S. M. Cameron, J. D. Getty and P. B. Kelly, Chem. Phys. Lett. **209**, 35 (1993).

[94] Appendix A.

[95] Appendix B.

[96] K. L. C. Hunt, J. Chem. Phys. **103**, 3552 (1995).

[97] X. Li and K. L. C. Hunt, J. Chem. Phys. **105**, 4076 (1996).

[98] D. A. Long, *Raman Spectroscopy* (McGraw-Hill, New York, 1977).

CHAPTER 3: RELATION OF POLARIZATION PROPAGATOR DERIVATIVES TO NONLINEAR POLARIZATION PROPAGATORS

Introduction

In quantum chemistry, calculation of molecular properties involves two quantities, operators and wavefunctions. Using perturbation theory, the value of a property is often found by operating a single operator upon a sum-over-eigenfunctions (sum-over-states). For example, the dipole polarizability can be calculated from the second-order perturbation expression[1]

$$\alpha_{\alpha\beta}(\omega) = -\sum_{n}{}' \left\{ \frac{\langle 0|\mu_\alpha|n\rangle\langle n|\mu_\beta|0\rangle}{E_0 - E_n + \hbar\omega} + \frac{\langle 0|\mu_\beta|n\rangle\langle n|\mu_\alpha|0\rangle}{E_0 - E_n - \hbar\omega} \right\}, \qquad (1)$$

where the $|n\rangle$ are the wavefunctions, μ_α is the dipole operator of the αth Cartesian coordinate and $\sum_{n}{}'$ indicates the sum over the excited states only. In general, accurate excited-state wavefunctions are more difficult to calculate than ground-state wavefunctions. Also for accurate property calculations, a large number of excited-state wavefunctions may be needed. Thus the sum-over-states method is often impractical, since its accuracy is dependent on the accuracy and number of the excited-state wavefunctions.

Use of the polarization propagator avoids the problem of needing excited-state wavefunctions. In a polarization propagator calculation, only an accurate ground-state wavefunction is necessary. To calculate a property, a sum is still needed; however, the sum is not over a complete space of excited-state wavefunctions but over a complete space of operators. The operator sums are found by applying the equation of motion of the polarization propagator. The equation of motion[2] for the polarization propagator $\langle\langle B;A\rangle\rangle$ that describes the effect of operator B on the molecular property of operator A is

$$\hbar\omega\langle\langle B;A\rangle\rangle = \langle 0|[B,A]|0\rangle - \langle\langle[\mathcal{H},B];A\rangle\rangle. \tag{2}$$

Equation (2) shows that the polarization propagator can be calculated in terms of the next higher order of polarization propagator. The same equation of motion is used for the higher order propagators. Therefore, the equation can be applied repeatedly to yield an infinite sum of nested commutators. In this form, the polarizability in Equation (1) becomes[2]

$$\alpha_{\alpha\beta}(\omega) = \frac{1}{\hbar\omega}\langle 0|\left[\mu_\alpha,\mu_\beta\right]|0\rangle + \left(\frac{-1}{\hbar\omega}\right)\langle 0|\left[[\mathcal{H},\mu_\alpha],\mu_\beta\right]|0\rangle + \left(\frac{-1}{\hbar\omega}\right)^2\langle 0|\left[[\mathcal{H},[\mathcal{H},\mu_\alpha]],\mu_\beta\right]|0\rangle + \cdots. \tag{3}$$

Thus, the problem of calculating molecular properties shifts from the calculation of excited states to the problem of calculating commutators. The commutators are calculated as algebraic sums using "superoperator" algebra. More details can be found in McWeeny's[2] text as well as Jørgensen and Simon's[3] text.

Indistinguishability

The indistinguishability of electrons in a molecular system is important to consider carefully since the polarization propagator employs a multi-electron wavefunction. The multi-electron wavefunction, in order to describe the state properly, needs to incorporate the indistinguishability of the electrons in the system. Indistinguishability is the name given to the concept that when two identical particles in a quantum mechanical system are exchanged, the exchanged state can not be distinguished from the original system. The consequence of indistinguishability for particles of half-integer spin such as electrons is adherence to a fundamental principle, the Pauli exclusion principle.

The Pauli exclusion principle states that identical half-integral spin particles must have wavefunctions that change sign when any two particles are exchanged. This property is called antisymmetry. The wavefunction describing the electronic state must be antisymmetric. Two formalisms are commonly used to ensure that the electronic state wavefunction is antisymmetric, Slater determinants and creation/annihilation operators.

Slater determinants

The first formalism used to ensure antisymmetry is the Slater determinant. For a two-electron system, an approximation to the total wave function can be written as

$$\Psi = \frac{1}{\sqrt{2}}\left[\psi_a(r_1)\psi_b(r_2) - \psi_b(r_1)\psi_a(r_2)\right]. \tag{4}$$

The $\psi_a(r_1)$ are the individual one-electron wavefunctions. If the two particles are exchanged by switching electronic coordinates r_1 and r_2, the total wavefunction changes its sign. Therefore, this wavefunction is antisymmetric. Using the definition of a determinant from linear algebra, the total wavefunction is written identically as

$$\Psi = \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_a(r_1) & \psi_a(r_2) \\ \psi_b(r_1) & \psi_b(r_2) \end{vmatrix}. \tag{5}$$

This determinant is an example of a Slater determinant. Similarly, an antisymmetric three-electron wavefunction can be written as

$$\Psi = \frac{1}{\sqrt{6}}\begin{vmatrix} \psi_a(r_1) & \psi_a(r_2) & \psi_a(r_3) \\ \psi_b(r_1) & \psi_b(r_2) & \psi_b(r_3) \\ \psi_c(r_1) & \psi_c(r_2) & \psi_c(r_3) \end{vmatrix}. \tag{6}$$

In general, a n-electron wavefunction is written as the following Slater determinant

$$\Psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_a(r_1) & \psi_a(r_2) & \cdots & \cdots & \psi_a(r_N) \\ \psi_b(r_1) & \psi_b(r_2) & \cdots & \cdots & \psi_b(r_N) \\ \vdots & \vdots & \ddots & & \vdots \\ \vdots & \vdots & & \ddots & \vdots \\ \psi_N(r_1) & \psi_N(r_2) & \cdots & \cdots & \psi_N(r_N) \end{vmatrix}. \tag{7}$$

Writing a multi-electron wavefunction in this fashion allows the Pauli exclusion principle to be satisfied. When any two columns of the determinant are exchanged, signifying the exchange of two particles, the magnitude of the determinant remains the same; however, the sign is changed.

Creation and Annihilation Operators/Second Quantization

The properties of creation and annihilation operators found in harmonic oscillator analysis[4], many-body solid state theory[5,6] and quantum field theory[7,8] are exploited to construct antisymmetric wavefunctions. Relating such operators to electrons in molecular systems,[2,3,9] a creation operator operates on the electronic wavefunction of a molecular system and creates an electron in a specific quantum state. As a simple example in an atomic system, the creation operator $a^{\dagger}(1s)$ is applied to the vacuum state $|\varnothing\rangle$ as follows:

$$a^{\dagger}(1s)\,|\varnothing\rangle = |1s\rangle\,. \tag{8}$$

The creation operator, $a^{\dagger}(1s)$, creates an electron in the 1s state. The annihilation operator destroys an electron as in the following examples.

$$a(1s)\,|1s^{2}\rangle = |1s^{1}\rangle \quad \text{or} \quad a(2s)\,|1s^{1}2s^{1}\rangle = -|1s^{1}\rangle\,. \tag{9}$$

The negative sign in Equation (9) is a consequence of antisymmetry. Both examples in Equation (9), the initial state had two electrons. In both cases, the annihilation operator destroyed an electron so that the final state had only one electron.

The creation and annihilation operators used above only had spatial labeling. Since the antisymmetry property is a function of spatial and spin coordinates, spatial and spin labels should be used to describe the electronic state. The examples in Equation (9) become

$$a^{\dagger}(1s_{\alpha})\,|\varnothing\rangle = |1s_{\alpha}\rangle, \quad a(1s_{\alpha})\,|1s_{\alpha}\,1s_{\beta}\rangle = |1s_{\beta}\rangle \quad \text{and} \quad a(2s_{\alpha})\,|1s_{\alpha}\,2s_{\alpha}\rangle = -|1s_{\alpha}\rangle\,. \tag{10}$$

What happens when we try to create an electron that is already present or annihilate an electron that is not present? The implication of the Pauli exclusion principle is that the maximum number of electrons in a given quantum state is one. In addition, the minimum number of electrons in a given state must be zero. Therefore, trying to create an electron in a state that is occupied or annihilating an electron that does not exist is not physical. Such operations are defined as zero, e. g.,

$$a^{\dagger}(1s_{\alpha})\,|1s_{\alpha}\,1s_{\beta}\rangle = 0 \quad \text{and} \quad a(2s_{\alpha})\,|1s_{\alpha}\,1s_{\beta}\rangle = 0\,. \tag{11}$$

These definitions ensure that the Pauli exclusion principle is satisfied. The operators can also be defined in an alternative, but equivalent fashion, using anticommutation rules to ensure antisymmetry. For states m and n, the anticommutation relations are

$$\begin{aligned} \left\{a_m^\dagger, a_n^\dagger\right\} &= a_m^\dagger a_n^\dagger + a_n^\dagger a_m^\dagger = 0 \\ \left\{a_m, a_n\right\} &= a_m a_n + a_n a_m = 0 \\ \left\{a_m^\dagger, a_n\right\} &= a_m^\dagger a_n + a_n a_m^\dagger = \delta_{mn} . \end{aligned} \tag{12}$$

These anticommutation relations demonstrate that when m = n, the same electronic state can not be created twice nor the same electronic state be annihilated twice.

A two-electron ground state that satisfies the antisymmetry requirement in terms creation operators is written as, e. g.

$$a^\dagger(1s_\beta)a^\dagger(1s_\alpha)|\varnothing\rangle = |1s_\beta 1s_\alpha\rangle . \tag{13}$$

An n-electron antisymmetric wavefunction is written as

$$a^\dagger(nlm_\beta)\cdots a^\dagger(1s_\beta)a^\dagger(1s_\alpha)|\varnothing\rangle = |nlm_\beta \cdots 1s_\beta 1s_\alpha\rangle . \tag{14}$$

An excited configuration of a multi-electron system can be constructed using a combination of creation and annihilation operators. First the annihilation operator destroys one of the electrons in the Hartree-Fock ground state, then the creation operator places an electron into an excited state. For example, creation and annihilation operators can be used to form an excited configuration of helium,

$$a^\dagger(2s_\alpha)a(1s_\beta)|1s_\beta 1s_\alpha\rangle = |2s_\alpha 1s_\alpha\rangle . \tag{15}$$

Because of the anticommutation relations of Equation (12), the order of the operators is very important. Appendix C explains in more detail the consequence of applying creation and annihilation operators to a multi-electron state.

Operators in the second quantized formulation of quantum chemistry are products of creation and annihilation operators with specific coefficients. The operators can involve any number of electrons, though only one and two electron operators are regularly used. A one-electron operator has the form,

$$\theta = \sum_{kl} \theta_{kl} a_k^{\dagger} a_l \text{ where } \theta_{kl} = \left\langle \phi_k(i) \middle| \theta(\bar{r}_i, \bar{p}_i) \middle| \phi_l(i) \right\rangle . \tag{16}$$

The coefficient θ_{kl} is the matrix element of a more traditional quantum mechanical operator with the basis functions ϕ_k and ϕ_l. The index i indicates the ith electron in the system. Examples of quantities described with one-electron operators are the kinetic energy, momentum, angular momentum, magnetic moment and polarization. Two electron operators have the form,

$$V = \sum_{klmn} a_k^{\dagger} a_l^{\dagger} a_m a_n \left\langle \phi_k(i) \phi_l(j) \middle| V(\bar{r}_i, \bar{r}_j, \bar{p}_i, \bar{p}_j) \middle| \phi_n(i) \phi_m(j) \right\rangle . \tag{17}$$

The indices i and j refer to different electrons, i. e. i and j can never refer to the same electron in the calculation of a single matrix element. The two electron operators are used for the calculation of Coulomb and exchange energies.

Occupation Number Formalism

When a basis set is used to describe the multi-electron wavefunction of a system, the wavefunction for a given state is written in terms of whether a particular basis function is used or not. For clarity of presentation, the one-electron spin-dependent hydrogenic wavefunctions are chosen as an example of a basis set. This basis set is $\{1s_{\alpha}, 1s_{\beta}, 2s_{\alpha}, 2s_{\beta}, 2p_{x\alpha}, 2p_{x\beta}, 2p_{y\alpha}, \ldots, \}$. The multi-electron wavefunction is derived from antisymmetrized products of these functions. In the occupation number formalism,[5,6,9] the wavefunction is constructed by counting the number of electrons in each state, e. g.

$$|\Psi\rangle = |n_{1s\alpha}\, n_{1s\beta}\, n_{2s\alpha}\, n_{2s\beta} \cdots n_{nlm\alpha}\, n_{nlm\beta}\rangle , \tag{18}$$

where the $n_{nlm\alpha}$ denotes the electrons with the basis function nlm_α, where nlm_α are the four quantum numbers needed to fully describe the hydrogenic single-electron state. Thus the Hartree-Fock ground state of the helium atom is rewritten in the occupation number formalism as

$$|1s_\alpha 1s_\beta\rangle = |1,1,0,0,0,\cdots,0\rangle . \tag{19}$$

The ones in the right side of Equation (19) indicate that the $1s_\alpha$ and $1s_\beta$ basis functions are occupied while the zeroes indicate that none of other basis functions are occupied. An excited configuration of helium can be rewritten as

$$|1s_\alpha 2s_\alpha\rangle = |1,0,1,0,0,\cdots,0\rangle . \tag{20}$$

A sum over a complete set of occupation numbers spans a complete multi-electron space; therefore, the completeness relation for multi-electron wavefunctions can be written as

$$\sum_i |i\rangle\langle i| = 1 = \sum_{n_{1s\alpha}} \sum_{n_{1s\beta}} \cdots \sum_{n_{nlm\beta}} |n_{1s\alpha}\, n_{1s\beta} \cdots n_{nlm\beta}\rangle\langle n_{nlm\beta} \cdots n_{1s\beta}\, n_{1s\alpha}| . \tag{21}$$

In the summations above, the only values that the occupation numbers may have is zero or one. This restriction is due to the Pauli exclusion principle. In terms of creation and annihilation operators, the sum-over-states becomes

$$|n_{1s\alpha}\, n_{1s\beta} \cdots n_{nlm\beta}\rangle = a^\dagger(1s_\alpha)\, a^\dagger(1s_\beta) \cdots a^\dagger(nlm_\beta)|\varnothing\rangle . \tag{22}$$

Further properties involving the importance of ordering of creation and annihilation operators in multi-electron states are found in Appendix C.

Foundations of the Polarization Propagator

The polarization propagator has its origins in the time correlation function of the density operator. The density operator is a statistical description of the state of an ensemble of quantum systems. One text describes the density operator as an averaging operator of single quantum systems over an ensemble.[4] A density operator can represent a mixed state, which does not have a specified wavefunction that can be constructed from a basis set. Therefore, to find numerical results involving a large number of quantum systems, the density operator is used. In conventional formalism, the N-electron density operator is expressed as

$$\rho(t) = |\Psi(t)\rangle\langle\Psi(t)|. \tag{23}$$

For calculations with single-electron operators, the N-electron density operator contains an overabundance of information. Therefore, the simpler single-electron density operator is used. In the language of second quantization, the single-particle density operator can be expressed as

$$\rho(\bar{r},t) = \sum_{i,j} \phi_i^*(\bar{r})\phi_j(\bar{r})a_i^\dagger(t)a_j(t) \text{ where the } \phi_i, \phi_j \text{ are basis functions.} \tag{24}$$

The relationship between the densities at two different times is found in the density correlation function constructed by Zubarev[10] and considered by others[11,12]. Correlation functions[13] describe how one quantity changes in response to a perturbation that couples to a second quantity. As a simple example, consider that an arbitrary charge distribution will deform in the presence of a time-dependent external electric field. The density time correlation function relates the charge distribution at one instant of time to the charge distribution at another instant of time. This charge density correlation function may be written using the Heaviside step function[14] as

$$\chi(t,t') = -i\theta(t-t')\{\langle\rho(t)\rho(t')\rangle - \langle\rho(t')\rangle\langle\rho(t)\rangle\} - i\theta(t'-t)\{\langle\rho(t')\rho(t)\rangle - \langle\rho(t)\rangle\langle\rho(t')\rangle\}. \quad (25)$$

Since the correlation function is written using the Heaviside step function, a charge distribution in the future never has an effect on a charge distribution in the past. Thus causality is ensured since the effects of a charge distribution propagate into the future, not into the past.

The Fourier transform of the time-dependent correlation function is the energy-dependent density correlation function $\chi_{\rho\rho}(E)$.[15]

$$\chi_{\rho\rho}(E) = \lim_{\varepsilon\to 0}\sum_{n\neq 0}\left\{\frac{\langle 0|\rho|n\rangle\langle n|\rho|0\rangle}{E-\hbar\omega_{n0}+i\varepsilon} - \frac{\langle 0|\rho|n\rangle\langle n|\rho|0\rangle}{E+\hbar\omega_{n0}-i\varepsilon}\right\} \text{ where } \hbar\omega_{n0} = E_n - E_0. \quad (26)$$

In terms of the points $\bar{r}$ and $\bar{r}'$, the time-dependent density correlation function is rewritten as

$$\chi_{\rho\rho}(\bar{r},\bar{r}';E) = \lim_{\varepsilon\to 0}\sum_{n\neq 0}\left\{\frac{\langle 0|\rho(\bar{r})|n\rangle\langle n|\rho(\bar{r}')|0\rangle}{E-\hbar\omega_{n0}+i\varepsilon} - \frac{\langle 0|\rho(\bar{r}')|n\rangle\langle n|\rho(\bar{r})|0\rangle}{E+\hbar\omega_{n0}-i\varepsilon}\right\} \quad (27)$$

where $\hbar\omega_{n0} = E_n - E_0$.

The imaginary infinitesimal amount added or subtracted to the energy denominator in the transformed density-correlation function is a result of taking the Fourier transform of the Heaviside step function. The imaginary infinitesimal allows causality to be maintained when the polarization propagator is contour-integrated to find the residues or poles of the propagator. The significance of finding the residue and poles will be explained in an upcoming section. The imaginary infinitesimal arises in the consideration of ensuring that a sinusoidal perturbation applied to system is zero at infinite time in the i

r

s

Th

past. Thus, the damping of the sinusoidal perturbation occurs when it is multiplied by a real exponential, $e^{\varepsilon t}$.

$$\lim_{t \to -\infty} H'(\omega) = \lim_{t \to -\infty} \frac{1}{2}\left(A_{\omega} e^{-i\omega t} + A_{-\omega} e^{i\omega t}\right) e^{\varepsilon t} = 0 . \tag{28}$$

The energy-dependent density correlation function can be rewritten in terms of the polarization propagator by substituting Equation (24), the definition of the density operator, into Equation (27).

$$\chi_{\rho\rho}(\bar{r},\bar{r}';E) = \sum_{i,j,k,l} \lim_{\varepsilon \to 0} \sum_{n \neq 0} \left\{ \frac{\langle 0|\phi_i^*(\bar{r})\phi_j(\bar{r}) a_i^\dagger(t) a_j(t)|n\rangle\langle n|\phi_k^*(\bar{r}')\phi_l(\bar{r}') a_k^\dagger(t) a_l(t)|0\rangle}{E - \hbar\omega_{n0} + i\varepsilon} - \frac{\langle 0|\phi_k^*(\bar{r}')\phi_l(\bar{r}') a_k^\dagger(t) a_l(t)|n\rangle\langle n|\phi_i^*(\bar{r})\phi_j(\bar{r}) a_i^\dagger(t) a_j(t)|0\rangle}{E + \hbar\omega_{n0} - i\varepsilon} \right\} . \tag{29}$$

Rearranging Equation (29) yields the energy-dependent density correlation function in terms of basis functions and the polarization propagator

$$\chi_{\rho\rho}(\bar{r},\bar{r}';E) = \sum_{i,j,k,l} \phi_i^*(\bar{r})\phi_j(\bar{r})\phi_k^*(\bar{r}')\phi_l(\bar{r}')\chi_{jl}^{ik}(E), \tag{30}$$

where $\chi_{jl}^{ik}(E)$ is defined as the polarization propagator.

$$\chi_{jl}^{ik}(E) = \sum_{n \neq 0} \left\{ \frac{\langle 0|a_i^\dagger a_j|n\rangle\langle n|a_k^\dagger a_l|0\rangle}{E - \hbar\omega_{n0} + i\varepsilon} - \frac{\langle 0|a_k^\dagger a_l|n\rangle\langle n|a_i^\dagger a_j|0\rangle}{E + \hbar\omega_{n0} - i\varepsilon} \right\} = \chi_{jl}^{ik}(\omega) . \tag{31}$$

Note $E = \hbar\omega$ is substituted to give the frequency-dependent polarization propagator. The imaginary infinitesimal portion of the propagator shall be dropped since only off-resonant response will be considered. The reduced resolvent operator $R(\omega)$ is defined to further simplify the expression.

$$R(\omega) = \left(-\hbar\omega_{0n} + \hbar\omega\right)^{-1}\left(1 - |0\rangle\langle 0|\right) \text{ where } 1 = \sum_n |n\rangle\langle n| . \tag{32}$$

Therefore, the polarization propagator becomes

$$\chi_{kl}^{ij}(\omega) = -\langle 0 | a_i^{\dagger} a_j R(-\omega) a_k^{\dagger} a_l | 0 \rangle - \langle 0 | a_k^{\dagger} a_l R(\omega) a_i^{\dagger} a_j | 0 \rangle . \tag{33}$$

Defining a_l^k as $a_l^k = a_k^{\dagger} a_l$ (the single-electron replacement operator) modifies the polarization propagator to become

$$\chi_{kl}^{ij}(\omega) = -\langle 0 | a_j^i R(-\omega) a_l^k | 0 \rangle - \langle 0 | a_l^k R(\omega) a_j^i | 0 \rangle . \tag{34}$$

The polarization propagator is rewritten as

$$\chi_{kl}^{ij}(\omega) = -\langle 0 | a_j^i R(-\omega) a_l^k | 0 \rangle - \langle 0 | a_l^k R(\omega) a_j^i | 0 \rangle \tag{35}$$

$$\text{or } \Pi_{\kappa,\kappa'}^{\lambda,\lambda'}(\omega) = -\langle 0 | a_{\kappa}^{\lambda} R(\omega) a_{\kappa'}^{\lambda'} | 0 \rangle - \langle 0 | a_{\kappa'}^{\lambda'} R(-\omega) a_{\kappa}^{\lambda} | 0 \rangle . \tag{36}$$

It is also possible to include the damping of excited states in the definition of the polarization propagator; however, such off-resonance damping is assumed negligible.

The Nonlinear Polarization Propagator

The polarization propagator is a general linear-response function meaning that it can be applied to any situation where the state density responds linearly to an applied perturbation. Specific examples include the polarizability as the linear-response function measuring the response to an applied electric field, and the paramagnetic susceptibility measuring the response to an applied magnetic field. When linear-response functions are inadequate to describe the response, nonlinear-response functions are used in addition. Nonlinear-response functions have been constructed by Olsen and Jørgensen[16] and have been reinterpreted using second-quantized operators by Hettema et. al.[17] and Moszynski et. al.[18] in terms of nonlinear polarization propagators. The nonlinear polarization propagator has the form

$$\Pi_{\kappa,\kappa',\kappa''}^{\lambda,\lambda',\lambda''}(\omega_1,\omega_2) = (1+P_{12}) \sum_{n,m\neq 0} \left\{ \begin{array}{l} \dfrac{\langle 0|a_\kappa^\lambda|n\rangle\langle n|\left(a_{\kappa'}^{\lambda'} - \rho_{\kappa'}^{\lambda'}\right)|m\rangle\langle m|a_{\kappa''}^{\lambda''}|0\rangle}{(-\hbar\omega_{0n} - \hbar\omega_1 - \hbar\omega_2)(-\hbar\omega_{0n} - \hbar\omega_2)} + \\ \dfrac{\langle 0|a_{\kappa''}^{\lambda''}|n\rangle\langle n|\left(a_{\kappa'}^{\lambda'} - \rho_{\kappa'}^{\lambda'}\right)|m\rangle\langle m|a_\kappa^\lambda|0\rangle}{(-\hbar\omega_{0n} + \hbar\omega_2)(-\hbar\omega_{0n} + \hbar\omega_1 + \hbar\omega_2)} + \\ \dfrac{\langle 0|a_{\kappa'}^{\lambda'}|n\rangle\langle n|\left(a_\kappa^\lambda - \rho_\kappa^\lambda\right)|m\rangle\langle m|a_{\kappa''}^{\lambda''}|0\rangle}{(-\hbar\omega_{0n} + \hbar\omega_1)(-\hbar\omega_{0n} - \hbar\omega_2)} \end{array} \right\} \tag{37}$$

where the permutator P_{12} permutes the following variables

$$P_{12} = \begin{pmatrix} \omega_1 \leftrightarrow \omega_2 \\ \lambda' \leftrightarrow \lambda'' \\ \kappa' \leftrightarrow \kappa'' \end{pmatrix} \tag{38}$$

and the operator ρ_κ^λ is defined as $\rho_\kappa^\lambda = \langle 0|a_\kappa^\lambda|0\rangle$. The nonlinear polarization propagator expressed in terms of the reduced resolvent operator becomes

$$\Pi_{\kappa,\kappa',\kappa''}^{\lambda,\lambda',\lambda''}(\omega_1,\omega_2) = (1+P_{12}) \left\{ \begin{array}{l} \langle 0|a_\kappa^\lambda R(-\omega_1 - \omega_2)\left(a_{\kappa'}^{\lambda'} - \rho_{\kappa'}^{\lambda'}\right)R(-\omega_2)a_{\kappa''}^{\lambda''}|0\rangle + \\ \langle 0|a_{\kappa''}^{\lambda''} R(\omega_2)\left(a_{\kappa'}^{\lambda'} - \rho_{\kappa'}^{\lambda'}\right)R(\omega_1 + \omega_2)a_\kappa^\lambda|0\rangle + \\ \langle 0|a_{\kappa'}^{\lambda'} R(\omega_1)\left(a_\kappa^\lambda - \rho_\kappa^\lambda\right)R(-\omega_2)a_{\kappa''}^{\lambda''}|0\rangle \end{array} \right\}. \tag{39}$$

The propagator that is Equation (39) is used to determine nonlinear molecular properties such as the hyperpolarizability.

The Derivative of the Polarization Propagator

The structure of the polarization propagator in the form of Equation (29) shows that for contour integration with respect to energy, its poles yield excitation energies of a molecular system while its residues yield transition matrix elements. Thus, the values of molecular properties can be found not only by applying the polarization propagator but also by finding its poles and residues.

The polarization propagator has been used to calculate a variety of molecular properties. Oddershede[12] mentions in his review article the following properties: oscillator strengths, Rayleigh scattering cross sections, photoionization cross sections, excitation energies, radiative lifetimes, static and dynamic polarizabilities, hyperpolarizabilities, dipole moment derivatives, potential energy curves, nuclear spin-spin coupling constants, nuclear magnetic shielding constants, magnetic susceptibilities, Verdet constants, spin-rotation constants, magnetic rotatory strengths, force constants and C_6 van der Waals coefficients. Most of these properties are calculated as single-point calculations at the equilibrium geometry of the molecule. However, in many cases, it is important to know the value of a property at several different molecular geometries about the equilibrium geometry. Also nuclear-coordinate derivatives of the properties are often calculated using numerical differentiation techniques.[19]

Magnetic Properties

The derivatives of magnetic properties with respect to a parameter have been examined, all using numerical methods. Several studies have examined the relationship of various orders of spin-spin coupling constants to changes in molecular geometry. $^1J(H, C)$ and $^2J(H, H)$ surfaces have been calculated for methane and perdeuteromethane using 49 distinct geometries.[20] Lazzeretti, Zanasi and Raynes also created surfaces from the contributions to the spin-spin coupling constants: Fermi contact terms, spin-dipole terms and orbital paramagnetic terms. The surface construction of $^1J(H, C)$ and $^2J(H, H)$ for methane has been repeated more recently using 51 distinct geometries.[21] Calculations of $^2J(H, H)$ have been done for CH_4, SiH_4, GeH_4 and SnH_4 at multiple geometries.[22] The calculations necessitated finding the normal-coordinate derivatives of the spin-spin coupling surface so that vibrational averages could be calculated. $^1J(H, C)$ and $^1J(H, N)$ have been computed for HCN and HNC at the equilibrium bond distance r_e and at $r_e \pm 0.1$Å.[23] Third-order, i. e. vicinal, spin-spin coupling constants $^3J(H, F)$ in substituted fluoroethanes have been determined as a function of the torsion angle between the hydrogen and fluorine atoms.[24] The through-space spin-spin coupling constants $^{TS}J(P, P)$ and $^{TS}J(Se, Se)$ in diphospho-methanes and diseleno-methanes have been calculated as a function of torsion angle using a simplified polarization propagator technique.[25] (The through-space contribution accounts only for that which is due to overlap of the lone pairs of the phosphorus or selenium atoms.) Spin-spin coupling constants have also been computed as a function of hydrogen-bond distance.[26]

Other magnetic properties have been calculated as a function as internuclear distance. The magnetizability and ^{13}C nuclear magnetic shielding surfaces for methane have been determined using 59 distinct geometries.[27] The spin-rotation constant has been computed in GaH[28] and AlH[29] as a function of internuclear distance. The nuclear magnetic shielding constant and spin-rotation constant of various isotopomers of second row hydrides have been calculated as function of internuclear distance.[30] Surfaces of the nuclear magnetic shielding of ^{17}O and H, the spin-rotation constant of ^{17}O and the rotational g-tensor in the oxonium ion H_3O^+ versus normal vibrational coordinates have been constructed.[31] Vibrational averages for Verdet constants have been found for N_2, H_2, CO and HF.[32]

Electric Properties

Electric properties that have been calculated using polarization propagators include Raman intensities, which depend on the normal-mode derivative of the polarizability, for CO, N_2, HCl and Cl_2.[33] The intensities were calculated using numerical differentiation techniques on polarizability calculations at three bond lengths. Potential energy curves of the ground state and various excited states of BH have been constructed.[34] Vibrational averages of the ground state energy, dipole moment and different Cartesian components of the polarizability, $\alpha_{zz}(\omega)$ and $\alpha_{xx}(\omega)$, and hyperpolarizabilities, $\beta_{zzz}(\omega)$, $\beta_{zxx}(\omega)$ and $\beta_{xzx}(\omega)$, have all been calculated using polarization propagator techniques.[35] The hyperpolarizabilities were computed by applying the finite-field technique[36] to calculations of the polarizability. Vibrational averages of the second hyperpolarizability $\gamma(\omega,\omega,0)$ of N_2 were found using finite-field techniques, applied to the polarizability calculated with the polarization propagator. The vibrational contributions to the hyperpolarizability and second hyperpolarizability of linear polymethine dyes (push-pull polyenes) have been determined and have been used to examine the change in nonlinear optical properties versus bond-length alternation (BLA).[37] Additionally, polarizability surfaces for $^{12}CH_4$ and $^{12}CD_4$ have been constructed using 49 distinct geometries.[38] The effect of vibronic coupling in the K-shell x-ray spectra of ethylene has been recently examined via calculation of normal-mode potential energy derivatives as vibronic coupling constants.[39] Oscillator strength sum rules of H_2 have been computed at 21 geometries to find their internuclear coordinate dependences.[40]

Uses of the Nonlinear Polarization Propagator

The nonlinear polarization propagator has been used in quadratic-response function theory[16, 17] to calculate quadratic-response properties and linear-response properties of excited states. Quadratic-response functions have been used to calculate quantities that are dependent upon vibronic coupling such as vibronic coupling constants, phosphorescence lifetimes and forbidden dipole-transition strengths. The nonlinear propagator is used to calculate the mixing of singlet and triplet spin states due to spin-orbit coupling. This spin mixing allows spin-forbidden dipole transitions and phosphorescence. Spin-forbidden transitions and phosphorescence lifetimes have been calculated for formaldehyde.[41,42] The vibrational structure of ground-state excitation bands has been determined by use of vibronic coupling constants for H_2O, NH_3, CH_4,[43] ethylene,[44] and pyrrole.[45] The effect of vibronic coupling on the two-photon spectra of benzene[46] and pyramidine[47] for dipole-forbidden two-photon transitions has been computed. Spin-orbit effects on the Auger spectrum of water have been examined.[48] Potential energy curves of the π^* state of the cyclopropenyl cation $C_3H_3^+$ have been calculated including the effects of vibronic coupling on the transition from the ground state to the π^* state.[49]

Derivation of the Polarization Propagator Derivative

Introduction

The derivation relating the derivative of the polarization propagator to the first order nonlinear polarization propagator is suggested by the relationship found by Hunt *et al.*[50,51]

v

p

Th

pa

ma

pol

the

term

idea

propa

allow

Inade

The

calcula

between the nuclear-coordinate derivative of the polarizability and the hyperpolarizability density,

$$\partial\alpha_{\alpha\beta}(\bar{r};\bar{r}',\omega)/\partial R_{\gamma}^{K} = \int d\bar{r}''\,\beta_{\alpha\beta\delta}(\bar{r};\bar{r}',\omega,\bar{r}'',0)Z^{K}\mathbf{T}_{\delta\gamma}(\bar{r}'',\bar{R}^{K})\,. \tag{40}$$

The polarizability density $\alpha_{\alpha\beta}(\bar{r};\bar{r}',\omega)$ can be calculated using the polarization propagator

$$\alpha_{\alpha\beta}(r,r';\omega) = -\left[p(r)_{\alpha}\right]_{\lambda}^{\kappa}\left[p(r')_{\beta}\right]_{\lambda'}^{\kappa'}\Pi_{\kappa,\kappa'}^{\lambda,\lambda'}(\omega) \quad \text{where} \quad \left[p(r)_{\alpha}\right]_{\lambda}^{\kappa} = \langle\lambda|p(r)_{\alpha}|\kappa\rangle\,, \tag{41}$$

whereas the hyperpolarizability density is calculated with the nonlinear polarization propagator

$$\beta_{\alpha\beta\gamma}(\bar{r},\bar{r}',\bar{r}'';\omega',\omega'') = \left[p(\bar{r})_{\alpha}\right]_{\lambda}^{\kappa}\left[p(\bar{r}')_{\beta}\right]_{\lambda'}^{\kappa'}\left[p(\bar{r}'')_{\gamma}\right]_{\lambda''}^{\kappa''}\Pi_{\kappa,\kappa',\kappa''}^{\lambda,\lambda',\lambda''}(\omega',\omega'')\,. \tag{42}$$

The matrix elements $\left[p(\bar{r})_{\alpha}\right]_{\lambda}^{\kappa} = \langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle$ may have a dependence on an arbitrary parameter and, as shown below, the replacement operators that comprise the propagators may also depend on the same parameter. Therefore, when the derivative of the polarization propagator is considered, the derivative must contain terms that differ from the nonlinear polarization propagator. These "extra" terms will be shown to cancel the terms from the derivatives of the standard matrix elements $\left[p(\bar{r})_{\alpha}\right]_{\lambda}^{\kappa}$ in Appendix D. The idea is emphasized that the extra terms arise in both the standard matrix elements and the propagators because the basis functions that comprise the basis set for the calculation are allowed to vary with respect to the arbitrary parameter η.

Inadequacies of Single-electron Wavefunctions

The derivation for the derivative of the polarization propagator is accomplished by calculating and manipulating the derivative of the ground-state wavefunction, the derivative of the reduced resolvent and the derivative of the Hamiltonian.[52] Finding the polarization propagator derivative involves also involves the derivatives of the creation and annihilation operators. The dependence of the creation and annihilation operators on an arbitrary parameter, such as nuclear coordinate, can be demonstrated by examining the derivative of the ground state wavefunction in the language of second quantization. The simple case of a one-electron ground state is now considered.

$$|0\rangle = a_0^\dagger|\varnothing\rangle \tag{43}$$

The derivative of the ground state is found to be[52]

$$\frac{\partial|0\rangle}{\partial\eta} = -G(0)\frac{\partial\mathcal{H}}{\partial\eta}|0\rangle \tag{44}$$

The reduced resolvent, G(0), can be expanded and simplified.

$$\begin{aligned}\frac{\partial|0\rangle}{\partial\eta} &= -(1-\wp)(\mathcal{H}-E_0)^{-1}(1-\wp)\frac{\partial\mathcal{H}}{\partial\eta}|0\rangle \\ &= -(\mathcal{H}-E_0)^{-1}(1-\wp)\frac{\partial\mathcal{H}}{\partial\eta}|0\rangle \\ &= -R(0)\frac{\partial\mathcal{H}}{\partial\eta}|0\rangle\end{aligned} \tag{45}$$

A new definition of the reduced resolvent is applied to Equation (45)

$$R(\omega) = (\mathcal{H}-E_0+\hbar\omega)^{-1}(1-\wp) \tag{46}$$

The derivative in the language of second quantization becomes

$$\frac{\partial|0\rangle}{\partial\eta} = -\sum_{\lambda}{}'\left[\frac{\partial\mathcal{H}}{\partial\eta}\right]_0^\lambda R(0)\,a_0^\lambda\, a_0^\dagger|\varnothing\rangle \tag{47}$$

where $\left[\frac{\partial\mathcal{H}}{\partial\eta}\right]_\kappa^\lambda = \langle\kappa|\frac{\partial\mathcal{H}}{\partial\eta}|\lambda\rangle$ are the matrix elements of the Hamiltonian derivative and $a_\kappa^\lambda = a_\lambda^\dagger a_\kappa$ is defined as the product of a creation and an annihilation operator.

This simple analogy between the ground state derivative in the second quantization formalism and the ground-state derivative in the standard formalism holds only for one electron systems. When two or more electrons comprise the ground state, the commutation relationship between the creation and annihilation operators becomes important and the simple analogy fails.[53] The antisymmetrical nature of the multi-electron wavefunction is taken into account by using occupation number wavefunctions. Thus the differences between the derivatives of Hunt *et. al.*[50,51] and this work lies in the nature of the polarization propagator which is defined in terms of single-electron basis states for a many-body system. Since the property is defined with a single-electron basis, the anti-commutation relationship between the single-electron states must be taken into account.

Derivative of the Polarization Propagator

The polarizability density, in the language of second quantization, is expressed as[54]

$$\alpha_{\alpha\beta}(\bar{r},\bar{r}';\omega) = -\left[p(\bar{r})_\alpha\right]_\lambda^\kappa \left[p(\bar{r}')_\beta\right]_{\lambda'}^{\kappa'} \Pi_{\kappa,\kappa'}^{\lambda,\lambda'}(\omega) \quad \text{where} \quad \left[p(\bar{r})_\alpha\right]_\lambda^\kappa = \langle \lambda | p(\bar{r})_\alpha | \kappa \rangle . \qquad (48)$$

To take the derivative of the polarizability density with respect to an arbitrary parameter, we need to consider what elements of the polarizability density may have parameter dependence. In this treatment, the electronic coordinate is the only parameter that will not be considered. First the matrix elements $\left[p(\bar{r})_\alpha\right]_\lambda^\kappa = \langle \lambda | p(\bar{r})_\alpha | \kappa \rangle$ are examined. Both the $\langle \lambda |$ and the $| \kappa \rangle$ wavefunctions may have parameter dependence that is easily calculated in terms of sums-over-states with single-electron states.

All of the elements of the polarization propagator may have parameter dependence. The derivative of the polarization propagator can be written as

$$\begin{aligned}\frac{\partial \Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)}{\partial \eta} = &-\frac{\partial \langle 0|}{\partial \eta} a^{\lambda}_{\kappa} R(\omega) a^{\lambda'}_{\kappa'}|0\rangle - \langle 0|\frac{\partial a^{\lambda}_{\kappa}}{\partial \eta} R(\omega) a^{\lambda'}_{\kappa'}|0\rangle - \langle 0|a^{\lambda}_{\kappa}\frac{\partial R(\omega)}{\partial \eta} a^{\lambda'}_{\kappa'}|0\rangle - \\ &\langle 0|a^{\lambda}_{\kappa} R(\omega)\frac{\partial a^{\lambda'}_{\kappa'}}{\partial \eta}|0\rangle - \langle 0|a^{\lambda}_{\kappa} R(\omega) a^{\lambda'}_{\kappa'}\frac{\partial |0\rangle}{\partial \eta} - \frac{\partial \langle 0|}{\partial \eta} a^{\lambda'}_{\kappa'} R(-\omega) a^{\lambda}_{\kappa}|0\rangle - \langle 0|\frac{\partial a^{\lambda'}_{\kappa'}}{\partial \eta} R(-\omega) a^{\lambda}_{\kappa}|0\rangle \\ &-\langle 0|a^{\lambda'}_{\kappa'}\frac{\partial R(-\omega)}{\partial \eta} a^{\lambda}_{\kappa}|0\rangle - \langle 0|a^{\lambda'}_{\kappa'} R(-\omega)\frac{\partial a^{\lambda}_{\kappa}}{\partial \eta}|0\rangle - \langle 0|a^{\lambda'}_{\kappa'} R(-\omega) a^{\lambda}_{\kappa}\frac{\partial |0\rangle}{\partial \eta}.\end{aligned} \tag{49}$$

The derivative with respect to any parameter η of the ground-state wavefunction and the derivative with respect to any parameter η of the reduced resolvent can be shown to be[52]

$$\frac{\partial |0\rangle}{\partial \eta} = -R(0)\frac{\partial \mathcal{H}}{\partial \eta}|0\rangle \tag{50}$$

$$\frac{\partial R(\omega)}{\partial \eta} = -R(\omega)\frac{\partial(\mathcal{H}-E_0)}{\partial \eta}R(\omega) + R(\omega)R(0)\frac{\partial \mathcal{H}}{\partial \eta}\wp + \wp\frac{\partial \mathcal{H}}{\partial \eta}R(0)R(\omega) \tag{51}$$

where $\wp = |0\rangle\langle 0|$.

Upon substitution, the polarization propagator derivative becomes

$$\begin{aligned}\frac{\partial \Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)}{\partial \eta} = &+\langle 0|\frac{\partial \mathcal{H}}{\partial \eta} R(0)\, a^{\lambda}_{\kappa} R(\omega)\, a^{\lambda'}_{\kappa'}|0\rangle - \langle 0|\frac{\partial a^{\lambda}_{\kappa}}{\partial \eta} R(\omega)\, a^{\lambda'}_{\kappa'}|0\rangle \\ &+\langle 0|a^{\lambda}_{\kappa} R(\omega)\frac{\partial(\mathcal{H}-E_0)}{\partial \eta} R(\omega)\, a^{\lambda'}_{\kappa'}|0\rangle - \langle 0|a^{\lambda}_{\kappa} R(\omega)R(0)\frac{\partial \mathcal{H}}{\partial \eta}\wp\, a^{\lambda'}_{\kappa'}|0\rangle \\ &-\langle 0|a^{\lambda}_{\kappa}\wp\frac{\partial \mathcal{H}}{\partial \eta} R(0)R(\omega)\, a^{\lambda'}_{\kappa'}|0\rangle - \langle 0|a^{\lambda}_{\kappa} R(\omega)\frac{\partial a^{\lambda'}_{\kappa'}}{\partial \eta}|0\rangle \\ &+\langle 0|a^{\lambda}_{\kappa} R(\omega)\, a^{\lambda'}_{\kappa'} R(0)\frac{\partial \mathcal{H}}{\partial \eta}|0\rangle + \langle 0|\frac{\partial \mathcal{H}}{\partial \eta} R(0)\, a^{\lambda'}_{\kappa'} R(-\omega)\, a^{\lambda}_{\kappa}|0\rangle \\ &-\langle 0|\frac{\partial a^{\lambda'}_{\kappa'}}{\partial \eta} R(-\omega)\, a^{\lambda}_{\kappa}|0\rangle + \langle 0|a^{\lambda'}_{\kappa'} R(-\omega)\frac{\partial(\mathcal{H}-E_0)}{\partial \eta} R(-\omega)\, a^{\lambda}_{\kappa}|0\rangle \\ &-\langle 0|a^{\lambda'}_{\kappa'} R(-\omega)R(0)\frac{\partial \mathcal{H}}{\partial \eta}\wp\, a^{\lambda}_{\kappa}|0\rangle' - \langle 0|a^{\lambda'}_{\kappa'}\wp\frac{\partial \mathcal{H}}{\partial \eta} R(0)R(-\omega)\, a^{\lambda}_{\kappa}|0\rangle \\ &-\langle 0|a^{\lambda'}_{\kappa'} R(-\omega)\frac{\partial a^{\lambda}_{\kappa}}{\partial \eta}|0\rangle + \langle 0|a^{\lambda'}_{\kappa'} R(-\omega)\, a^{\lambda}_{\kappa} R(0)\frac{\partial \mathcal{H}}{\partial \eta}|0\rangle\end{aligned} \tag{52}$$

Terms (1, 5), (4, 7), (8, 12) and (11, 14) in Equation (52) are combined using the definition $\rho_\kappa^\lambda = \langle 0|a_\kappa^\lambda|0\rangle$. As an example, terms 1 and 5 are combined.

$$\begin{aligned}
&\langle 0|\frac{\partial \mathcal{H}}{\partial \eta} R(0)\, a_\kappa^\lambda R(\omega)\, a_{\kappa'}^{\lambda'}|0\rangle - \langle 0|a_\kappa^\lambda \wp \frac{\partial \mathcal{H}}{\partial \eta} R(0) R(\omega)\, a_{\kappa'}^{\lambda'}|0\rangle \\
&= \langle 0|\frac{\partial \mathcal{H}}{\partial \eta} R(0)\, a_\kappa^\lambda R(\omega)\, a_{\kappa'}^{\lambda'}|0\rangle - \langle 0|a_\kappa^\lambda|0\rangle\langle 0|\frac{\partial \mathcal{H}}{\partial \eta} R(0) R(\omega)\, a_{\kappa'}^{\lambda'}|0\rangle \\
&= \langle 0|\frac{\partial \mathcal{H}}{\partial \eta} R(0)\, a_\kappa^\lambda R(\omega)\, a_{\kappa'}^{\lambda'}|0\rangle - \langle 0|\frac{\partial \mathcal{H}}{\partial \eta} R(0)\langle 0|a_\kappa^\lambda|0\rangle R(\omega)\, a_{\kappa'}^{\lambda'}|0\rangle \\
&= \langle 0|\frac{\partial \mathcal{H}}{\partial \eta} R(0)\left(a_\kappa^\lambda - \rho_\kappa^\lambda\right) R(\omega)\, a_{\kappa'}^{\lambda'}|0\rangle
\end{aligned} \tag{53}$$

Completing the combination of terms (1, 5), (4, 7), (8, 12) and (11, 14) yields

$$\begin{aligned}
\frac{\partial \Pi_{\kappa,\kappa'}^{\lambda,\lambda'}(\omega)}{\partial \eta} = &+\langle 0|\frac{\partial \mathcal{H}}{\partial \eta} R(0)\left(a_\kappa^\lambda - \rho_\kappa^\lambda\right) R(\omega)\, a_{\kappa'}^{\lambda'}|0\rangle - \langle 0|\frac{\partial a_\kappa^\lambda}{\partial \eta} R(\omega)\, a_{\kappa'}^{\lambda'}|0\rangle \\
&+ \langle 0|a_\kappa^\lambda R(\omega) \frac{\partial(\mathcal{H} - E_0)}{\partial \eta} R(\omega)\, a_{\kappa'}^{\lambda'}|0\rangle - \langle 0|a_\kappa^\lambda R(\omega) \frac{\partial a_{\kappa'}^{\lambda'}}{\partial \eta}|0\rangle \\
&+ \langle 0|a_\kappa^\lambda R(\omega)\left(a_{\kappa'}^{\lambda'} - \rho_{\kappa'}^{\lambda'}\right) R(0) \frac{\partial \mathcal{H}}{\partial \eta}|0\rangle + \langle 0|\frac{\partial \mathcal{H}}{\partial \eta} R(0)\left(a_{\kappa'}^{\lambda'} - \rho_{\kappa'}^{\lambda'}\right) R(-\omega)\, a_\kappa^\lambda|0\rangle \\
&- \langle 0|\frac{\partial a_{\kappa'}^{\lambda'}}{\partial \eta} R(-\omega)\, a_\kappa^\lambda|0\rangle + \langle 0|a_{\kappa'}^{\lambda'} R(-\omega) \frac{\partial(\mathcal{H} - E_0)}{\partial \eta} R(-\omega)\, a_\kappa^\lambda|0\rangle \\
&- \langle 0|a_{\kappa'}^{\lambda'} R(-\omega) \frac{\partial a_\kappa^\lambda}{\partial \eta}|0\rangle + \langle 0|a_{\kappa'}^{\lambda'} R(-\omega)\left(a_\kappa^\lambda - \rho_\kappa^\lambda\right) R(0) \frac{\partial \mathcal{H}}{\partial \eta}|0\rangle
\end{aligned} \tag{54}$$

We limit consideration to the set of parameters η such that $\partial\mathcal{H}/\partial\eta$ can be written as a sum of one-electron operators $\partial h/\partial\eta$, so that the Hamiltonian derivatives become

$$\frac{\partial \mathcal{H}_0}{\partial \eta} = \left[\frac{\partial h_0}{\partial \eta}\right]_{\lambda''}^{\kappa''} a_{\kappa''}^{\lambda''} \tag{55}$$

and

$$\frac{\partial(\mathcal{H}_0 - E_0)}{\partial \eta} = \left[\frac{\partial h_0}{\partial \eta}\right]_{\lambda''}^{\kappa''} \left(a_{\kappa''}^{\lambda''} - \rho_{\kappa''}^{\lambda''}\right) \tag{56}$$

The expression $\left[\frac{\partial h_0}{\partial \eta}\right]_{\lambda''}^{\kappa''}$ is a multiplicative term that relates the nonlinear polarization propagator to the quadratic response function of a specific molecular property. After substitution of Equations (55) and (56) into Equation (54), the polarization propagator derivative becomes

$$\begin{aligned}
\frac{\partial \Pi_{\kappa,\kappa'}^{\lambda,\lambda'}(\omega)}{\partial \eta} = {} & \left[\frac{\partial h_0}{\partial \eta}\right]_{\lambda''}^{\kappa''} \\
& \times \{\langle 0|a_{\kappa''}^{\lambda''} R(0)\left(a_{\kappa}^{\lambda} - \rho_{\kappa}^{\lambda}\right)R(\omega)\,a_{\kappa'}^{\lambda'}|0\rangle + \langle 0|a_{\kappa}^{\lambda} R(\omega)\left(a_{\kappa''}^{\lambda''} - \rho_{\kappa''}^{\lambda''}\right)R(\omega)\,a_{\kappa'}^{\lambda'}|0\rangle \\
& + \langle 0|a_{\kappa}^{\lambda} R(\omega)\left(a_{\kappa'}^{\lambda'} - \rho_{\kappa'}^{\lambda'}\right)R(0)\,a_{\kappa''}^{\lambda''}|0\rangle + \langle 0|a_{\kappa''}^{\lambda''} R(0)\left(a_{\kappa'}^{\lambda'} - \rho_{\kappa'}^{\lambda'}\right)R(-\omega)\,a_{\kappa}^{\lambda}|0\rangle \qquad (57) \\
& + \langle 0|a_{\kappa'}^{\lambda'} R(-\omega)\left(a_{\kappa''}^{\lambda''} - \rho_{\kappa''}^{\lambda''}\right)R(-\omega)\,a_{\kappa}^{\lambda}|0\rangle + \langle 0|a_{\kappa'}^{\lambda'} R(-\omega)\left(a_{\kappa}^{\lambda} - \rho_{\kappa}^{\lambda}\right)R(0)\,a_{\kappa''}^{\lambda''}|0\rangle\} \\
& - \langle 0|\frac{\partial a_{\kappa}^{\lambda}}{\partial \eta} R(\omega)\,a_{\kappa'}^{\lambda'}|0\rangle - \langle 0|a_{\kappa}^{\lambda} R(\omega)\frac{\partial a_{\kappa'}^{\lambda'}}{\partial \eta}|0\rangle \\
& - \langle 0|\frac{\partial a_{\kappa'}^{\lambda'}}{\partial \eta} R(-\omega)\,a_{\kappa}^{\lambda}|0\rangle - \langle 0|a_{\kappa'}^{\lambda'} R(-\omega)\frac{\partial a_{\kappa}^{\lambda}}{\partial \eta}|0\rangle.
\end{aligned}$$

The first six terms of the polarization propagator derivative have a structure analogous to the hyperpolarizability[55]

$$\begin{aligned}
\beta_{\alpha\beta\gamma}(\bar{r},\bar{r}',\omega,\bar{r}'',0) = {} & \langle 0|P_{\alpha}(\bar{r})G(\omega)P_{\gamma}^{0}(\bar{r}'')G(\omega)P_{\beta}(\bar{r}')|0\rangle \\
& + \langle 0|P_{\beta}(\bar{r}')G(-\omega)P_{\gamma}^{0}(\bar{r}'')G(-\omega)P_{\alpha}(\bar{r})|0\rangle \\
& + \langle 0|P_{\alpha}(\bar{r})G(\omega)P_{\beta}^{0}(\bar{r}')G(0)P_{\gamma}(\bar{r}'')|0\rangle \qquad (58) \\
& + \langle 0|P_{\gamma}(\bar{r}'')G(0)P_{\beta}^{0}(\bar{r}')G(-\omega)P_{\alpha}(\bar{r})|0\rangle \\
& + \langle 0|P_{\gamma}(\bar{r}'')G(0)P_{\alpha}^{0}(\bar{r})G(\omega)P_{\beta}(\bar{r}')|0\rangle \\
& + \langle 0|P_{\beta}(\bar{r}')G(-\omega)P_{\alpha}^{0}(\bar{r})G(0)P_{\gamma}(\bar{r}'')|0\rangle.
\end{aligned}$$

In fact, the hyperpolarizability can be expressed in terms of the nonlinear polarization propagator.

$$\beta_{\alpha\beta\gamma}(\bar{r},\bar{r}',\bar{r}'';\omega',\omega'') = \left[p(\bar{r})_{\alpha}\right]_{\lambda}^{\kappa}\left[p(\bar{r}')_{\beta}\right]_{\lambda'}^{\kappa'}\left[p(\bar{r}'')_{\gamma}\right]_{\lambda''}^{\kappa''}\Pi_{\kappa,\kappa',\kappa''}^{\lambda,\lambda',\lambda''}(\omega',\omega''). \qquad (59)$$

However, Equation (57) contains more than just the nonlinear polarization propagator. The terms which depend on the derivatives of the replacement operator must also be considered.

Derivative of the Replacement Operator

To consider the derivative of the replacement operator $a_\kappa^\lambda = a_\lambda^\dagger a_\kappa$, the operator is transformed into the occupation number basis set. First, two different complete sum-over-single-electron-states are inserted, one preceding the operator and one following it.[53]

$$\begin{aligned} a_\kappa^\lambda = a_\lambda^\dagger a_\kappa &= \sum_{\{n_k\}} \sum_{\{n'_k\}} |n'_1 n'_2 \cdots n'_\lambda \cdots n'_\kappa \cdots\rangle \\ &\times \langle n'_1 n'_2 \cdots n'_\lambda \cdots n'_\kappa \cdots | a_\lambda^\dagger a_\kappa | n_1 n_2 \cdots n_\lambda \cdots n_\kappa \cdots \rangle \langle n_1 n_2 \cdots n_\lambda \cdots n_\kappa \cdots | \\ &= \sum_{\{n_k\}} \sum_{\{n'_k\}} (-1)^{S_\lambda} (-1)^{S_\kappa} \delta_{0,n_\lambda} \delta_{1,n_\kappa} |n'_1 n'_2 \cdots n'_\lambda \cdots n'_\kappa \cdots\rangle \\ &\times \langle n'_1 n'_2 \cdots n'_\lambda \cdots n'_\kappa \cdots | n_1 n_2 \cdots n_\lambda + 1 \cdots n_\kappa - 1 \cdots \rangle \langle n_1 n_2 \cdots n_\lambda \cdots n_\kappa \cdots |. \end{aligned} \tag{60}$$

Therefore,

$$\begin{aligned} a_\kappa^\lambda = a_\lambda^\dagger a_\kappa = \sum_{\{n_k\}} \sum_{\{n'_k\}} (-1)^{S_\lambda} (-1)^{S_\kappa} \delta_{0,n_\lambda} \delta_{1,n_\kappa} |n'_1 n'_2 \cdots n'_\lambda \cdots n'_\kappa \cdots\rangle \\ \times \delta_{n'_1,n_1} \delta_{n'_2,n_2} \cdots \delta_{n'_\kappa,n_\kappa - 1} \cdots \delta_{n'_\lambda,n_\lambda + 1} \cdots \langle n_1 n_2 \cdots n_\lambda \cdots n_\kappa \cdots |. \end{aligned} \tag{61}$$

Summation over the primed occupation numbers yields

$$a_\kappa^\lambda = \sum_{\{n_k\}} (-1)^{S_\lambda - S_\kappa} \delta_{0,n_\lambda} \delta_{1,n_\kappa} |n_1 n_2 \cdots n_\lambda + 1 \cdots n_\kappa - 1 \cdots\rangle \langle n_1 n_2 \cdots n_\lambda \cdots n_\kappa \cdots |. \tag{62}$$

The right side of Equation (62) is necessarily equal to the left side; therefore, the right side is an occupation number representation of the replacement operator.

To calculate the derivative of the replacement operator, the occupation number representation of the replacement operator in Equation (62) is used. Thus the derivative of the replacement operator is the sum of derivatives of the ket·bra products.

$$\frac{\partial a_\kappa^\lambda}{\partial \eta} = \sum_{\{n_k\}} (-1)^{S_\lambda - S_\kappa} \delta_{0,n_\lambda} \delta_{1,n_\kappa} \left\{ \begin{array}{l} \dfrac{\partial | n_1 n_2 \cdots n_\lambda + 1 \cdots n_\kappa - 1 \cdots \rangle}{\partial \eta} \langle n_1 n_2 \cdots n_\lambda \cdots n_\kappa \cdots | \\ | n_1 n_2 \cdots n_\lambda + 1 \cdots n_\kappa - 1 \cdots \rangle \dfrac{\partial \langle n_1 n_2 \cdots n_\lambda \cdots n_\kappa \cdots |}{\partial \eta} \end{array} \right\}. \quad (63)$$

Equation (63) necessitates the calculation of the derivative of the multi-electron states.

Derivative of the Multi-electron State

The derivative of the multi-electron state is different from that of the single-electron wavefunction, since antisymmetry must be preserved in the multi-electron derivative. For clarity, the derivative of the multi-electron state will be found by using the Slater determinant formalism rather than the occupation number formalism. Comparing Equations (7) and (18) yields the identity

$$| 1_1 1_2 1_3 \cdots 1_N 0_{N+1} 0_{N+2} \cdots \rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1) & \psi_1(r_2) & \cdots & \cdots & \psi_1(r_N) \\ \psi_2(r_1) & \psi_2(r_2) & \cdots & \cdots & \psi_2(r_N) \\ \vdots & \vdots & \ddots & & \vdots \\ \vdots & \vdots & & \ddots & \vdots \\ \psi_N(r_1) & \psi_N(r_2) & \cdots & \cdots & \psi_N(r_N) \end{vmatrix}. \quad (64)$$

The multi-electron wavefunction is a sum of products of single-electron wavefunctions. Therefore, the derivative of the multi-electron wavefunction is a sum of sums of derivatives of single-electron wavefunctions. (The first sum is represented by the determinant notation.)

$$
\begin{aligned}
\frac{\partial\left|1_1 1_2 1_3 \cdots 1_N 0_{N+1} 0_{N+2} \cdots\right\rangle}{\partial\eta} = \frac{1}{\sqrt{N!}}
&\begin{vmatrix}
\frac{\partial\psi_1(r_1)}{\partial\eta} & \frac{\partial\psi_1(r_2)}{\partial\eta} & \cdots & \cdots & \frac{\partial\psi_1(r_N)}{\partial\eta} \\
\psi_2(r_1) & \psi_2(r_2) & \cdots & \cdots & \psi_2(r_N) \\
\vdots & \vdots & \ddots & & \vdots \\
\vdots & \vdots & & \ddots & \vdots \\
\psi_N(r_1) & \psi_N(r_2) & \cdots & \cdots & \psi_N(r_N)
\end{vmatrix} \\
+\frac{1}{\sqrt{N!}}
&\begin{vmatrix}
\psi_1(r_1) & \psi_1(r_2) & \cdots & \cdots & \psi_1(r_N) \\
\frac{\partial\psi_2(r_1)}{\partial\eta} & \frac{\partial\psi_2(r_2)}{\partial\eta} & \cdots & \cdots & \frac{\partial\psi_2(r_N)}{\partial\eta} \\
\vdots & \vdots & \ddots & & \vdots \\
\vdots & \vdots & & \ddots & \vdots \\
\psi_N(r_1) & \psi_N(r_2) & \cdots & \cdots & \psi_N(r_N)
\end{vmatrix} + \cdots \\
+\frac{1}{\sqrt{N!}}
&\begin{vmatrix}
\psi_1(r_1) & \psi_1(r_2) & \cdots & \cdots & \psi_1(r_N) \\
\psi_2(r_1) & \psi_2(r_2) & \cdots & \cdots & \psi_2(r_N) \\
\vdots & \vdots & \ddots & & \vdots \\
\vdots & \vdots & & \ddots & \vdots \\
\frac{\partial\psi_N(r_1)}{\partial\eta} & \frac{\partial\psi_N(r_2)}{\partial\eta} & \cdots & \cdots & \frac{\partial\psi_N(r_N)}{\partial\eta}
\end{vmatrix}
\end{aligned}
\tag{65}
$$

The derivatives of the single electron wavefunctions in Equation (65) can be expressed as a sum-over-states.

$$
\frac{\partial|k\rangle}{\partial\eta} = \sum_{m\neq k} C_{km}|m\rangle \tag{66}
$$

The prime on the summation of Equation (66) indicates exclusion of the $|k\rangle$ function. Substitution of Equation (66) into Equation (65) yields

$$\frac{\partial|1_1 1_2 1_3 \cdots 1_N 0_{N+1} 0_{N+2} \cdots\rangle}{\partial\eta} = \frac{1}{\sqrt{N!}} \sum_{m \neq 1} C_{1m} \begin{vmatrix} \psi_m(r_1) & \psi_m(r_2) & \cdots & \cdots & \psi_m(r_N) \\ \psi_2(r_1) & \psi_2(r_2) & \cdots & \cdots & \psi_2(r_N) \\ \vdots & \vdots & \ddots & & \vdots \\ \vdots & \vdots & & \ddots & \vdots \\ \psi_N(r_1) & \psi_N(r_2) & \cdots & \cdots & \psi_N(r_N) \end{vmatrix}$$

$$+ \frac{1}{\sqrt{N!}} \sum_{m \neq 2} C_{2m} \begin{vmatrix} \psi_1(r_1) & \psi_1(r_2) & \cdots & \cdots & \psi_1(r_N) \\ \psi_m(r_1) & \psi_m(r_2) & \cdots & \cdots & \psi_m(r_N) \\ \vdots & \vdots & \ddots & & \vdots \\ \vdots & \vdots & & \ddots & \vdots \\ \psi_N(r_1) & \psi_N(r_2) & \cdots & \cdots & \psi_N(r_N) \end{vmatrix} + \cdots$$

$$+ \frac{1}{\sqrt{N!}} \sum_{m \neq N} C_{Nm} \begin{vmatrix} \psi_1(r_1) & \psi_1(r_2) & \cdots & \cdots & \psi_1(r_N) \\ \psi_2(r_1) & \psi_2(r_2) & \cdots & \cdots & \psi_2(r_N) \\ \vdots & \vdots & \ddots & & \vdots \\ \vdots & \vdots & & \ddots & \vdots \\ \psi_m(r_1) & \psi_m(r_2) & \cdots & \cdots & \psi_m(r_N) \end{vmatrix} . \tag{67}$$

Note that if there is a determinant where the $|m\rangle$ functions are included in the set of single electron functions used to construct the multi-electron configuration, i. e. $|m\rangle \in \{|p\rangle : p = 1, 2 \cdots N\}$, then that determinant is zero. In addition, no assumptions have been placed upon the determinants; they may be ground or excited configurations. Before converting Equation (67) back into an occupation number representation, the $|m\rangle$ functions in the determinant must be put into standard order. The ordering is done by exchanging the $|m\rangle$ wavefunction row with as other rows as necessary. Each exchange of rows introduces a sign change, giving an overall factor that can be symbolized as $(-1)^{S_m - S_k}$. The quantity S_m-S_k indicates the number of row exchanges. Equation (67) is written as a double sum, the k sum indicating the sum of determinants and the m sum indicating the sum of single electron states.

$$\frac{\partial|1_1 1_2 1_3 \cdots 1_N 0_{N+1} 0_{N+2} \cdots\rangle}{\partial\eta} = \frac{1}{\sqrt{N!}} \sum_{k} \sum_{m \neq k} (-1)^{S_m - S_k} C_{km} \begin{vmatrix} \psi_1(r_1) & \psi_1(r_2) & \cdots & \cdots & \psi_1(r_N) \\ \vdots & \vdots & \cdots & \cdots & \vdots \\ \psi_m(r_1) & \psi_m(r_2) & \ddots & & \psi_m(r_N) \\ \vdots & \vdots & & \ddots & \vdots \\ \psi_N(r_1) & \psi_N(r_2) & \cdots & \cdots & \psi_N(r_N) \end{vmatrix} . \tag{68}$$

In the occupation number formalism, Equation (68) becomes

$$\frac{\partial|1_1 1_2 1_3 \cdots 1_N 0_{N+1} 0_{N+2} \cdots\rangle}{\partial\eta} = \sum_{k} \sum_{m \neq k} (-1)^{S_m - S_k} \delta_{0,n_m} \delta_{1,n_k} C_{km} |n_1 n_2 \cdots n_k - 1 \cdots n_m + 1 \cdots n_N\rangle \tag{69}$$

<u>Continuation of the Replacement Operator Derivative</u>

Equation (69) is the derivative of the multi-electron wavefunction. Thus Equation (69) is substituted into Equation (63) to continue calculating the derivative of the replacement operator.

$$\begin{aligned} \frac{\partial a_\kappa^\lambda}{\partial\eta} = \sum_{\{n_k\}} \sum_{k} \sum_{m \neq k} (-1)^{S_m - S_k} (-1)^{S_\lambda - S_\kappa} \delta_{0,n_\lambda} \delta_{1,n_\kappa} \delta_{0,n_m} \delta_{1,n_k} \\ \times \left\{ \begin{array}{l} C_{km} |n_1 n_2 \cdots n_k - 1 \cdots n_\lambda + 1 \cdots n_\kappa - 1 \cdots n_m + 1 \cdots n_N\rangle\langle n_1 n_2 \cdots n_\lambda \cdots n_\kappa \cdots | \\ + C_{km}^{*} |n_1 n_2 \cdots n_\lambda + 1 \cdots n_\kappa - 1 \cdots\rangle\langle n_1 n_2 \cdots n_k - 1 \cdots n_\lambda \cdots n_\kappa \cdots n_m + 1 \cdots n_N| \end{array} \right\} . \end{aligned} \tag{70}$$

Now the right hand side of Equation (70) is cast back into replacement operator formalism.

$$\frac{\partial a_\kappa^\lambda}{\partial\eta} = \sum_{k} \sum_{m \neq k} C_{km} a_k^m a_\kappa^\lambda + \sum_{m} \sum_{m \neq k} C_{km}^{*} a_\kappa^\lambda a_m^k \cdot \tag{71}$$

Note that in the first term of Equation (71), the effect of the derivative is to annihilate an electron in the k state and create an electron in the m state; whereas, in the second term, the effect of the derivative is to annihilate an electron in the m state and create an electron in the k state. Since k and m are only labels, they can be interchanged in the second term.

$$\frac{\partial a_\kappa^\lambda}{\partial \eta} = \sum_k \sum_{m \neq k} C_{km} a_k^m a_\kappa^\lambda + \sum_k \sum_{m \neq k} C_{mk}^* a_\kappa^\lambda a_k^m \cdot \tag{72}$$

The replacement operators are expanded as creation/annihilation operator products and the anticommutation relationships of Equation (12) are applied

$$\begin{aligned} \frac{\partial a_\kappa^\lambda}{\partial \eta} &= \sum_k \sum_{m \neq k} C_{km} a_m^\dagger a_k a_\lambda^\dagger a_\kappa + \sum_k \sum_{m \neq k} C_{mk}^* a_\lambda^\dagger a_\kappa a_m^\dagger a_k \\ &= \sum_k \sum_{m \neq k} \left\{ C_{km} \left[a_m^\dagger a_\kappa \delta_{\lambda k} - a_m^\dagger a_\lambda^\dagger a_k a_\kappa \right] + C_{mk}^* \left[a_\lambda^\dagger a_k \delta_{\kappa m} - a_\lambda^\dagger a_m^\dagger a_\kappa a_k \right] \right\} \\ &= \sum_k \sum_{m \neq k} \left\{ C_{km} \left[a_m^\dagger a_\kappa \delta_{\lambda k} - a_m^\dagger a_\lambda^\dagger a_k a_\kappa \right] + C_{mk}^* \left[a_\lambda^\dagger a_k \delta_{\kappa m} - a_m^\dagger a_\lambda^\dagger a_k a_\kappa \right] \right\} \\ &= \sum_k \sum_{m \neq k} \left\{ C_{km} a_m^\dagger a_\kappa \delta_{\lambda k} + C_{mk}^* a_\lambda^\dagger a_k \delta_{\kappa m} - \left(C_{km} + C_{mk}^* \right) a_m^\dagger a_\lambda^\dagger a_k a_\kappa \right\}. \end{aligned} \tag{73}$$

Now the quantity $C_{km} + C_{mk}^*$ must be examined. The C_{km} coefficients indicate the amount that the m state mixes into the k state when a perturbation is applied. Thus the perturbed k state $|k'\rangle$ can be written as

$$|k'\rangle = |k\rangle + \cdots + C_{km} |m\rangle + \cdots. \tag{74}$$

Accordingly, the perturbed m state $\langle m'|$ can be written as

$$\langle m'| = \langle m| + \cdots + C_{mk}^* \langle k| + \cdots. \tag{75}$$

The perturbed states can be constructed to be still orthogonal when perturbed if certain conditions are met.

$$\begin{aligned} \langle m' | k' \rangle = \langle m | k \rangle + \cdots + C_{km} \langle m | m \rangle + \cdots + C_{mk}^* \langle k | k \rangle + \cdots = 0 \\ = 0 + \cdots + C_{km} \cdot 1 + \cdots + C_{mk}^* \cdot 1 + \cdots = 0 \end{aligned} \tag{76}$$

The conditions on the perturbed wavefunctions that insure orthonormality are that for all $k \neq m$, $C_{km} + C_{mk}^* = 0$. Thus continuing from Equation (73), the derivative of the replacement operator is found by substituting the orthonormality condition and performing a summation over a single index.

$$\begin{aligned}\frac{\partial a_{\kappa}^{\lambda}}{\partial \eta} &= \sum_{m\neq\lambda} C_{\lambda m}\, a_{m}^{\dagger} a_{\kappa} + \sum_{k\neq\kappa} C_{\kappa k}^{*}\, a_{\lambda}^{\dagger} a_{k} \\ &= \sum_{m\neq\lambda} C_{\lambda m}\, a_{\kappa}^{m} + \sum_{k\neq\kappa} C_{\kappa k}^{*}\, a_{k}^{\lambda}.\end{aligned} \tag{77}$$

<u>Continuation of the Polarization Propagator Derivative</u>

To finish calculating the derivative of the polarization propagator, we re-examine Equation (57), specifically the last four terms.

$$\begin{aligned}\frac{\partial \Pi_{\kappa,\kappa'}^{\lambda,\lambda'}(\omega)}{\partial \eta} &= \left[\frac{\partial h_0}{\partial \lambda}\right]_{\lambda''}^{\kappa''} \Pi_{\kappa,\kappa',\kappa''}^{\lambda,\lambda',\lambda''}(\omega,0) \\ &- \langle 0|\frac{\partial a_{\kappa}^{\lambda}}{\partial \eta} R(\omega) a_{\kappa'}^{\lambda'}|0\rangle - \langle 0|a_{\kappa}^{\lambda} R(\omega) \frac{\partial a_{\kappa'}^{\lambda'}}{\partial \eta}|0\rangle \\ &- \langle 0|\frac{\partial a_{\kappa'}^{\lambda'}}{\partial \eta} R(-\omega) a_{\kappa}^{\lambda}|0\rangle - \langle 0|a_{\kappa'}^{\lambda'} R(-\omega) \frac{\partial a_{\kappa}^{\lambda}}{\partial \eta}|0\rangle.\end{aligned} \tag{78}$$

The derivative of the replacement operator is substituted to yield

$$\begin{aligned}\frac{\partial \Pi_{\kappa,\kappa'}^{\lambda,\lambda'}(\omega)}{\partial \eta} &= \left[\frac{\partial h_0}{\partial \eta}\right]_{\lambda''}^{\kappa''} \Pi_{\kappa,\kappa',\kappa''}^{\lambda,\lambda',\lambda''}(\omega,0) \\ &- \sum_{m\neq\lambda} C_{\lambda m} \langle 0|a_{\kappa}^{m} R(\omega) a_{\kappa'}^{\lambda'}|0\rangle - \sum_{k\neq\kappa} C_{\kappa k}^{*} \langle 0|a_{k}^{\lambda} R(\omega) a_{\kappa'}^{\lambda'}|0\rangle \\ &- \sum_{m\neq\lambda'} C_{\lambda' m} \langle 0|a_{\kappa}^{\lambda} R(\omega) a_{\kappa'}^{m}|0\rangle - \sum_{k\neq\kappa'} C_{\kappa' k}^{*} \langle 0|a_{\kappa}^{\lambda} R(\omega) a_{k}^{\lambda'}|0\rangle \\ &- \sum_{m\neq\lambda} C_{\lambda' m} \langle 0|a_{\kappa'}^{m} R(-\omega) a_{\kappa}^{\lambda}|0\rangle - \sum_{k\neq\kappa'} C_{\kappa' k}^{*} \langle 0|a_{k}^{\lambda'} R(-\omega) a_{\kappa}^{\lambda}|0\rangle \\ &- \sum_{m\neq\lambda'} C_{\lambda m} \langle 0|a_{\kappa'}^{\lambda'} R(-\omega) a_{\kappa}^{m}|0\rangle - \sum_{k\neq\kappa} C_{\kappa k}^{*} \langle 0|a_{\kappa'}^{\lambda'} R(-\omega) a_{k}^{\lambda}|0\rangle.\end{aligned} \tag{79}$$

The terms are rearranged and the definition of the polarization propagator, Equation (36) is applied to yield the final result.

$$
\begin{aligned}
\frac{\partial \Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)}{\partial \eta} &= \left[\frac{\partial h_0}{\partial \eta}\right]^{\kappa''}_{\lambda''} \Pi^{\lambda,\lambda',\lambda''}_{\kappa,\kappa',\kappa''}(\omega,0) \\
&- \sum_{m\neq\lambda} C_{\lambda m}\langle 0|a^{m}_{\kappa} R(\omega)\, a^{\lambda'}_{\kappa'}|0\rangle - \sum_{m\neq\lambda} C_{\lambda m}\langle 0|a^{\lambda'}_{\kappa'} R(-\omega)\, a^{m}_{\kappa}|0\rangle \\
&- \sum_{m\neq\lambda'} C_{\lambda' m}\langle 0|a^{\lambda}_{\kappa} R(\omega)\, a^{m}_{\kappa'}|0\rangle - \sum_{m\neq\lambda'} C_{\lambda' m}\langle 0|a^{m}_{\kappa'} R(-\omega)\, a^{\lambda}_{\kappa}|0\rangle \\
&- \sum_{k\neq\kappa'} C^{*}_{\kappa' k}\langle 0|a^{\lambda}_{\kappa} R(\omega)\, a^{\lambda'}_{k}|0\rangle - \sum_{k\neq\kappa'} C^{*}_{\kappa' k}\langle 0|a^{\lambda'}_{k} R(-\omega)\, a^{\lambda}_{\kappa}|0\rangle \\
&- \sum_{k\neq\kappa} C^{*}_{\kappa k}\langle 0|a^{\lambda}_{k} R(\omega)\, a^{\lambda'}_{\kappa'}|0\rangle - \sum_{k\neq\kappa} C^{*}_{\kappa k}\langle 0|a^{\lambda'}_{\kappa'} R(-\omega)\, a^{\lambda}_{k}|0\rangle \\
&= \left[\frac{\partial h_0}{\partial \eta}\right]^{\kappa''}_{\lambda''} \Pi^{\lambda,\lambda',\lambda''}_{\kappa,\kappa',\kappa''}(\omega,0) \\
&+ \sum_{m\neq\lambda} C_{\lambda m}\Pi^{m,\lambda'}_{\kappa,\kappa'}(\omega) + \sum_{m\neq\lambda} C_{\lambda' m}\Pi^{\lambda,m}_{\kappa,\kappa'}(\omega) \\
&+ \sum_{k\neq\kappa'} C^{*}_{\kappa' k}\Pi^{\lambda,\lambda'}_{\kappa,k}(\omega) + \sum_{k\neq\kappa} C^{*}_{\kappa k}\Pi^{\lambda,\lambda'}_{k,\kappa'}(\omega).
\end{aligned}
\tag{80}
$$

Discussion

The result in Equation (80) demonstrates a new relationship between response functions. The equation of motion for the linear-response function, Equation (2), shows a relationship between linear and quadratic-response functions; however, the relationship is not a derivative relationship. (Parkinson[56] has used this relationship to calculate the dipole polarizability of H_2O with the quadratic-response function. Since the polarizability is more easily calculated using the linear-response function, using the quadratic-response function is not advantageous.)

This work demonstrates that the calculation of molecular properties from energy derivatives with respect to an electric or magnetic field such as hyperpolarizabilities or hypermagnetizabilities can be calculated without finite-field techniques. Only response functions are used. Since the relationship in Equation (80) is general, the equation may suggest an efficient method for the calculation of the parameter dependence of electromagnetic properties allowing for frequency dependence.

The chief advantage of Equation (80) is in the calculation of derivatives of linear-response properties via the nonlinear polarization propagator. The calculation of energy derivatives with respect to nuclear-coordinate molecular gradients and energy second derivatives with respect to nuclear-coordinate molecular Hessians is essential in the calculation of molecular structure.[57] The derivatives are also important in the calculation of vibrational energies via harmonic and anharmonic force constants. Much effort has been used to find efficient methods to calculate these quantities.[58,59]

Though the calculation of the derivative of the polarization propagator via calculation of the second-quantized one-electron replacement operator appears to be novel, the calculation of derivatives of individual creation and annihilation operators is not. The derivative of the creation operator appears first in the paper by Bak *et al.*[60] where the authors calculated first-order nonadiabatic coupling matrix elements necessary for accurate accountings of phenomena such as Λ-doubling[61] and spin-orbit coupling. The theory was also applied in the calculation of atomic polar and axial tensors of Stephens[62] in work on the rotational strengths necessary for describing vibrational circular dichroism.[63] The result of this chapter differs from the work of Bak *et. al.* in that the derivative of the number-preserving replacement operator has been found rather than the derivative of the number-changing creation and annihilation operators and that the result of this chapter is expressed in terms of polarization propagators rather than molecular gradients.

The result in Equation (80) was suggested by the relationship found by Hunt *et al.*[50,51] relating the derivative of polarizability to the hyperpolarizability density. In published work[64] and Chapter 2 of this thesis, a similar relationship has been found between the derivative of the hyperpolarizability and the second hyperpolarizability density. This relationship suggests a relationship between the derivative of the quadratic polarization propagator and the cubic polarization propagator. Such a relationship would be useful as cubic polarization propagators constructed for the random phase approximation are already being used to find various cubic electric response tensors such as those responsible for third harmonic generation, DC-electric field induced second harmonic generation, degenerate four-wave mixing, etc.[65] The cubic propagators[65] and mixed analytical-numerical techniques[66] have also been used in the calculation of hypermagnetizabilities which are responsible for magnetic field induced birefringence or the Cotton-Mouton effect, a magnetic analogue of the Kerr Effect. In their review, Rizzo, Rizzo and Bishop[67] mention that the calculation of the vibrational corrections to nonlinear properties, such as the hypermagnetizability, remains a nontrivial problem. The extension of the results of this chapter to the next order could aid in the calculation of such corrections.

REFERENCES

[1] Peter W. Atkins, *Molecular Quantum Mechanics*, 2nd. ed. (Oxford University Press, Oxford, 1983).

[2] Roy McWeeny, *Methods of Molecular Quantum Mechanics*, 2nd ed. (Academic Press, New York, 1981).

[3] Poul Jørgensen and Jack Simons, *Second Quantization-Based Methods in Quantum Chemistry* (Academic Press, New York, 1981).

[4] Claude Cohen-Tannoudji, Bernard Diu and Franck Laloë, *Quantum Mechanics, Vol. 1* (John Wiley and Sons, New York, 1977).

[5] Alexander L. Fetter and John Dirk Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill Publishing Co, New York, 1971).

[6] Richard D. Mattuck, A *Guide to Feynman Diagrams in the Many-Body Problem*, 2nd. ed. (Dover Publications, Inc., New York, 1992).

[7] Michio Kaku, *Quantum Field Theory* (Oxford University Press, Oxford, 1993).

[8] Michael E. Peskin and Daniel V. Schroeder, *An Introduction to Quantum Field Theory* (Addison-Wesley Publishing Co., Reading, Massachusetts, 1995).

[9] George C. Schatz and Mark A. Ratner, *Quantum Mechanics in Chemistry* (Prentice-Hall, Englewood Cliffs, New Jersey, 1993).

[10] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) - Sov. Phys. Usp. (Eng. Trans.) **3**, 320 (1960).

[11] Jan Linderberg and Yngve Öhrn, *Propagators in Quantum Chemistry* (Academic Press, New York, 1973).

[12] J. Oddershede, Adv. Quant. Chem. **11,** 275 (1978).

[13] L. D. Landau and E. M. Lifshitz, *Statistical Physics: Part 1*, 3rd ed. (Pergamon Press, Oxford, 1980).

[14] George Arfken, *Mathematical Methods for Physicists*, 3rd Ed. (Academic Press, San Diego, 1985) pg. 490.

[15] The following replacement may be made $-\hbar\omega_{0n} \rightarrow \mathcal{H}-E_{0.}$

[16] J. Olsen and P. Jørgensen, J. Chem. Phys. **82,** 3235 (1985).

[17] H. Hettema, H. J. A. Jensen, P. Jørgensen and J. Olsen, J. Chem. Phys. **97,** 1174 (1992).

[18] R. Moszynski, P. E. S. Wormer, B. Jeziorski and A. van der Avoird, J. Chem. Phys. **103,** 8058 (1995).

[19] Douglas R. Hartree, *Numerical Analysis*, 2nd. ed. (Oxford University Press, Oxford, 1958).

[20] P. Lazzeretti, R. Zanasi and W. T. Raynes, Molec. Phys. **66,** 831 (1989).

[21] J. Geersten, J. Oddershede, W. T. Raynes and T. L. Marvin, Molec. Phys. **82,** 29 (1994).

[22] S. Kirpekar, T. Enevoldsen, J. Oddershede and W. T. Raynes, Molec. Phys. **91,** 897 (1997).

[23] A. Barszczewicz, T. Helgaker, M. Jaszunski, P. Jørgensen, and K. Ruud, J. Mag. Res. A **114,** 212 (1995).

[24] J. San Fabian and J. Guilleme, Chem. Phys. **206,** 325 (1996).

[25] C. G. Giribet, M. C. R. DeAzua, R. H. Contreras, R. L. Debonczak, G. A. Aucar and S. Gomez, J. Mol. Struct. **300**, 467 (1993).

[26] C. Vizioli, M. C. R. DeAzua, C. G. Giribet, R. H. Contreras, L. Turi, J. J. Dannenberg, I. D. Rae, J. A. Weigold, M. Malagoli, R. Zanasi and P. Lazzeretti, J. Phys. Chem. **98**, 8858 (1994).

[27] P. Lazzeretti, R. Zanasi, A. J. Sadlej, and W. T. Raynes, Molec. Phys. **62**, 605 (1987).

[28] S. P. A. Sauer, Chem. Phys. Lett. **260**, 271 (1996).

[29] S. P. A. Sauer, J. Phys. Chem. **98**, 8617 (1994).

[30] S. P. A. Sauer and I. Paidarová, Chem. Phys. **201**, 405 (1995).

[31] S. P. A. Sauer, V. Špirko, I. Paidarová and J. Oddershede, Chem. Phys. **184**, 1 (1994).

[32] W. A. Parkinson, S. P. A. Sauer, J. Oddershede and D. M. Bishop, J. Chem. Phys. **98**, 487 (1993).

[33] J. Oddershede and E. N. Svendsen, Chem. Phys. **64**, 359 (1982).

[34] M. Jaszunski, Int. J. Quant. Chem. **51**, 307 (1994).

[35] M. Jaszunski, P. Jørgensen and H. J. A. Jensen, Chem. Phys. Lett. **191**, 293 (1992).

[36] H. D. Cohen and C. C. J. Roothaan, J. Chem. Phys. **43**, S34 (1965); A. D. Buckingham, Adv. Chem. Phys. **12**, 107 (1967); D. M. Bishop and G. Maroulis, J. Chem. Phys. **82**, 2380 (1985); M. Jaszunski, Chem. Phys. Lett. **140**, 130 (1987).

[37] M. Cho, J. Phys. Chem. **102**, 703 (1998).

[38] W. T. Raynes, P. Lazzeretti and R. Zanasi, Molec. Phys. **64**, 1061 (1988).

[39] H. Köppel, F. X. Gadea, G. Klatt, J. Schirmer and L. S. Cederbaum, J. Chem. Phys. **106**, 4415 (1997).

[40] J. R. Sabin, I. Paidarová, and J. Oddershede, Theor. Chim. Acta **89**, 375 (1994).

[41] O. Vahtras, H. Ågren, P. Jørgensen, J. Jorgen, A. Jensen, T. Helgaker, and J. Olsen, J. Chem. Phys. **97**, 9178 (1992).

[42] B. F. Minaev, S. Knuts, H. Ågren and O. Vahtras, Chem. Phys. **175**, 245 (1993).

[43] J. Schirmer, A. B. Trofimov, K. J. Randall, I. Feldhaus, A. M. Bradshaw, Y. Ma, C. T. Chen and F. Sette, Phys. Rev. A **47**, 1136 (1993).

[44] F. X. Gadea, H. Köppel, J. Schirmer, L. S. Cederbaum, K. J. Randall, A. M. Bradshaw, Y. Ma, F. Sette and C. T. Chen, Phys. Rev. Lett. **66**, 883 (1991).

[45] A. B. Trofimov and J. Schirmer, Chem. Phys. **214**, 153 (1997).

[46] Y. Luo, H. Ågren, S. Knuts, B. F. Minaev and P. Jørgensen, Chem. Phys. Lett. **209**, 513 (1993).

[47] Y. Luo, H. Ågren, S. Knuts and P. Jørgensen, Chem. Phys. Lett. **213**, 356 (1993).

[48] H. Ågren, and O. Vahtras, J. Phys. B - Atom. Mol. and Opt. Phys. **26**, 913 (1993).

[49] H. D. Schulte and L. S. Cederbaum, J. Chem. Phys. **103**, 698 (1995).

[50] K. L. C. Hunt, J. Chem. Phys. **90**, 4909 (1989).

[51] K. L. C. Hunt, Y. Q. Liang, R. Nimalakirthi, and R. A. Harris, J. Chem. Phys. **91**, 5251 (1989).

[52] Appendix A.

[53] Appendix C.

[54] X. Li and K. L. C. Hunt, J. Chem. Phys. **105**, 4076 (1996).

[55] B. J. Orr and J. F. Ward, Molec. Phys. **33**, 513 (1971).

[56] William A. Parkinson, Int. J. Quant. Chem. Symp. **26**, 487 (1992).

[57] Attila Szabo and Neil S. Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, New York, 1992).

[58] *Geometrical Derivatives of Energy Surfaces and Molecular Properties* P. Jørgensen and J. Simons, eds. NATO ASI Series C: Vol. **166** (D. Reidel Pub. Co., Dordrecht, 1985).

[59] H. B. Schlegel, Adv. Chem. Phys. **67**, 249 (1987).

[60] K. L. Bak, P. Jørgensen, H. J. A. Jensen, J. Olsen, and T. Helgaker, J. Chem. Phys. **97**, 7573 (1992).

[61] Jack D. Graybeal, *Molecular Spectroscopy*, 1st Rev. ed. (McGraw-Hill, New York, 1988).

[62] P. J. Stephens and M. A. Lowe, Annu. Rev. Phys. Chem. **36**, 213 (1985).

[63] K. L. Bak, P. Jørgensen, H. J. A. Jensen, J. Olsen, and T. Helgaker, J. Chem. Phys. **98**, 8873 (1993).

[64] E. L. Tisko, X. Li and K. L. C. Hunt, J. Chem. Phys. **103**, 6873 (1995).

[65] P. Norman, D. Jonsson, O. Vahtras and H. Ågren, Chem. Phys. **203**, 23 (1996).

[66] S. Coriani, A. Rizzo, K. Ruud and T. Helgaker, Chem. Phys. **216**, 53 (1997).

[67] C. Rizzo, A. Rizzo and D. M. Bishop, Int. Rev. Phys. Chem. **16**, 81 (1997).

CHAPTER 4: FIRST ORDER APPROXIMATION TO THE ELECTRONIC MAGNETIC MOMENT DERIVATIVE

Introduction

Intramolecular response to internal electromagnetic fields has been described by the same electromagnetic response tensors that describe intramolecular response to external electromagnetic fields. The first example of this equivalence was derived by Hunt[1] who showed that the derivative of the electronic dipole moment with respect to nuclear coordinate is connected to the nonlocal polarizability density.

$$\partial \mu_\beta / \partial R_\alpha^K = \int d\bar{r}\, d\bar{r}'\, \alpha_{\beta\delta}(\bar{r};\bar{r}',0)\, Z^K\, \mathbf{T}_{\delta\alpha}(\bar{r}',\bar{R}^K)\,. \tag{1}$$

The physical interpretation of this connection can be discerned by examining the balance of electric fields in the molecule at its equilibrium geometry. The electric field at the nucleus in a molecule at equilibrium is zero since the electric field from the other positive nuclei in the molecule must balance the electric field from the negative electronic charge distribution. When a nucleus is perturbed away from equilibrium, the Coulomb field changes throughout the molecule. The electronic charge distribution responds to this change in the electric field via the nonlocal polarizability density. This response is weighted by a distance relationship between the position of the nucleus and the point in the electronic charge distribution where the change in the nuclear Coulomb field is computed. This distance relationship, known as the dipole propagator, is defined as

$$\mathbf{T}_{\alpha\beta}(\bar{r},\bar{r}') = \nabla_\alpha \nabla_\beta \left(\frac{1}{|\bar{r} - \bar{r}'|} \right) = \frac{3(r_\alpha - r'_\alpha)(r_\beta - r'_\beta) - \delta_{\alpha\beta}|\bar{r} - \bar{r}'|^2}{|\bar{r} - \bar{r}'|^5} - \frac{4\pi}{3}\delta_{\alpha\beta}\delta(\bar{r} - \bar{r}'). \quad (2)$$

The nonlocal polarizability density that characterizes the intramolecular response is the same tensor used to describe the electronic molecular response to an external electric field. Other such relationships have been found and will be discussed, subsequently.

Nonlocal Susceptibility Densities

The distinction between the polarizability and nonlocal polarizability density should be clarified. The nonlocal polarizability density yields the response of the molecule at a single point due to an applied field at another point. When an electric field interacts with a point of charge distribution, the charge distribution at the field point becomes polarized. This polarization field in turn polarizes the charge distribution at the response point. To find the total response at a single point in the molecule, the effect of the field at all field points in the molecules must be summed. To calculate the total collective response, i. e. the total polarizability, from all points, all the response points must be summed. Thus, the relationship between the polarizability and nonlocal polarizability density is that the polarizability is equal to the nonlocal polarizability density integrated over all field and response points.

$$\alpha_{\alpha\beta}(\omega) = \int d\bar{r}\, d\bar{r}'\, \alpha_{\alpha\beta}(\bar{r},\bar{r}';\omega). \quad (3)$$

Intramolecular Electric Response

The intramolecular responses of the polarizability[2] and hyperpolarizability[3] due to an applied electric field are related to external response tensors.

$$\partial\alpha_{\beta\gamma}(\omega) / \partial\bar{R}^{K}_{\alpha} = \int d\bar{r}d\bar{r}'d\bar{r}''\ \beta_{\beta\gamma\delta}(\bar{r};\bar{r}',\omega,\bar{r}'',0)\, Z^{K}\, \mathbf{T}_{\delta\alpha}(\bar{r}'',\bar{R}^{K})\,. \tag{4}$$

$$\begin{aligned} &\partial\beta_{\alpha\beta\gamma}(-\omega_{\sigma};\omega',\omega'') / \partial R^{K}_{\delta} \\ &\quad = \int d\bar{r}d\bar{r}'d\bar{r}''d\bar{r}'''\gamma_{\alpha\beta\gamma\varepsilon}(\bar{r};\bar{r}',\omega',\bar{r}'',\omega'',\bar{r}''',0)\, Z^{K}\, \mathbf{T}_{\varepsilon\delta}(\bar{r}''',\bar{R}^{K}). \end{aligned} \tag{5}$$

Equation (4) shows that the electronic polarizability responds to an internal electric field via the nonlocal hyperpolarizability density, whereas Equation (5) demonstrates that the hyperpolarizability responds via the second hyperpolarizability density.

Intramolecular Magnetic Response

Derivatives of the electronic magnetic moment with respect to nuclear linear momentum have been related to nonlocal charge-current susceptibility densities.[4]

$$\frac{\partial m^{e}_{\alpha}}{\partial p^{K}_{\beta}} = -\frac{\hbar Z^{K} e}{M^{K} c}\int d\bar{r}\, d\bar{r}'\, \mathrm{Im}\langle 0|\rho(r')G(\omega)G(-\omega)\left[\bar{r}\times\bar{j}(\bar{r})\right]_{\alpha}|0\rangle\, \nabla^{K}_{\beta}\frac{1}{|\bar{R}^{K}-\bar{r}'|} \tag{6}$$

In Equation (6), G(ω) represents the reduced resolvent from standard perturbation theory.

$$G(\omega) = (1-\wp)(\mathcal{H} - E_0 - \hbar\omega)^{-1}(1-\wp),\ \text{where}\ \wp = |0\rangle\langle 0|, \tag{7}$$

Z^K is the charge and M^K is the mass on nucleus K while ∇^{K}_{β} is the gradient operator with respect to the nuclear coordinate R^K. p^{K}_{β} represents the βth Cartesian coordinate of the linear momentum of nucleus K while m^{e}_{α} is the αth Cartesian coordinate of the electronic magnetic moment. Equation (6) demonstrates that the change of the electronic magnetic moment due to an internal electric field is related to a charge-current susceptibility density, $\chi_{\alpha}^{\rho m} = \langle 0|\rho(r')G(\omega)G(-\omega)\left[\bar{r}\times\bar{j}(\bar{r})\right]_{\alpha}|0\rangle$. This susceptibility tensor is the nonlocal density analog of the rotational strength, the quantity calculated to find the intensities of the transitions associated with vibrational circular dichroism, VCD.

VCD[5,6,7] is the phenomenon when light of one circular polarization has a different degree of vibrational absorption than light of the other circular polarization. The effect occurs only in chiral molecules or molecules with chiral crystal symmetry. Heuristically, VCD can be understood by considering the electric field of the nuclei during a vibration. As the nuclei move, a time-dependent electric field is produced. The electric field produces a time-dependent deformation of the charge density that induces a magnetic moment within the molecule. The intensity of the absorption is determined by a quantity called the rotational strength that couples the electronic electric-dipole transition matrix element to electronic magnetic-dipole transition matrix element.

The charge-current susceptibility $\chi_{\alpha}^{\rho m}$ used in the theory of VCD relates a change in the electronic magnetic moment at one point in a molecule to the change in the polarization due to an applied electric field at another point in the molecule. Thus, the derivative of the electronic magnetic moment with respect to nuclear linear momentum can be calculated from a change in the current density due to electric field perturbations. The work in this chapter also calculates the derivative of the electronic magnetic moment with respect to nuclear linear momentum. However, the result differs because the susceptibility density used to calculate the response is different. The response of the magnetic moment due to an applied magnetic field is considered, rather than an applied electric field.

In this chapter, the magnetic moment derivative with respect to nuclear linear momentum is related to the paramagnetic nonlocal chemical shift density. The nonlocal chemical shift density describes how a magnetic field at one point in the molecule affects a magnetic moment at another point in the molecule. Magnetic moments are created in the molecule when magnetic fields induce the charge density to circulate. This induction of circulation is termed the magnetization. In macroscopic terms, the magnetization is defined as an average of magnetic dipole moments just as the polarization of a molecule is defined as an average of electric dipole moments.[8] One can understand a magnetic dipole as a loop of current in the same way that an electric dipole is pictured as two oppositely charged particles separated at a distance.

Molecular Electromagnetism

Background

Many texts[9] and monographs[10,11] provide an introduction to molecular electromagnetism, i. e., the interaction of molecules with electric and magnetic fields. Molecules interact with magnetic fields differently than they do with electric fields. Viewed figuratively, the electronic charge distribution of a molecule 'stretches' when perturbed by an electric field. When a magnetic field is applied to a molecule, the electronic charge distribution becomes 'twisted'. The twisting of the electronic distribution produces two different effects. Diamagnetism is produced when the twisting causes circulation of the electrons in currents. These induced currents circulate as to decrease the total magnetic field. Paramagnetism may be produced when the applied magnetic field torques the electrons that cause their magnetic moments to align with the magnetic field. The alignment of the magnetic moments increases the total magnetic field. In molecules without unpaired electrons or net orbital angular momentum, the response to an applied magnetic field is diamagnetic. However, the description of the response is inherently quantum mechanical and has an unequivocal dependence upon an arbitrary function named the gauge whose value changes the quantum mechanical description of the magnetic response but not its actual value. The next section discusses the basic theory of the gauge function and its relationship to the vector potential and magnetic fields.

Vector Potentials, Gauge Functions and Magnetic Fields

The simplest magnetic object found in nature is a magnetic dipole. This contrasts with the electric case where the simplest particle is a monopole. Because magnetic monopoles do not exist, the magnetic field can not emanate from a point source, thus the divergence of a magnetic field is always zero.

$$\nabla \cdot \overline{B} = 0 . \tag{8}$$

When the divergence of a vector is zero, the vector can be described as the curl of a second vector.[12,13] In the case of a magnetic field, this vector is named the vector potential.

$$\overline{B} = \nabla \times \overline{A} . \tag{9}$$

The curl of a gradient of a scalar function is always zero. Therefore, the vector potential can be parameterized with the gradient of a scalar function.

$$\overline{B} = \nabla \times (\overline{A}' + \nabla\lambda), \qquad \text{where} \qquad \overline{A} = \overline{A}' + \nabla\lambda . \tag{10}$$

This scalar function λ is known as a gauge function. The gauge function does not affect measurable quantities but may ease their calculation.

Applied Magnetic Fields and the Hamiltonian

The application of a magnetic field to a molecule changes the Lagrangian of the molecule. If the nuclei are fixed and there are no spin interactions between the nuclei and the electrons, the Lagrangian[9] of a single electron within a molecule with applied electric and magnetic fields in SI units[14] is

$$\mathcal{L} = \frac{1}{2} m_e \dot{r}^2 + V + e\phi - e\dot{\overline{r}} \cdot \overline{A} \tag{11}$$

where ϕ is the electric scalar potential and **A** is the magnetic vector potential. The canonical linear momentum associated with the Lagrangian is defined and subsequently calculated as

$$p_k = \frac{\partial \mathcal{L}}{\partial r_k} = m_e \dot{r}_k - eA_k . \tag{12}$$

The canonical linear momentum is seen to depend on the vector potential. Using this canonical momentum, the Hamiltonian of the molecule becomes

$$\mathcal{H} = \frac{1}{2m_e} (\overline{p} + e\overline{A})^2 + V - e\phi \tag{13}$$

When p is replaced by $p = -i\hbar\nabla$, the Hamiltonian after expansion becomes

$$\mathcal{H} = \frac{-\hbar^2}{2m_e}\nabla^2 + \frac{e\hbar}{im_e}\overline{A}\cdot\nabla + \frac{e\hbar}{2im_e}\nabla\cdot\overline{A} + \frac{e^2}{2m_e}A^2 + V - e\phi . \qquad (14)$$

For convenience in calculation, a gauge for the vector potential is often chosen such that $\nabla\cdot\overline{A} = 0$. This gauge choice is referred to as the Coulomb gauge. After applying the Coulomb gauge and assuming that only magnetic fields are acting on the molecule, the Hamiltonian becomes

$$\mathcal{H} = \frac{-\hbar^2}{2m_e}\nabla^2 + \frac{e\hbar}{im_e}\overline{A}\cdot\nabla + \frac{e^2}{2m_e}A^2 + V . \qquad (15)$$

The Hamiltonian can be examined in orders of the vector potential where

$$\mathcal{H}^{(0)} = \frac{-\hbar^2}{2m_e}\nabla^2 + V,\ \mathcal{H}^{(1)} = \frac{e\hbar}{im_e}\overline{A}\cdot\nabla \text{ and } \mathcal{H}^{(2)} = \frac{e^2}{2m_e}A^2 . \qquad (16)$$

The two different magnetic effects mentioned earlier can be seen with the division of the Hamiltonian into first and second-order terms. The first-order term is the paramagnetic term. Its energy depends on the alignment of magnetic dipoles with the magnetic field thus increasing the total magnetic field away from the molecule. In molecules with zero spin angular momentum, the magnetic dipoles originate from the net orbital angular momentum of the molecule. The second-order term can be considered the diamagnetic term where the applied magnetic field induces electronic currents in the molecule. These currents produce magnetic fields that oppose the applied magnetic field and thus decrease the total magnetic field away from the molecule.

The distinction made between paramagnetic and diamagnetic effects is not rigorous. While the first-order paramagnetic effects are independent of the gauge, the second-order paramagnetic effects are dependent on the choice of the gauge. How the total second-order magnetic effects are described can be changed by adjusting the gauge of the vector potential. Because of choosing the proper gauge, the total second-order magnetic effects can be described using different combinations of first-order perturbation theory applied to $\mathcal{H}^{(2)}$ in Equation (16) and second-order perturbation theory applied to $\mathcal{H}^{(1)}$ in Equation (16). Therefore, division of magnetic effects in a molecule into diamagnetic and paramagnetic effects is illusory, but conventional. Adjusting the gauge will not affect the second-order energy of the system. In this work, only the first-order effects are considered, therefore the specific choice of gauge, within the general Coulomb gauge, is of minor importance.

Construction of the Nonlocal Chemical Shift Tensor

Magnetic Field of the Nuclear Current

A nonlocal magnetizability tensor will be constructed in this chapter via finding the derivative of the electronic magnetic moment with respect to nuclear linear momentum. The theory presented will consider only the zeroth and first-order parts of the Hamiltonian from Equation (16). The second-order contribution will not be included. To find the magnetic moment derivative, the expectation value of the magnetization operator is calculated. However, the expectation value is calculated with wavefunctions from first-order perturbation theory, where the perturbation is the first-order portion of the Hamiltonian from Equation (16).

When a charged particle moves rectilinearly relative to a fixed reference frame, the particle produces a magnetic field.[8]

$$\overline{B}(\overline{R}) = -\frac{\mu_0 Ze}{4\pi}\frac{\overline{R}\times\overline{v}}{|\overline{R}|^3} = -\frac{\mu_0 Ze}{4\pi M}\frac{\overline{R}\times\overline{p}}{|\overline{R}|^3}. \qquad (17)$$

In equation (17), μ_0 is the vacuum permeability associated with SI units, $\overline{R}$ is the vector distance from the particle, Ze is the particle's charge, M is the particle's mass and $\overline{p}$ is the particle's mechanical linear momentum. When a nucleus inside a molecule moves, it creates a magnetic field. The electronic charge distribution changes in response to the magnetic field of the moving nucleus. The effect on the ground-state wavefunction is calculated by applying standard nondegenerate time-independent perturbation theory.

First-order Ground State Wavefunction

The first-order correction to the ground state wavefunction from standard perturbation theory is found to be[9]

$$|\Psi'\rangle = \sum_i{}' \frac{\langle\psi_i|\mathcal{H}'|\psi_0\rangle}{\mathcal{E}_0 - \mathcal{E}_i}|\psi_i\rangle \qquad (18)$$

where the $|\psi_i\rangle$ are the unperturbed wavefunctions from the zeroth-order Hamiltonian, the $\mathcal{E}_i$ are unperturbed energies and the prime on the summation indicates summation over all states except the ground state. When the first-order perturbation of Equation (16) is substituted, the ground-state perturbed wavefunction becomes

$$|\Psi\rangle = |\psi_0\rangle + \sum_i{}' \frac{\langle\psi_i|\frac{e}{m}\overline{A}\cdot\overline{p}|\psi_0\rangle}{\mathcal{E}_0 - \mathcal{E}_i}|\psi_i\rangle. \qquad (19)$$

At this point, the nature of the perturbation $\overline{A} \cdot \overline{p}$ needs to be considered. For a uniform applied magnetic field, the vector potential can be written as

$$\overline{A}(\overline{r}) = \frac{1}{2}\left(\overline{B} \times \overline{r}\right). \tag{20}$$

Substituting Equation (20) into the perturbation $\overline{A} \cdot \overline{p}$ yields

$$\overline{A} \cdot \overline{p} = \frac{1}{2}\left(\overline{B} \times \overline{r}\right) \cdot \overline{p}. \tag{21}$$

Applying the vector identity $\left(\overline{a} \times \overline{b}\right) \cdot \overline{c} = \left(\overline{c} \times \overline{a}\right) \cdot \overline{b} = \left(\overline{b} \times \overline{c}\right) \cdot \overline{a}$ yields

$$\frac{1}{2}\left(\overline{B} \times \overline{r}\right) \cdot \overline{p} = \frac{1}{2}\left(\overline{r} \times \overline{p}\right) \cdot \overline{B} = \frac{1}{2}\overline{l} \cdot \overline{B}, \tag{22}$$

where the electronic angular momentum operator has been defined as $\overline{l} = \overline{r} \times \overline{p}$. The electronic magnetic moment operator is defined as $\overline{\mu} = -\frac{1}{2}\frac{e}{m}\overline{l}$. Thus for a uniform magnetic field, the first-order perturbation of Equation (16) can be written in terms of the electronic magnetic moment operator.

$$\mathcal{H}^{(1)} = -\overline{\mu} \cdot \overline{B} \tag{23}$$

One can arrive at a similar result if, for the magnetic interaction between a nucleus and the electronic charge distribution, the perturbation Hamiltonian used is[15]

$$\mathcal{H}^{(1)} = -\int \overline{j}_e \cdot \overline{A}_n \, d\tau \tag{24}$$

In Equation (24), the e and n subscripts represent electronic and nuclear quantities, respectively. This form of the interaction Hamiltonian is written in terms of the electronic current density rather the current. The density formulation is vital to the construction of the nonlocal magnetizability density. The divergence of the electronic current density is zero for steady currents, i. e. where the charge density is not permitted to fluctuate over time. Thus, the current density can be written in terms of the magnetization density:

$$\bar{j}_e = \nabla \times \bar{m}_e \cdot \tag{25}$$

Note that the magnetization density $\bar{m}_e$ is written as a vector whereas the electron mass m_e is written as a scalar. The magnetization in Equation (25) is more than only the magnetic dipole density, because it includes all the information about the electronic current distribution under the influence of an applied magnetic field. Substitution of Equation (25) into Equation (24) yields

$$\mathcal{H}^{(1)} = -\int \left(\nabla \times \bar{m}_e \right) \cdot \bar{A}_n d\tau \, . \tag{26}$$

The vector potential due to the linear momentum of the nucleus and the electronic magnetization density are finite for a finite molecule. Therefore, for a surface surrounding the molecule at an infinite boundary, the following integral is zero.

$$-\int \left(\bar{A}_n \times \bar{m}_e \right) \cdot d\bar{S}_e = 0 \, . \tag{27}$$

By application of the divergence theorem, Equation (27) becomes

$$-\int \nabla \cdot \left(\bar{A}_n \times \bar{m}_e \right) d\tau = 0 \, . \tag{28}$$

Adding Equation (28) to Equation (26) and using the vector identity

$\nabla \cdot \left(\bar{a} \times \bar{b} \right) = \bar{b} \cdot \left(\nabla \times \bar{a} \right) - \bar{a} \cdot \left(\nabla \times \bar{b} \right)$ yields

$$\mathcal{H}^{(1)} = -\int \nabla \cdot \left(\bar{A}_n \times \bar{m}_e \right) d\tau - \int \left(\nabla \times \bar{m}_e \right) \cdot \bar{A}_n d\tau = -\int \bar{m}_e \cdot \left(\nabla \times \bar{A}_n \right) d\tau = -\int \bar{m}_e \cdot B_n d\tau \tag{29}$$

where B_n is the magnetic field due to the motion of the nucleus.

The interaction Hamiltonian of Equation (29) can be substituted into the expression for the first-order ground-state wavefunction of Equation (18) to yield

$$|\Psi\rangle = |\psi_0\rangle - \sum_i{}' \frac{\int \langle \psi_i | \bar{m}_e(\bar{r}) \cdot \bar{B}_n(\bar{r}) | \psi_0 \rangle d^3 r}{\mathcal{E}_0 - \mathcal{E}_i} |\psi_i\rangle . \tag{30}$$

Substituting Equation (17), the expression for the magnetic field produced by a nucleus undergoing rectilinear motion, into Equation (30) yields

$$|\Psi\rangle = |\psi_0\rangle + \frac{\mu_0 Ze}{4\pi M} \sum_i{}' \frac{\int \left\langle \psi_i \middle| \frac{\bar{m}_e(\bar{r}) \cdot \left(\bar{r} \times \bar{p}^K\right)}{|\bar{r}|^3} \middle| \psi_0 \right\rangle d^3 r}{\mathcal{E}_0 - \mathcal{E}_i} |\psi_i\rangle \tag{31}$$

Equation (31) has the implicit assumption that the origin in the three-dimensional space considered is at the nucleus. This choice is arbitrary and differs from the choice of origin for the electronic coordinates which affects the gauge of the magnetic field and is often intentionally varied for ease of calculation.[16,17,18,19] This wavefunction is the new ground state wavefunction corrected to first order for magnetic fields produced by a moving zero-spin nucleus.

Electronic Magnetic Moment Derivative

The wavefunction found in Equation (31) is now used to calculate the expectation value of the electronic magnetic moment density at point $\bar{r}'$. The expectation value is computed by calculating the ground state matrix element of the magnetization operator $\bar{m}_e(\bar{r}')$.

$$
\begin{aligned}
\langle\Psi|\bar{m}_e(\bar{r}')|\Psi\rangle &= \langle\psi_0|\bar{m}_e(\bar{r}')|\psi_0\rangle \\
&+ \frac{\mu_0 Ze}{4\pi M}\sum_i{}' \frac{\int\langle\psi_i|\frac{\bar{m}_e(\bar{r})\cdot\left(\bar{r}\times\bar{p}^K\right)}{|\bar{r}|^3}|\psi_0\rangle d^3r\langle\psi_0|\bar{m}_e(\bar{r}')|\psi_i\rangle}{\mathcal{E}_0-\mathcal{E}_i} \\
&+ \frac{\mu_0 Ze}{4\pi M}\sum_i{}' \frac{\int\langle\psi_0|\frac{\bar{m}_e(\bar{r})\cdot\left(\bar{r}\times\bar{p}^K\right)}{|\bar{r}|^3}|\psi_i\rangle d^3r\langle\psi_i|\bar{m}_e(\bar{r}')|\psi_0\rangle}{\mathcal{E}_0-\mathcal{E}_i} \qquad (32)\\
&+ \left(\frac{\mu_0 Ze}{4\pi M}\right)^2 \sum_{i,i'}{}' \frac{\int\langle\psi_0|\frac{\bar{m}_e(\bar{r})\cdot\left(\bar{r}\times\bar{p}^K\right)}{|\bar{r}|^3}|\psi_{i'}\rangle\langle\psi_i|\frac{\bar{m}_e(\bar{r})\cdot\left(\bar{r}\times\bar{p}^K\right)}{|\bar{r}|^3}|\psi_0\rangle d^3r\langle\psi_{i'}|\bar{m}_e(\bar{r}')|\psi_i\rangle}{\left(\mathcal{E}_0-\mathcal{E}_i\right)\left(\mathcal{E}_0-\mathcal{E}_{i'}\right)}.
\end{aligned}
$$

The derivative of Equation (32) with respect to the nuclear linear momentum $\bar{p}$ is performed while also neglecting the fourth term. The electronic wavefunctions used are the complete adiabatic wavefunctions formulated by Nafie and Freedman,[20] which only have parametric dependence on the nuclear momentum $\bar{p}^K$. Therefore, the only quantity in the expression for the electronic magnetic moment with functional nuclear linear momentum dependence is the quantity $\bar{r}\times\bar{p}^K$. As a lemma, the derivative of $\bar{r}\times\bar{p}^K$ with respect to the z-component nuclear linear momentum is calculated.

$$
\begin{aligned}
\frac{\partial\left(\bar{r}\times\bar{p}^K\right)}{\partial p_z^K} &= \frac{\partial}{\partial p_z^K}\left[\left(yp_z^K - zp_y^K\right)\hat{i} + \left(zp_x^K - xp_z^K\right)\hat{j} + \left(xp_y^K - yp_x^K\right)\hat{k}\right] \qquad (33)\\
&= y\hat{i} - x\hat{j} = -\bar{V}.
\end{aligned}
$$

In Equation (33), the vortex function $\overline{V}$ has been defined[9] as $\overline{V} = -y\hat{i} + x\hat{j}$. Applying this result within the derivative of the electronic magnetic moment yields

$$\frac{\partial \overline{m}_e(\bar{r}')}{\partial p_z} = \frac{\partial \langle \Psi | \overline{m}_e(\bar{r}') | \Psi \rangle}{\partial p_z} =$$
$$-\frac{\mu_0 Ze}{4\pi M}\sum_i{}' \frac{\int \langle \psi_0 | \overline{m}_e(\bar{r}') | \psi_i \rangle \langle \psi_i | \frac{\overline{m}_e(\bar{r}) \cdot \overline{V}}{|\bar{r}|^3} | \psi_0 \rangle d^3r}{\mathcal{E}_0 - \mathcal{E}_i}$$
$$-\frac{\mu_0 Ze}{4\pi M}\sum_i{}' \frac{\int \langle \psi_0 | \frac{\overline{m}_e(\bar{r}) \cdot \overline{V}}{|\bar{r}|^3} | \psi_i \rangle \langle \psi_i | \overline{m}_e(\bar{r}') | \psi_0 \rangle d^3r}{\mathcal{E}_0 - \mathcal{E}_i}. \tag{34}$$

Because the vortex function is a function of three dimensional space but not of electronic coordinates, the matrix elements in Equation (34) of the form $\langle \psi_i | \frac{\overline{m}_e(\bar{r}) \cdot \overline{V}}{|\bar{r}|^3} | \psi_0 \rangle$ can be rewritten as $\langle \psi_i | \frac{\overline{m}_e(\bar{r})}{|\bar{r}|^3} | \psi_0 \rangle \cdot \overline{V}$. Thus, Equation (34) becomes

$$\frac{\partial \overline{m}_e(\bar{r}')}{\partial p_z} = -\frac{\mu_0 Ze}{4\pi M}$$
$$\times \int \sum_i{}' \left[\frac{\langle \psi_0 | \overline{m}_e(\bar{r}') | \psi_i \rangle \langle \psi_i | \frac{\overline{m}_e(\bar{r})}{|\bar{r}|^3} | \psi_0 \rangle + \langle \psi_0 | \frac{\overline{m}_e(\bar{r})}{|\bar{r}|^3} | \psi_i \rangle \langle \psi_i | \overline{m}_e(\bar{r}') | \psi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_i} \right] \cdot \overline{V} d^3r. \tag{35}$$

The quantity in the brackets [] is the high-frequency or "paramagnetic" chemical shift of Ramsey's nuclear magnetic resonance theory.[15,21,22] Equation (34) neglects all effects of spin.[23]

$$\sigma_{\alpha\beta}^{HF}(\bar{r}, \bar{r}') = \sum_i{}' \left[\frac{\langle \psi_0 | \overline{m}_{e\alpha}(\bar{r}') | \psi_i \rangle \langle \psi_i | \frac{\overline{m}_{e\beta}(\bar{r})}{|\bar{r}|^3} | \psi_0 \rangle + \langle \psi_0 | \frac{\overline{m}_{e\beta}(\bar{r})}{|\bar{r}|^3} | \psi_i \rangle \langle \psi_i | \overline{m}_{e\alpha}(\bar{r}') | \psi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_i} \right]. \tag{36}$$

Substituting Equation (36) into Equation (35) and putting the equation in component form yields the final result.

$$\frac{\partial \overline{m}_{e\alpha}(\bar{r}')}{\partial p_z} = -\frac{\mu_0 Ze}{4\pi M} \times \int \sigma^{HF}_{\alpha\beta}(\bar{r},\bar{r}')\overline{V}_\beta \, d^3r . \tag{37}$$

In Equation (37) and all subsequent equations, the Einstein summation convention is used where summation over repeated coordinate indices is assumed.

As mentioned briefly in the above derivation, the wavefunctions in the derivation have a parametric dependence on the nuclear momenta in addition to the nuclear coordinates. The need for such wavefunctions arises from the observation that the use of adiabatic wavefunctions from the Born-Oppenheimer approximation[24] to calculate electronic velocities results in zero.[25,26] This lack of computability necessitates the use of wavefunctions beyond the zeroth-order Born-Oppenheimer approximation. Nafie and Freedman have constructed complete adiabatic electronic wavefunctions that include a parametric dependence on the nuclear motion for use in theories of vibronic coupling[20] and vibrational circular dichroism.[27] These wavefunctions are adiabatic because the electronic portion is separable from the nuclear portion. The wavefunctions have the utility of calculating electronic momenta without using the nuclear portion of the wavefunction.

Discussion

The physical interpretation of Equation (37) is not completely transparent. However, Equation (37) does demonstrate that molecular electronic current densities respond to internal magnetic fields with the same molecular properties used to describe the response to external magnetic fields. The chemical shift tensor describes how an external magnetic field induces magnetic moments in the electronic distribution, which affect the true magnetic field at a nucleus. The induced magnetic moments create magnetic fields that oppose the external field. Thus, the total magnetic field seen by the nucleus is a sum of contributions from the fields of the induced magnetic moments and the applied field. Equation (37) shows that the chemical shift tensor not only relates magnetic field information from the electrons to the nuclei, but that it also relates magnetic field information from the nuclei to the electrons.

This calculation of the nuclear linear momentum derivative incorporates a magnetization-magnetization mechanism for the response of magnetic perturbations within the molecule. The calculation differs from other calculations done for the nuclear linear momentum derivative of the electronic magnetic moment in theories of vibrational circular dichroism. In their nonlocal theory of VCD, Hunt and Harris[4] consider the response to a magnetic field via a magnetization-polarization mechanism in the construction of a nonlocal charge susceptibility density. This susceptibility is related to the magnetoelectric shielding tensor that describes the electric field shielding to due an applied magnetic field[28]. Their result was derived with the assumption of a homogeneous magnetic field. In contrast, the result of Equation (37) was derived with an inhomogeneous magnetic field though the field used was not general but it was specific to the rectilinear motion of charged particle.

The derivative of the electronic magnetic moment with respect to nuclear linear momentum is an important quantity in theories of VCD. Buckingham, Fowler and Galwas[29] have examined the velocity dependence of molecular property surfaces. They generalize property surfaces to include imaginary operators such as the momentum and apply the theory to a nuclear momentum surface of the electronic magnetic moment for use in a description of VCD. In work on the electromagnetic effects of nuclei upon electrons, Lazzeretti *et al.*[30,31] have investigated how vibrational motion of nuclei affects the average electronic magnetic dipole. The effects of the nuclear spin on the electronic magnetic dipole were also studied.[30] Extension of this work led to a sum rule for the electromagnetic nuclear shieldings in terms of the paramagnetic susceptibility.[32] Walnut has examined how radiation interacts with a molecule under the influence of a magnetic field generated by nuclear motion.[33] In a novel application of the velocity surface theory of Buckingham, Fowler and Galwas, a theory of antisymmetric nonresonant vibrational Raman scattering has been constructed using the nuclear linear momentum derivative of the antisymmetric portion of the polarizability tensor.[34]

In the theories above, the susceptibility tensors used have not been densities. Chemical shift densities, i. e., nuclear magnetic shielding densities have been constructed by Jameson and Buckingham.[35] Their chemical shift density is a local density and differs from the nonlocal density found in this chapter. A local chemical shift density has been calculated for several small molecules. The method involves constructing a neutron magnetic shielding tensor via calculating the magnetic response of a "probe" neutron within the molecular volume.[36]

The theory constructed in this chapter relating internal magnetic fields to molecular properties is incomplete. Only the paramagnetic response to a spinless charged particle has been considered. The diamagnetic response is the same order of magnitude as the paramagnetic response. To include the diamagnetic response, an appropriate treatment of the second order Hamiltonian of Equation (16), which contains the square of the vector potential, is necessary. In addition, the spin of the nucleus has been neglected which is also a nontrivial contributor to the magnetic interactions within a molecule. In Chapter 5, possible avenues of research are presented to produce a more complete theory of intramolecular magnetic interactions and even a unified electromagnetic theory of intramolecular interactions.

REFERENCES

[1] K. L. C. Hunt, J. Chem. Phys. **90**, 4909 (1989).

[2] K. L. C. Hunt, Y. Q. Liang, R. Nimalakirthi and R. A. Harris, J. Chem. Phys. **91**, 5251 (1989).

[3] E. L. Tisko, X. Li, and K. L. C. Hunt, J. Chem. Phys. **103**, 6873 (1995); Chapter 2.

[4] K. L. C. Hunt and R. A. Harris, J. Chem. Phys. **94**, 6995 (1991).

[5] L. D. Barron, *Molecular Light Scattering and Optical Activity* (Cambridge University Press, Cambridge, 1982).

[6] A. D. Buckingham, Faraday Discuss. **99**, 1 (1994).

[7] P. J. Stephens, J. Phys. Chem. **89**, 748 (1985); **91**, 1712 (1987).

[8] J. D. Jackson, *Classical Electrodynamics*, 2nd ed. (John Wiley and Sons, New York, 1975).

[9] P. W. Atkins, *Molecular Quantum Mechanics*, 2nd. ed. (Oxford, Oxford University Press, 1983).

[10] J. H. van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford, Oxford University Press, 1932).

[11] D. W. Davies, *The Theory of the Electric and Magnetic Properties of Molecules* (John Wiley and Sons, London, 1967).

[12] G. Arfken, *Mathematical Methods for Physicists*, 3rd ed. (Academic Press, San Diego, 1985).

[13] M. L. Boas, *Mathematical Methods in the Physical Sciences*, 2nd ed. (John Wiley and Sons, New York, 1983).

[14] See the Appendix in Jackson's text for a discussion of electromagnetic units.

[15] N. F. Ramsey, *Molecular Beams* (Oxford University Press, Oxford, 1956).

[16] R. Ditchfield, Molec. Phys. **27**, 789 (1974).

[17] K. Wolinski, J. F. Hinton and P. Pulay, J. Am. Chem. Soc. **112**, 8251 (1990).

[18] K. Ruud, T. Helgaker, R. Kobayashi, P. Jørgensen, K. L. Bak and H. J. A. Jensen, J. Chem. Phys. **100**, 8178 (1994).

[19] R. Zanasi, P. Lazzeretti, M. Malagoli and F. Piccinini, J. Chem. Phys. **102**, 7150 (1995).

[20] L. A. Nafie and T. B. Freedman, J. Chem. Phys. **78**, 7108 (1983).

[21] N. F. Ramsey, Phys. Rev. **77**, 567 (1950); **78**, 699 (1950); **86**, 243 (1952); **87**, 1075 (1952).

[22] C. P. Slichter, *Principles of Magnetic Resonance*, 2nd ed. (Springer-Verlag, Berlin, 1978).

[23] N. F. Ramsey and E. M. Purcell, Phys. Rev. **85**, 143 (1952); N. F. Ramsey, Phys. Rev. **90**, 232 (1953); **91**, 303 (1953).

[24] M. Born and R. Oppenheimer, Ann. Phys. **84**, 457 (1927); M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* Oxford University Press, London, 1954).

[25] N. V. Cohan and H. F. Hameka, J. Chem. Phys. **45**, 4392 (1966).

[26] C. A. Mead and A. Moscowitz, Int. J. Quantum Chem. **1**, 243 (1967).

[27] L. A. Nafie, J. Chem. Phys. **79**, 4950 (1983).

[28] P. Lazzeretti, Adv. Chem. Phys. **12**, 507 (1989).

[29] A. D. Buckingham, P. W. Fowler and P. A. Galwas, Chem. Phys. **112**, 1 (1987).

[30] P. Lazzeretti, Chem. Phys. **134**, 269 (1989).

[31] P. Lazzeretti, M. Maligoli and R. Zanasi, Chem. Phys. Lett. **179**, 297 (1991).

[32] P. Lazzeretti, M. Maligoli and R. Zanasi, Chem. Phys. **150**, 173 (1991).

[33] T. H. Walnut, Int. J. Quantum Chem., Symp. **22**, 99 (1988).

[34] F.-C. Liu, J. Phys. Chem. **95**, 7180 (1991).

[35] C. J. Jameson and A. D. Buckingham, J. Chem. Phys. **73**, 5684 (1980).

[36] K. Wolinski, J. Chem. Phys. **106**, 6061 (1997).

CHAPTER 5: TOWARD A COMPLETE ELECTROMAGNETIC SUSCEPTIBILITY DENSITY

Introduction

In Chapter 4, the derivative of the electronic magnetic moment with respect to the rectilinear nuclear momentum was related to the paramagnetic or high-frequency nonlocal magnetizability density

$$\frac{\partial m_{e\alpha}(\bar{r}')}{\partial p_z} = -\frac{\mu_0 Ze}{4\pi M} \times \int \sigma_{\alpha\beta}^{HF}(\bar{r},\bar{r}') V_\beta \, d^3r \tag{1}$$

where $\bar{V}$ is the vortex function defined[1] for the magnetic axis in the z-direction as $\bar{V} = -y\hat{i} + x\hat{j}$. In other words, Equation (1) shows that the electronic magnetic moment changes due to the influence from the magnetic field of a moving nucleus via the response of the nonlocal magnetizability density. The intramolecular response to magnetic fields is described with the same molecular property used to describe molecular response to external magnetic fields.

Two unfinished aspects of the treatment of response of the electronic charge distribution by intramolecular magnetic fields are the treatment of diamagnetic response and the response due to the nuclear magnetic moment. Initial possibilities to extend the theory include manipulation of the diamagnetic portion of the interaction Hamiltonian, which is essentially the square of the vector potential, into a form that is the square of the magnetic field.

The intramolecular magnetic response theory can be extended by including the magnetic moment of a nucleus with spin angular momentum. This extension should yield an explanation of nuclear spin-spin coupling using a nonlocal susceptibility density. Though this idea has not been adequately investigated, the addition of the magnetic field due to a nuclear magnetic moment would not appear to contribute to the nuclear momentum derivative since the nuclear dipolar field is independent of the nuclear momentum. However, this independence is only to first order in a relativistic electromagnetic theory. Thus, further investigations into intramolecular magnetic response seem to necessitate the introduction of special relativity.

Most of the remaining discussion in this chapter will present two possible paths to pursue using special relativity in the context of molecular interactions. The first path involves using the original formulation of the nonlocal polarizability density in terms of 3-dimensional current densities and using the ansatz of replacing the 3-dimensional current densities with 4-dimensional current densities from special relativity. Manipulation of this pseudo-relativistic polarizability density to relate it to electromagnetic properties is nontrivial since the tensor calculus of the 4-dimensional space-time is much different from the vector calculus of the 3-dimensional "3-space".

The second path involves the construction of a nonlocal electromagnetic susceptibility density using the nonrelativistic expansion of the interaction Hamiltonian of the fully relativistic Dirac equation. Such an expansion contains interesting terms such as spin-other-orbit terms that have a dependence on the nuclear momentum. If such terms can be included within an intramolecular response theory, new insights into what electromagnetic properties are affected by nuclear magnetic fields may be found.

The Special Relativity of Electromagnetic Theory

Relativistic Mechanics

Special relativity is a consequence of two axioms concerning physical laws.[2,3] The first axiom is that the laws of nature are same in any inertial reference frame. The second axiom is that the speed of light is the same in all inertial reference frames. Heuristically stated, the second axiom says that one can never ride on the crest of light wave unless one is a light wave. The two axioms together change the intuitive notion of time and space. As brief example, consider two observers observing wave motion on a body of water. A stationary observer on a riverbank measures the time interval for a wavecrest to travel 20 feet. An observer in a 20-foot boat traveling in the direction of the wave measures the time interval needed for the wave to travel from stern to bow. The time interval measured by the moving observer is longer than that measured by the stationary observer. This agrees with our intuition. The conflict with our intuition arises in the second axiom of special relativity for the case of light waves. In this case, the measured time interval for each observer is identical. Consequently, the time interval between two events is no longer an invariant quantity. Time measured on the shore differs from time measured on the boat. The effect of relativity is that time and space are no longer absolute and independent quantities, but they are fused into geometry of four-dimensional space-time.

In Newtonian mechanics, the transformation between a stationary reference frame and a reference frame moving exclusively in the x-direction is dictated by the Galilean transformation

$$t' = t\,,\ x' = x - vt\,,\ y' = y \text{ and } z' = z\,, \tag{2}$$

where the primed coordinates refer to the moving reference frame. Within a Galilean transformation, time is absolute; i. e. time has no dependence on the position in space. In relativistic mechanics, the transformation between stationary and moving frames (in the x-direction) is dictated by the Lorentz transformation

$$t' = \gamma\left(t - \frac{vx}{c^2}\right),\ x' = \gamma\left(x - vt\right),\ y' = y \text{ and } z' = z \text{ where } \gamma = \left(1 - \frac{v^2}{c^2}\right)^{-\frac{1}{2}}. \quad (3)$$

Quantities in space-time must be expressed four-dimensionally to retain the same structure in different inertial reference frames. This retention of structure is known as Lorentz invariance. In other words, the structure must be the same after a Lorentz transformation. All physical quantities and laws must be Lorentz invariant. Thus the position vector is not a three-dimensional vector $\bar{x} = \left(x_1 \quad x_2 \quad x_3\right)$ but rather a four-dimensional vector that includes time $\mathbf{x} = \left(ct \quad x \quad y \quad z\right)$ or $\mathbf{x} = x_\mu = \left(x_0 \quad x_1 \quad x_2 \quad x_3\right)$. (Greek subscripts are usually used to indicate a four-dimensional vector or tensor. Also note that the time component is often referred as the zeroth component in space-time. This convention is not absolute and depends on the formalism chosen to describe space-time.) A Lorentz invariant vector is also known as a 4-vector. A 4-vector differential operator can also be constructed which is known as the 4-gradient

$$\frac{\partial}{\partial x^\mu} = \partial^\mu = \left(\frac{1}{c}\frac{\partial}{\partial t} \quad \frac{\partial}{\partial x} \quad \frac{\partial}{\partial y} \quad \frac{\partial}{\partial z}\right) = \left(\frac{\partial}{\partial x^0} \quad \frac{\partial}{\partial x^1} \quad \frac{\partial}{\partial x^2} \quad \frac{\partial}{\partial x^3}\right). \quad (4)$$

The abbreviated notation for the gradient ∂^μ will be used in this chapter.

Distances and time intervals measured separately in a stationary frame and in a moving frame will differ. The difference will be slight when speeds are small compared to the speed of light. As the speed of the moving frame approaches the speed of light, the differences in the values of length and time measurements become more pronounced. In contrast, four-dimensional space-time intervals are Lorentz invariant, i. e. the value of the interval will be the same in all reference frames, moving or not. This invariance of the space-time interval can be expressed as

$$\left(c^2 t'^2 - x'^2 - y'^2 - z'^2\right) = \left(c^2 t^2 - x^2 - y^2 - z^2\right). \tag{5}$$

The mixed signs in the space-time interval are contrasted with the uniformity of signs within the invariant space interval of Newtonian mechanics $\left(x^2 + y^2 + z^2\right)$. This additional complication is tackled using two formalisms. The first formalism is the use of pseudo-Euclidean space where the time component of 4-vectors is made an imaginary number. The second formalism uses Minkowski space where a distinction is made between contravariant and covariant vectors and dot products between the two 4-vectors are performed via contraction with a diagonal matrix called the metric tensor. The use of Minkowski space is more accurate since it is derived from the differential geometry used in Einstein's theory of gravitation, the general theory of relativity. These issues of metric choice are ignored in this chapter.

Relativistic Electromagnetic Theory

The fusing of quantities naively considered to be independent also occurs in the electromagnetic theory.[4,5] Before the advent of relativity theory, the fundamental equations of electrodynamics, Maxwell's equations, were known to be the same in stationary and moving reference frames. Maxwell's equations in SI units[6] are

$$\nabla \cdot \bar{E} = \frac{\rho}{\varepsilon_0}, \tag{6}$$

$$\nabla \times \bar{E} + \frac{\partial \bar{B}}{\partial t} = 0, \tag{7}$$

$$\nabla \cdot \bar{B} = 0, \tag{8}$$

$$\nabla \times \bar{B} = \mu_0 \bar{j} + \mu_0 \varepsilon_0 \frac{\partial \bar{E}}{\partial t}. \tag{9}$$

Equations (6) and (8) are static equations indicating that in a stationary frame, the source of the electric field is the charge whereas the magnetic field has no source. Equations (7) and (9) are dynamic equations showing that electric fields can be created from time-dependent magnetic fields and that magnetic fields are created from moving charges and time-dependent electric fields.

In relativity theory, the electric and magnetic fields are components of a single quantity called the electromagnetic field tensor.

$$F_{\mu\nu} = \begin{pmatrix} 0 & -E_x & -E_y & -E_z \\ E_x & 0 & -B_z & B_y \\ E_y & B_z & 0 & -B_x \\ E_z & -B_y & B_x & 0 \end{pmatrix}. \tag{11}$$

The charge density and the current density are merged into a four-dimensional current density or 4-current density. The 4-current density is written as

$$\mathbf{j}(\mathbf{r}) = j_\mu(\mathbf{r}) = \left(c\rho(\bar{r},t), j_x(\bar{r},t), j_y(\bar{r},t), j_z(\bar{r},t)\right). \tag{12}$$

The convention used in this chapter is bold type to indicate a four-dimensional quantity and an overhead bar to indicate a three-dimensional quantity. The constant c is the speed of light that can be considered a proportionality constant between electric and magnetic quantities. Maxwell's equations can be rewritten in terms of the electromagnetic field tensor and the 4-current density as

$$\partial_\mu F^{\mu\nu} = \mu_0 j^\nu \tag{13}$$

$$\partial^\sigma F^{\mu\nu} + \partial^\mu F^{\nu\sigma} + \partial^\nu F^{\sigma\mu} = 0 \tag{14}$$

where ∂_μ represents the 4-gradient from Equation (4) and the Einstein summation convention of summation over repeated Greek indices is followed. Equation (13) is the relativistic equivalent of Equations (6) and (9) whereas Equation (14) is the equivalent of the Equations (7) and (8). The relativistic formulation of Maxwell's equations is an example of the compactness of the relativistic electromagnetic theory. As a further example of the compactness of the theory, the electrostatic scalar potential and magnetic vector potential can be fused into a single quantity, the 4-potential.

$$\mathbf{A} = A^\mu = \begin{pmatrix} \frac{\phi}{c} & A^x & A^y & A^z \end{pmatrix} \tag{15}$$

where ϕ is the scalar potential and A^i are the components of the vector potential. All of the components of the electromagnetic field tensor can be derived with the Equation (16)

$$F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu \tag{16}$$

The relativistic formulation of electrodynamics is not limited to Maxwell's equations of microscopic matter but can be extended to Maxwell's equations of macroscopic matter.

$$\nabla \cdot \overline{D} = \rho, \tag{17}$$

$$\nabla \times \overline{E} + \frac{\partial \overline{B}}{\partial t} = 0, \tag{7}$$

$$\nabla \cdot \overline{B} = 0, \tag{8}$$

$$\nabla \times \overline{H} = \bar{j} + \frac{\partial \overline{D}}{\partial t}. \qquad (18)$$

The relationship between the microscopic equations and the macroscopic equations is established with the constitutive relations

$$\overline{D} = \varepsilon_0 \overline{E} + \overline{P} \quad \text{and} \quad \overline{H} = \frac{1}{\mu_0}\overline{B} - \overline{M}. \qquad (19)$$

The macroscopic fields $\overline{D}$ and $\overline{H}$ include the effects of polarization $\overline{P}$ and magnetization $\overline{M}$ of a system. Relativistically, the polarization and magnetization can be fused into a single electromagnetization tensor,[7,8] $M_{\mu\nu}$

$$M_{\mu\nu} = \begin{pmatrix} 0 & cP_x & cP_y & cP_z \\ -cP_x & 0 & M_z & -M_y \\ -cP_y & -M_z & 0 & M_x \\ -cP_z & M_y & -M_x & 0 \end{pmatrix} \qquad (20)$$

Similarly a second rank tensor $H_{\mu\nu}$ can be constructed from the displacement field $\overline{D}$ and the magnetic field $\overline{H}$.

$$H_{\mu\nu} = \begin{pmatrix} 0 & -cD_x & -cD_y & -cD_z \\ cD_x & 0 & H_z & -H_y \\ cD_y & -H_z & 0 & H_x \\ cD_z & H_y & -H_x & 0 \end{pmatrix} \qquad (21)$$

Using Equations (11), (20) and (21), the constitutive relations of Equation (18) can be rewritten relativistically as

$$F_{\mu\nu} = \mu_0 \left(H_{\mu\nu} + M_{\mu\nu} \right) \qquad (22)$$

Relativistic Adaptation of Nonlocal Polarizability Density

The lack of independence between the polarization and magnetization exhibited by Equation (20) suggests that response tensors that describe the changes in polarization within a molecule could be extended within a relativistic formulation to describe also the magnetic response. Nonlocal polarizability densities[9,10,11,12] have been used to describe the effect of polarization at a point upon the polarization at another point. Hunt[9] has used the nonlocal polarizability densities of Maaskant and Oosterhoff,[13] originally created for use in the theory of optical rotation tensors, in a theory of intermolecular and intramolecular electric response. Maaskant and Oosterhoff's nonlocal polarizability density was fashioned with current densities.

$$\begin{aligned}\alpha_{\alpha\beta}(\bar{r},\bar{r}';\omega) = \frac{1}{\omega^2}\sum_{n\neq 0}\left\{\frac{\langle 0|j_\alpha(\bar{r})|n\rangle\langle n|j_\beta(\bar{r}')|0\rangle}{\mathcal{E}_0-\mathcal{E}_n-\hbar\omega}+\frac{\langle 0|j_\beta(\bar{r}')|n\rangle\langle n|j_\alpha(\bar{r})|0\rangle}{\mathcal{E}_0-\mathcal{E}_n+\hbar\omega}\right\} \\ -\frac{1}{\omega^2}\zeta_{00}(\bar{r})\delta(\bar{r}-r')\,\delta_{\alpha\beta}.\end{aligned} \tag{23}$$

In Equation (23), the current density is defined quantum mechanically as

$$\langle 0|j_\alpha(\bar{r})|n\rangle = \frac{1}{2}\left[\langle 0|\sum_j\frac{q_j}{m_j}\delta(\bar{r}-\bar{r}_j)\frac{\hbar}{i}\nabla_{j\alpha}|m\rangle + \langle 0|\sum_j\frac{q_j}{m_j}\delta(\bar{r}-\bar{r}_j)\frac{\hbar}{i}\nabla_{j\alpha}|m\rangle^*\right] \tag{24}$$

and $\zeta_{00}(\bar{r})$ is defined as

$$\zeta_{00}(\bar{r}) = \langle 0|\sum_j\frac{q_j^2}{m_j^2}\delta(\bar{r}-\bar{r}_j)|0\rangle\,. \tag{25}$$

The index j indicates both electrons and nuclei with charge q_j, mass m_j and position r_j.

Hunt demonstrated that the nonlocal polarizability density formulated in terms of current densities could be reformulated in terms of polarization operators as long as the field incident upon the molecule could be derived from a scalar potential.[9]

$$\alpha_{\alpha\beta}(\bar{r},\bar{r}';\omega)=\sum_{n\neq 0}\left\{\frac{\langle 0|P_\alpha(\bar{r})|n\rangle\langle n|P_\beta(\bar{r}')|0\rangle}{\mathcal{E}_0-\mathcal{E}_n-\hbar\omega}+\frac{\langle 0|P_\beta(\bar{r}')|n\rangle\langle n|P_\alpha(\bar{r})|0\rangle}{\mathcal{E}_0-\mathcal{E}_n+\hbar\omega}\right\} \tag{26}$$

Since the electric field is derivable from a scalar potential, Hunt's formulation of the nonlocal polarizability density is able to describe the molecular response to external[9,10] and internal[11,12] electric fields. A complete theory of nonlocal susceptibility densities would describe electric, magnetic and mixed electric-magnetic response.

One approach to extending nonlocal susceptibility density theory is to substitute into Equation (23), as an ansatz, classical 4-current densities.

$$\begin{aligned}\alpha_{\mu\nu}(\bar{r},\bar{r}',t,t')=\frac{1}{\omega^2}\sum_{n\neq 0}&\left\{\frac{\langle 0|j_\mu(\bar{r},t)|n\rangle\langle n|j_\nu(\bar{r}',t')|0\rangle}{\mathcal{E}_0-\mathcal{E}_n}+\frac{\langle 0|j_\nu(\bar{r}',t')|n\rangle\langle n|j_\mu(\bar{r},t)|0\rangle}{\mathcal{E}_0-\mathcal{E}_n}\right\}\\&-\frac{1}{\omega^2}\zeta_{00}(\bar{r},t)\delta(\bar{r}-\bar{r}',t-t')\delta_{\alpha\beta}.\end{aligned} \tag{27}$$

Substituting the 4-current densities does not make Equation (27) relativistically rigorous. Such rigor would need to be developed from the first principles of quantum electrodynamics. This approach is discussed further in the next section. Since the zeroth component of the 4-current density is the electric charge density, the α_{00} component of the "relativistic" nonlocal polarizability density of Equation (27) would include Hunt's formulation of the nonlocal polarizability density plus additional terms associated with the time dependence of the charge density. The applications of the 4-polarizability density may follow from analogies with Hunt's earlier work. However, such analogies would be indirect since the tensor calculus of relativistic electrodynamics is different from the calculus of Coulombic electrostatics. Application of the four-dimensional tensor calculus upon Equation (27) may uncover interesting and unknown relationships between the responses of electric and magnetic fields with molecules.

Four-dimensional susceptibility tensors have been used by McLachlan to describe retardation effects in the theory of long-range intermolecular forces.[14]

$$\alpha_{\mu\nu}(\bar{r},\bar{r}';\omega) = \sum_{n\neq 0}\left\{\frac{\langle 0|\,j_\mu(\bar{r})|\,n\rangle\langle n|\,j_\nu(\bar{r}')|\,0\rangle}{\mathcal{E}_0-\mathcal{E}_n-\hbar\omega}+\frac{\langle 0|\,j_\nu(\bar{r}')|\,n\rangle\langle n|\,j_\mu(\bar{r})|\,0\rangle}{\mathcal{E}_0-\mathcal{E}_n+\hbar\omega}\right\}. \qquad (28)$$

This form of the susceptibility density describes the response of the relativistic interaction perturbation

$$V = -\int J_\mu(\bar{r})\,A_\mu(\bar{r},t)\,d\bar{r} \qquad (29)$$

where the current densities are assumed to be time independent. McLachlan's susceptibility density was constructed from the generalized susceptibility discussed by Landau and Lifshitz.[15] The susceptibility of Equation (28) is simpler than the susceptibility of Equation (27) since the 4-currents in Equation (28) are time-independent. However, McLachlan's equation suggests the ansatz used in the creation of Equation (27) is not too unphysical.

Relativistic Quantum Mechanics

Klein-Gordon Equation

As coordinates in the space-time of relativistic mechanics, space and time belong to the same class. This equivalence contrasts with 3-space where the x, y, and z coordinates belong to the same class but the time coordinate is different. The energies of most non-relativistic phenomena can be calculated with the Schrödinger equation.

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x_\alpha^2}\Psi + V\Psi = i\hbar\frac{\partial}{\partial t}\Psi \tag{30}$$

The Schrödinger equation treats the spatial and time coordinates differently as it has a second order spatial derivative and a first order time derivative. A relativistic equation would have identical orders of derivatives for the time and spatial coordinates. The Klein-Gordon equation[16,17] is a relativistic equation that has second order time and space derivatives.

$$\hbar^2\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} - \frac{\partial^2}{\partial z^2}\right)\Psi - m_0^2c^2\Psi = 0. \tag{31}$$

The negative signs in the spatial derivative arise from the special relativistic tensor calculus needed to describe invariance of the space-time interval, Equation (5). Also, note that in Equation (31), m_0 is the rest mass. (In special relativity, the total energy includes the kinetic energy and the potential energy of the rest mass, i. e., $E^2 = \left(p^2 + m_0^2c^2\right)c^2$ or for a particle with no kinetic energy, $E = m_0c^2$.) Analysis of the Klein-Gordon equation demonstrates that it is an inadequate description for particles with half-integral spin such as the electron but it provides an excellent description of exotic massive zero-spin particles of high-energy particle physics.

Dirac Equation

Dirac formulated a relativistic wave equation based on first order derivatives

$$i\hbar c\frac{\partial}{\partial t}\Psi = \left[-i\hbar c\left(\alpha_1\frac{\partial}{\partial x} + \alpha_2\frac{\partial}{\partial y} + \alpha_3\frac{\partial}{\partial z}\right) + \beta m_0 c^2\right]\Psi \tag{32}$$

where the α_i and β are coefficients. Dirac put the condition on the solutions of Equation (32) that they must satisfy the Klein-Gordon equation as well. For Equation (32), the Dirac equation, to have well defined solutions, the α_i and β coefficients must be 4 x 4 matrices.

$$\alpha_1 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \alpha_2 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix}, \alpha_3 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \quad (33)$$

These matrices can be written as matrices of the Pauli matrices and the unit matrix

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \text{ and } \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (34)$$

To make the Dirac equation truly Lorentz invariant, the Dirac matrices γ_μ are used rather than the α_i and β matrices.

$$\gamma_i = \begin{pmatrix} 0 & \sigma_i \\ -\sigma_i & 0 \end{pmatrix} \text{ and } \gamma_0 = \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (35)$$

Using these matrices in the Dirac equation yields solutions that are vectors. These vectors are four-component spinors. To examine some of the consequences of having these four-component spinors as solutions, let us investigate the solutions for a free electron with a specified momentum. The four solutions to the Dirac equation are

$$\Psi_1 = \begin{pmatrix} 1 \\ 0 \\ \dfrac{c\bar{\sigma}\cdot\bar{p}}{m_0c^2+E} \\ 0 \end{pmatrix} e^{i(\bar{p}\cdot\bar{r}-Et)}, \qquad \Psi_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \dfrac{c\bar{\sigma}\cdot\bar{p}}{m_0c^2+E} \end{pmatrix} e^{i(\bar{p}\cdot\bar{r}-Et)},$$

$$\Psi_3 = \begin{pmatrix} 1 \\ 0 \\ \dfrac{c\bar{\sigma}\cdot\bar{p}}{m_0c^2-E} \\ 0 \end{pmatrix} e^{i(\bar{p}\cdot\bar{r}+Et)} \quad \text{and} \quad \Psi_4 = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \dfrac{c\bar{\sigma}\cdot\bar{p}}{m_0c^2-E} \end{pmatrix} e^{i(\bar{p}\cdot\bar{r}+Et)}. \tag{36}$$

Ψ_1 and Ψ_2 are called the positive energy solutions and Ψ_3 and Ψ_4 are the negative energy solutions. When Dirac first published his equation, the interpretation of a negative energy state for the electron was mystifying since the negative energy state of an electron is unobservable. With the discovery of antimatter, the negative energy states were reinterpreted as positive energy states of antielectrons or positrons.

Within each solution there are two sets of components. The upper two components are called the large components and the lower two components are called the small components. At low energies, i. e., most chemical energies, the rest mass energy m_0c^2 is much greater than the kinetic energy E. Therefore the quantity $\dfrac{c\bar{\sigma}\cdot\bar{p}}{m_0c^2+E}$ within the lower two components is much less than one. Thus the lower two components are much smaller than the upper two components and their labeling as large and small components is natural.

At first glance, ignoring the negative energy states and the small components might prove to be useful. However, the Dirac equation is actually four coupled wave equations. One could start with a solution from the free Hamiltonian that neglects the small components and positron energies. However, when an interaction Hamiltonian is added, the small components and positron energies reappear. In a fully relativistic calculation, the electron energies are inextricably connected with the positron energies.

Gordon Decomposition

In relativistic quantum mechanics, the current density is written as

$$\mathbf{j} = c\overline{\Psi}\cdot\gamma_\mu\cdot\Psi \tag{37}$$

where $\overline{\Psi}=\Psi^\dagger\cdot\gamma_0$ and $\Psi^\dagger$ is the Hermitian conjugate of Ψ. Using substitutions of the Dirac equation and the calculus of 4-component spinors, Equation (37) can be rewritten as[18,19]

$$\begin{aligned}\mathbf{j} &= \frac{ie\hbar}{2m}\frac{\partial}{\partial x_\mu}\left(\overline{\Psi}\gamma_\mu\gamma_\nu\Psi\right)+\frac{ie\hbar}{2m}\left\{\left(\frac{\partial\overline{\Psi}}{\partial x_\mu}-\frac{ie}{\hbar c}A_\mu\overline{\Psi}\right)\Psi+\overline{\Psi}\left(\frac{\partial}{\partial x_\mu}-\frac{ie}{\hbar c}A_\mu\right)\Psi\right\} \\ &= \mathbf{j}_{\mathrm{int}}+\mathbf{j}_{\mathrm{conv}}.\end{aligned} \tag{38}$$

In Equation (38), $\mathbf{j}_{\mathrm{int}}$ is interpreted as an internal current analogous to the internal currents and charges that arise from magnetizations and polarizations. The convection current density $\mathbf{j}_{\mathrm{conv}}$ describes currents analogous to the currents created by moving charges. The currents in the Gordon decomposition are still fully relativistic; that is, the currents calculated involve positron states in addition to electron states. However, the technique is included in this chapter for consideration when trying to separate applied fields from their molecular responses. Nonrelativistic transformations would still be needed for chemical applications.

Nonrelativistic Approximations to the Dirac Equation

Chemically, the concept of electrons having positron 'shadows' is mysterious. Even for relativistic effects that become observable in molecules with high-Z nuclei, chemists are not accustomed to searching for positrons within molecules. Fortunately, methods exist where the positron portions of relativistic equations can be approximated by expansions of the electron portions of the equations. One technique, the Foldy-Wouthuysen transformation, will be briefly examined.

Foldy-Wouthuysen Transformation

For molecular systems, fully relativistic calculations are impossible since the interaction Hamiltonian between electrons is not well defined. Even under relativistic approximations molecular calculations quickly become intractable. In a relativistic calculation, each electron in the system does not have just four components but instead has 4^n components where n is the number of electrons within the system. For example, calculation of energies of the helium atom involves 16 x 16 Dirac matrices as well as 16 component spinors. Calculation of energies of the lithium atom uses 64 x 64 Dirac matrices and 64 component spinors. This problem is avoided by finding a transformation that removes the effects of the positron states so that relativistic energies can be calculated from a series expansion using only electron states. The expansion that is considered in this thesis is the Foldy-Wouthuysen transformation.[20,21]

Operators within the Dirac equation can be classified according to how they couple the components of the wavefunction and their parity. Operators that couple the electron and positron states have odd parity. Operators that couple the electron states with other electron states (or positron states with positron states) have even parity. Thus uncoupling the effects of positron states on the electron states involves finding a transformation for the odd operators in terms of even operators and higher-order odd operators. The Foldy-Wouthuysen transformation achieves this uncoupling. The method involves a unitary transformation where the generator of the transformation is a specific odd operator. The essence of the transformation involves commutation relations between even and odd operators.

Non-relativistic Hamiltonian

Before stating the molecular Hamiltonian from the result of a Foldy-Wouthuysen transformation on the Dirac Hamiltonian, the two-body interaction between charged particles must be considered. There exists no fully relativistic closed expression for the two-body interaction. However, relativistic approximations such as the Breit equation[19,21] can be made for low energy systems such as molecular systems. Moss presents a nonrelativistic expression based on the Foldy-Wouthuysen transformation of a single electron system, a relativistic expansion of the vector potential and the requirement that the interaction be symmetric with respect to the interchange of electrons. Moss states that his *ad hoc* Hamiltonian is accurate to $mc^2\alpha^5$ where α is the fine structure constant and that it agrees with the Hamiltonian rigorously derived by Itoh[22] from quantum electrodynamics. In the Hamiltonian below, nuclei are treated as Dirac particles; however, their anomalous magnetic moment is considered in an *ad hoc* fashion.

Moss[20] gives the nonrelativistic molecular Hamiltonian as

$\mathrm{H} = \sum_{i}\{mc^2$	the electron's rest mass energy,
$-e\phi_i$	the electron's interaction with external electric potential,
$+\pi_i^2/2m$	the electron's kinetic energy,
$+g\mu_B\left(\bar{s}_i \cdot \bar{B}_i\right)$	Zeeman interaction of e^- spin with magnetic field,
$-\left(g\mu_B/4mc^2\right)\bar{s}_i \cdot \left[\bar{\pi}_i \times \bar{E}_i - \bar{E}_i \times \bar{\pi}_i\right]$	interaction of electron spin with magnetic field caused by movement through external electric field,
$+\left(e\hbar^2/8m^2c^2\right)\nabla \cdot \bar{E}$	the Darwin term, an effect of the positrons,
$-\left(1/8m^3c^2\right)\pi_i^4$	relativistic correction to electronic kinetic energy,
$-\left(g\mu_B/2m^2c^2\right)\left(\bar{s}_i \cdot \bar{B}_i\right)\pi_i^2$	relativistic correction to Zeeman interaction,
$+\sum_{j \neq i}\{e^2/8\pi\varepsilon_0 r_{ij}$	Coulomb interaction between electrons,
$-\left(e^2/16\pi\varepsilon_0 m^2c^2\right)\bar{\pi}_i \cdot \left(r_{ij}^{-1}\bar{\pi}_j\right)$	orbit-orbit interaction,
$-\left(e^2/16\pi\varepsilon_0 m^2c^2\right)\left(\bar{\pi}_i \cdot \bar{r}_{ij}\right)r_{ij}^{-3}\left(\bar{\pi}_j \cdot \bar{r}_{ij}\right)$	retarded orbit-orbit interaction,
$-\left(eg\mu_B/8\pi\varepsilon_0 mc^2 r_{ij}^3\right)\bar{s}_i \cdot \left(\bar{r}_{ij} \times \bar{\pi}_i\right)$	spin-orbit interaction of an electron's spin interacting with magnetic field arising from motion relative to the electric field of a another electron,
$+\left(eg\mu_B/4\pi\varepsilon_0 mc^2 r_{ij}^3\right)\bar{s}_i \cdot \left(\bar{r}_{ij} \times \bar{\pi}_j\right)$	spin-other-orbit interaction of an electron's spin with the magnetic field created by another electron's orbital motion,

$+\left(g^2\mu_B^2/8\pi\varepsilon_0 c^2\right)$	
$\times\begin{bmatrix}\left(\bar{s}_i\cdot\bar{s}_j\right)/r_{ij}^3 \\ -3\left(\bar{s}_i\cdot\bar{r}_{ij}\right)\left(\bar{r}_{ij}\cdot\bar{s}_j\right)/r_{ij}^5\end{bmatrix}$	dipolar spin-spin interaction,
$-\left(g^2\mu_B^2/3\varepsilon_0 c^2\right)\delta\left(\bar{r}_{ij}\right)\left(\bar{s}_i\cdot\bar{s}_j\right)$	Fermi contact term of spin-spin interaction,
$-\left(e^2\hbar^2/8\varepsilon_0 m^2 c^2\right)\delta\left(\bar{r}_{ij}\right)+\cdots\}$	relativistic correction to Coulomb interaction,
$+\sum\limits_{\alpha}\{m_\alpha c^2$	rest mass energy of the nucleus,
$+Z_\alpha e\phi_\alpha$	the nucleus' interaction with external electric potential,
$+\pi_\alpha^2/2m_\alpha$	the nucleus' kinetic energy,
$-g\mu_N\left(\bar{I}_\alpha\cdot\bar{B}_\alpha\right)$	Zeeman interaction of nuclear spin with external magnetic field,
$+\sum\limits_{\beta\neq\alpha}\left[Z_\alpha Z_\beta e^2/8\pi\varepsilon_0 r_{\alpha\beta}+\cdots\right]$	nucleus-nucleus Coulomb interaction,
$-Z_\alpha e^2/4\pi\varepsilon_0 r_{i\alpha}$	electron-nucleus Coulomb interaction,
$+\left(Z_\alpha e^2/8\pi\varepsilon_0 m m_\alpha c^2\right)\bar{\pi}_i\cdot\left(r_{i\alpha}^{-1}\bar{\pi}_\alpha\right)$	electron-orbit-nuclear-orbit interaction,
$+\left(Z_\alpha e^2/8\pi\varepsilon_0 m m_\alpha c^2\right)\left(\bar{\pi}_i\cdot\bar{r}_{i\alpha}\right)r_{i\alpha}^{-3}\left(\bar{\pi}_\alpha\cdot\bar{r}_{i\alpha}\right)$	retarded electric-orbit-nuclear-orbit interaction,
$-\left(Z_\alpha e g\mu_B/8\pi\varepsilon_0 m c^2 r_{i\alpha}^3\right)\bar{s}_i\cdot\left(\bar{r}_{i\alpha}\times\bar{\pi}_i\right)$	spin-orbit interaction of an electron's spin interacting with magnetic field arising from motion relative to the electric field of nucleus,

$-\left(Z_\alpha e g \mu_B / 4\pi\varepsilon_0 m_\alpha c^2 r_{i\alpha}^3\right) \bar{s}_i \cdot \left(\bar{r}_{i\alpha} \times \bar{\pi}_\alpha\right)$ spin-other-orbit interaction of an electron's spin with the magnetic field created by a nucleus' orbital motion,

$+\left(e g_\alpha \mu_N / 4\pi\varepsilon_0 m c^2 r_{i\alpha}^3\right) \bar{I}_\alpha \cdot \left(\bar{r}_{i\alpha} \times \bar{\pi}_i\right)$ spin-other-orbit interaction of a nucleus' spin with the magnetic field created by an electron's orbital motion,

$-\left(g g_\alpha \mu_B \mu_N / 4\pi\varepsilon_0 c^2\right) \times \begin{bmatrix} \left(\bar{s}_i \cdot \bar{I}_\alpha\right)/r_{i\alpha}^3 \\ -3\left(\bar{s}_i \cdot \bar{r}_{i\alpha}\right)\left(\bar{r}_{i\alpha} \cdot \bar{I}_\alpha\right)/r_{i\alpha}^5 \end{bmatrix}$ dipolar electron-spin-nucleus-spin interaction,

$+\left(g g_\alpha \mu_B \mu_N / 3\varepsilon_0 c^2\right) \delta\left(\bar{r}_{i\alpha}\right)\left(\bar{s}_i \cdot \bar{I}_\alpha\right)$ Fermi contact term of electron-spin-nucleus spin interaction,

$-\left(Z_\alpha e^2 \hbar^2 / 8\varepsilon_0 m^2 c^2\right)\delta\left(\bar{r}_{i\alpha}\right) + \cdots \} + \cdots \}$ relativistic correction to Coulomb interaction, etc.,

$+\mathcal{H}_Q + \cdots$ nuclear quadrupole interaction, etc., (39)

where the i and j indices indicate electrons, the α index indicates nuclei, $\bar{s}_i$ is the electron spin, $\bar{I}_\alpha$ is the nuclear spin, g is the magnetogyric ratio, μ_B and μ_N are the Bohr and nuclear magnetons, respectively, and the momenta $\bar{\pi}$ are canonical momenta, $\bar{\pi} = \bar{p} - e\overline{A}$.

Higher Order Magnetic Susceptibilities

Vibrational effects can be very important in chemical shifts of light nuclei.[23] Rovibrational effects on chemical shifts have been calculated for $^1H^{19}F$,[24] ^{14}N[25] and ^{13}C.[26] These calculations are done readily using numerical differentiation techniques. However, they lack a physical interpretation in terms of the electromagnetic phenomena occurring during the course of a vibration. A higher-order magnetic susceptibility density may offer such interpretations. Intramolecular response due to mixed electric-magnetic effects such as the effect of hydrogen bonding on the chemical shift[27,28,29] may also find a physical explanation.

A physical interpretation of vibrational averaging of magnetic properties may include the effects of nuclear motion via the nuclear canonical momenta. The terms in equation (39) that involve the nuclear canonical momenta are

$$\begin{aligned}\mathcal{H}' = \sum_i \sum_\alpha + \pi_\alpha^2/2m_\alpha + \left(Z_\alpha e^2/8\pi\varepsilon_0 m m_\alpha c^2\right)\left[\bar{\pi}_i \cdot \left(r_{i\alpha}^{-1}\bar{\pi}_\alpha\right) + \left(\bar{\pi}_i \cdot \bar{r}_{i\alpha}\right) r_{i\alpha}^{-3}\left(\bar{\pi}_\alpha \cdot \bar{r}_{i\alpha}\right)\right] \\ -\left(Z_\alpha e g \mu_B/4\pi\varepsilon_0 m_\alpha c^2 r_{i\alpha}^3\right)\bar{s}_i \cdot \left(\bar{r}_{i\alpha} \times \bar{\pi}_\alpha\right).\end{aligned} \tag{40}$$

These terms describe the nuclear kinetic energy, the retarded electron-orbit-nuclear-orbit interaction and the spin-other-orbit interaction of the spin of an electron with the magnetic field created by a nucleus' orbital motion. The creation of a higher-order susceptibility density that would have the ability to describe intramolecular magnetic response to moving nuclei could involve Equation (40). This Hamiltonian could be used in a first-order perturbation theory similar to that used to create the magnetic susceptibility density found in Chapter 4 or in a second-order perturbation theory.

Relativistic effects have been incorporated into *ab initio* calculations in the chemical shift of high-Z nuclei, ^{119}Sn,[30] ^{183}W,[31] and non-zero spin isotopomers of the halides.[32] Relativistic theories of the chemical shift by Pyykkö[33], Pyper[34] and Zhang and Webb[35] have been formulated. These theories consider the relativistic effects on the core electrons of heavy atoms within molecules. The effects arise from the high velocities that are created through interaction with the large electric fields that originate from the high-Z nuclei. Effects of the nuclear momentum on the molecular magnetizability are not specifically considered.

REFERENCES

[1] P. W. Atkins, *Molecular Quantum Mechanics*, 2nd. ed. (Oxford University Press, Oxford, 1983).

[2] W. Rindler, *Introduction to Special Relativity*, 2nd. ed. (Oxford University Press, Oxford, 1991).

[3] E. F. Taylor and J. A. Wheeler, *Spacetime Physics*, 2nd ed. (W. H. Freeman and Co., New York, 1991).

[4] H. C. Ohanian, *Classical Electrodynamics* (Allyn and Bacon, Boston, 1988).

[5] J. D. Jackson, *Classical Electrodynamics*, 2nd ed. (John Wiley and Sons, New York, 1974).

[6] Refer to the Appendix in Jackson for a discussion of units.

[7] R. Becker, *Electromagnetic Fields and Interactions* (Dover Publications, New York, 1982).

[8] M. H. Nayfeh and M. K. Brussel, *Electricity and Magnetism* (John Wiley and Sons, New York, 1985).

[9] K. L. C. Hunt, J. Chem. Phys. **78,** 6149 (1983).

[10] K. L. C. Hunt, J. Chem. Phys. **80**, 393 (1984).

[11] K. L. C. Hunt, J. Chem. Phys. **90**, 4909 (1989).

[12] K. L. C. Hunt, Y. Q. Liang, R. Nimalakirthi and R. A. Harris, J. Chem. Phys. **91**, 5251 (1989).

[13] W. J. A. Maaskant and L. J. Oosterhoff, Molec. Phys. **8**, 319 (1964).

[14] A. D. McLachlan, Proc. R. Soc. London, Ser. A **271**, 387 (1963); **274**, 80 (1963).

[15] L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part 1*, 3rd ed. (Pergamon Press, Oxford, 1980).

[16] W. Greiner, *Relativistic Quantum Mechanics: Wave Equations* (Springer-Verlag, Berlin, 1990).

[17] M. E. Peskin and D. V. Schroeder, *An Introduction to Quantum Field Theory* (Addison-Wesley, Reading, MA, 1995).

[18] R. H. Landau, *Quantum Mechanics II* (John Wiley and Sons, New York, 1996).

[19] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-electron Atoms* (Academic Press, New York, 1957).

[20] R. E. Moss, *Advanced Molecular Quantum Mechanics* (Chapman and Hall, London, 1973).

[21] M. E. Rose, *Relativistic Electron Theory* (John Wiley and Sons, New York, 1961).

[22] T. Itoh, Rev. Mod. Phys. **37**, 159 (1965).

[23] D. B. Chesnut, Chem. Phys. **214**, 73 (1997).

[24] D. M. Bishop and S. M. Cybulski, J. Chem. Phys. **101**, 2180 (1994).

[25] C. J. Jameson, A. C. de Dios and A. K. Jameson, J. Chem. Phys. **95**, 1069 (1991).

[26] A. K. Jameson and C. J. Jameson, Chem. Phys. Lett. **134**, 461 (1987).

[27] M. J. Stephen, Molec. Phys. **1**, 223 (1958).

[28] T. W. Marshall and J. A. Pople, Molec. Phys. **1**, 199 (1958).

[29] J. A. Pople, Molec. Phys. **1**, 216 (1958).

[30] C. C. Ballard, M. Hada, H. Kaneko and H. Nakatsuji, Chem. Phys. Lett. **261**, 1 (1996).

[31] M. Hada, H. Kaneko and H. Nakatsuji, Chem. Phys. Lett. **261**, 7 (1996).

[32] C. C. Ballard, M. Hada, H. Kaneko and H. Nakatsuji, Chem. Phys. Lett. **254,** 170 (1996).

[33] P. Pyykkö, Chem. Phys. **74,** 1 (1983).

[34] N. C. Pyper, Chem. Phys. Lett. **96,** 204 (1983); **96,** 211 (1983).

[35] Z. C. Zhang and G. A. Webb, J. Mol. Struct.-Theochem. **104,** 439 (1983).

APPENDIX A: DERIVATIVES OF WAVEFUNCTIONS AND OPERATORS

A. Derivative of the ground state wavefunction

In deriving the derivative of the ground state wavefunction with respect to an arbitrary parameter, the orthonormality of wavefunctions that are eigenfunctions of a Hamiltonian is exploited. The proof begins by considering the following off-diagonal Hamiltonian matrix element in a basis of eigenfunctions of the Hamiltonian.

$$n \neq 0 \quad \langle n|\mathcal{H}|0\rangle = E_0\langle n|0\rangle = 0\,. \tag{A1}$$

The derivative of this matrix element is also zero.

$$\frac{\partial\langle n|\mathcal{H}|0\rangle}{\partial\lambda} = 0\,. \tag{A2}$$

The derivative of the matrix element becomes the sum of three derivatives.

$$\frac{\partial\langle n|\mathcal{H}|0\rangle}{\partial\lambda} = \frac{\partial\langle n|}{\partial\lambda}\mathcal{H}|0\rangle + \langle n|\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle + \langle n|\mathcal{H}\frac{\partial|0\rangle}{\partial\lambda}\,. \tag{A3}$$

The Hamiltonian (which is Hermitian) operates on the wavefunctions $|0\rangle$ and $\langle n|$ and yields Equation (A4).

$$\frac{\partial\langle n|\mathcal{H}|0\rangle}{\partial\lambda} = E_0\frac{\partial\langle n|}{\partial\lambda}|0\rangle + \langle n|\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle + E_n\langle n|\frac{\partial|0\rangle}{\partial\lambda}\,. \tag{A4}$$

Lemma 1:

$$\begin{aligned} &\langle n|0\rangle = 0 \quad \text{where } n \neq 0 \quad \Rightarrow \\ &\frac{\partial\langle n|0\rangle}{\partial\lambda} = \frac{\partial\langle n|}{\partial\lambda}|0\rangle + \langle n|\frac{\partial|0\rangle}{\partial\lambda} = 0 \\ &\Rightarrow \frac{\partial\langle n|}{\partial\lambda}|0\rangle = -\langle n|\frac{\partial|0\rangle}{\partial\lambda}. \end{aligned} \qquad \text{(A5)}$$

Using Lemma 1, the derivative of the matrix element becomes

$$\begin{aligned} &\frac{\partial\langle n|\mathcal{H}|0\rangle}{\partial\lambda} = (E_n - E_0)\langle n|\frac{\partial|0\rangle}{\partial\lambda} + \langle n|\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle = 0 \\ &\Rightarrow \langle n|\frac{\partial|0\rangle}{\partial\lambda} = (E_n - E_0)^{-1}\langle n|\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle. \end{aligned} \qquad \text{(A6)}$$

Multiply Equation (A6) on the left by $|n\rangle$ and sum over all the excited states $\sum\limits_{n\neq 0}$

$$\sum_{n\neq 0}|n\rangle\langle n|\frac{\partial|0\rangle}{\partial\lambda} = -\sum_{n\neq 0}|n\rangle\langle n|(E_n - E_0)^{-1}\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle. \qquad \text{(A7)}$$

Recall that the complete sum-over-states of projection operators $|m\rangle\langle m|$ is one.

$$\sum_m |m\rangle\langle m| = 1. \qquad \text{(A8)}$$

Now insert one, as a complete sum-over-states into the equation between the energy denominator and the Hamiltonian derivative.

$$\sum_{n\neq 0}|n\rangle\langle n|\frac{\partial|0\rangle}{\partial\lambda} = -\sum_{n\neq 0}\sum_{m}|n\rangle\langle n|(E_n - E_0)^{-1}|m\rangle\langle m|\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle. \qquad \text{(A9)}$$

In the summation over m, the m = 0 term vanishes. Therefore, the sums can be rewritten

$$\sum_{n\neq 0}|n\rangle\langle n|\frac{\partial|0\rangle}{\partial\lambda} = -\sum_{n\neq 0}\sum_{m\neq 0}|n\rangle\langle n|(E_n - E_0)^{-1}|m\rangle\langle m|\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle. \qquad \text{(A10)}$$

The expression is simplified by defining the reduced resolvent operator $G(\omega)$ (the prime on the summation implies neglect of the ground state) as follows:

$$G(\omega) = \sum_m{}' \sum_n{}' |n\rangle\langle n|(E_n - E_0 - \hbar\omega)^{-1}|m\rangle\langle m| = (1-|0\rangle\langle 0|)(E_n - E_0 - \hbar\omega)^{-1}(1-|0\rangle\langle 0|). \quad \text{(A11)}$$

Thus by using the zero frequency expression for the reduced resolvent, Equation (A10) becomes

$$\begin{aligned} \sum_n{}' |n\rangle\langle n|\frac{\partial|0\rangle}{\partial\lambda} &= -(1-|0\rangle\langle 0|)(E_n - E_0)^{-1}(1-|0\rangle\langle 0|)\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle \\ &= -G(0)\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle. \end{aligned} \quad \text{(A12)}$$

To find the derivative of the ground state, the left side of Equation (A12) must be manipulated. First, the sum-over-excited-states is rewritten as sum-over-states minus the ground state term.

$$\begin{aligned} \sum_n{}' |n\rangle\langle n|\frac{\partial|0\rangle}{\partial\lambda} &= \sum_n |n\rangle\langle n|\frac{\partial|0\rangle}{\partial\lambda} - |0\rangle\langle 0|\frac{\partial|0\rangle}{\partial\lambda} \\ &= \frac{\partial|0\rangle}{\partial\lambda} - |0\rangle\langle 0|\frac{\partial|0\rangle}{\partial\lambda}. \end{aligned} \quad \text{(A13)}$$

<u>Lemma 2</u>

As a lemma, calculate $\langle 0|\frac{\partial|0\rangle}{\partial\lambda}$.

$$\begin{aligned} &\langle 0|0\rangle = 1 \Rightarrow \\ &\frac{\partial\langle 0|0\rangle}{\partial\lambda} = \frac{\partial\langle 0|}{\partial\lambda}|0\rangle + \langle 0|\frac{\partial|0\rangle}{\partial\lambda} = 0 \\ &\langle 0|\frac{\partial|0\rangle}{\partial\lambda} = -\frac{\partial\langle 0|}{\partial\lambda}|0\rangle. \end{aligned} \quad \text{(A14)}$$

If the ground state is real, (not complex), then

$$\left(\langle 0|\frac{\partial|0\rangle}{\partial\lambda}\right)^{*} = \frac{\partial\langle 0|}{\partial\lambda}|0\rangle . \tag{A15}$$

Thus substituting Equation (A15) into the last line of Equation (A14) yields

$$\langle 0|\frac{\partial|0\rangle}{\partial\lambda} = -\left(\langle 0|\frac{\partial|0\rangle}{\partial\lambda}\right)^{*} . \tag{A16}$$

The only time a complex number Z = -Z* is when Z is purely imaginary; however, we are assuming that the ground state is real. Therefore Z = -Z ⇒ Z = 0.

$$\langle 0|\frac{\partial|0\rangle}{\partial\lambda} = 0 \tag{A17}$$

Using Lemma 2, Equation (A13) becomes

$$\sum_{n}{}'|n\rangle\langle n|\frac{\partial|0\rangle}{\partial\lambda} = \frac{\partial|0\rangle}{\partial\lambda} - |0\rangle\langle 0|\frac{\partial|0\rangle}{\partial\lambda} = \frac{\partial|0\rangle}{\partial\lambda} . \tag{A18}$$

Substituting Equation (A18) into Equation (A12) yields the result

$$\frac{\partial|0\rangle}{\partial\lambda} = -G(0)\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle . \tag{A19}$$

B. Derivative of the reduced resolvent

The proof starts with the definition of the reduced resolvent from Equation (A11), noting that the Hamiltonian operator $\mathcal{H}$ can be substituted for the energy E_n when the wavefunctions are eigenfunctions of the Hamiltonian operator. The symbol $\wp$ is used to represent the ground state projection operator $|0\rangle\langle 0|$.

$$\begin{aligned} G(\omega) &= \sum_m{}' \sum_n{}' |n\rangle\langle n| \left(E_n - E_0 - \hbar\omega\right)^{-1} |m\rangle\langle m| = \left(1 - |0\rangle\langle 0|\right)\left(E_n - E_0 - \hbar\omega\right)^{-1}\left(1 - |0\rangle\langle 0|\right) \\ &= \left(1 - \wp\right)\left(\mathcal{H} - E_0 - \hbar\omega\right)^{-1}\left(1 - \wp\right). \end{aligned} \tag{B1}$$

Initially the derivative with respect to arbitrary parameter λ is found to be

$$\begin{aligned} \frac{\partial G(\omega)}{\partial\lambda} &= \frac{\partial(1-\wp)}{\partial\lambda}\left(\mathcal{H} - E_0 - \hbar\omega\right)^{-1}\left(1-\wp\right) \\ &+ \left(1-\wp\right)\frac{\partial\left(\mathcal{H} - E_0 - \hbar\omega\right)^{-1}}{\partial\lambda}\left(1-\wp\right) \\ &+ \left(1-\wp\right)\left(\mathcal{H} - E_0 - \hbar\omega\right)^{-1}\frac{\partial(1-\wp)}{\partial\lambda}. \end{aligned} \tag{B2}$$

Lemma 1

$$\begin{aligned} \frac{\partial(1-\wp)}{\partial\lambda} &= -\frac{\partial\wp}{\partial\lambda} = -\frac{\partial|0\rangle\langle 0|}{\partial\lambda} \\ &= -\frac{\partial|0\rangle}{\partial\lambda}\langle 0| - |0\rangle\frac{\partial\langle 0|}{\partial\lambda} \\ &= G(0)\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle\langle 0| + |0\rangle\langle 0|\frac{\partial\mathcal{H}}{\partial\lambda}G(0) \\ &= G(0)\frac{\partial\mathcal{H}}{\partial\lambda}\wp + \wp\frac{\partial\mathcal{H}}{\partial\lambda}G(0). \end{aligned} \tag{B3}$$

Lemma 2

$$\begin{aligned} \wp(1-\wp) &= \sum_m |0\rangle\langle 0|\left(|m\rangle\langle m| - |0\rangle\langle 0|\right) = \sum_m |0\rangle\langle 0|m\rangle\langle m| - |0\rangle\langle 0|0\rangle\langle 0| \\ &= \sum_m |0\rangle\delta_{0m}\langle m| - |0\rangle\langle 0| = |0\rangle\langle 0| - |0\rangle\langle 0| \\ &= 0. \end{aligned} \tag{B4}$$

Lemma 3

$$\begin{aligned}(1-\wp)(1-\wp) &= \sum_{m}\big(|m\rangle\langle m|-|0\rangle\langle 0|\big)\sum_{n}\big(|n\rangle\langle n|-|0\rangle\langle 0|\big)\\ &= \sum_{m}\sum_{n}|m\rangle\langle m|n\rangle\langle n|-|m\rangle\langle m|0\rangle\langle 0|-|0\rangle\langle 0|n\rangle\langle n|+|0\rangle\langle 0|0\rangle\langle 0|\\ &= \sum_{m}\sum_{n}|m\rangle\delta_{mn}\langle n|-|m\rangle\delta_{m0}\langle 0|-|0\rangle\delta_{n0}\langle n|+|0\rangle\langle 0|\\ &= \sum_{m}|m\rangle\langle m|-|0\rangle\langle 0|-|0\rangle\langle 0|+|0\rangle\langle 0| = \sum_{m}|m\rangle\langle m|-|0\rangle\langle 0|\\ &= (1-\wp).\end{aligned} \tag{B5}$$

Substituting Lemma 1 into Equation (B2) yields

$$\begin{aligned}\frac{\partial G(\omega)}{\partial\lambda} &= \left[G(0)\frac{\partial\mathcal{H}}{\partial\lambda}\wp+\wp\frac{\partial\mathcal{H}}{\partial\lambda}G(0)\right](\mathcal{H}-E_0-\hbar\omega)^{-1}(1-\wp)\\ &\quad-(1-\wp)(\mathcal{H}-E_0-\hbar\omega)^{-1}\frac{\partial(\mathcal{H}-E_0)}{\partial\lambda}(\mathcal{H}-E_0-\hbar\omega)^{-1}(1-\wp)\\ &\quad+(1-\wp)(\mathcal{H}-E_0-\hbar\omega)^{-1}\left[G(0)\frac{\partial\mathcal{H}}{\partial\lambda}\wp+\wp\frac{\partial\mathcal{H}}{\partial\lambda}G(0)\right].\end{aligned} \tag{B6}$$

Distributing the quantities in Equation (B6) yields

$$\begin{aligned}\frac{\partial G(\omega)}{\partial\lambda} &= G(0)\frac{\partial\mathcal{H}}{\partial\lambda}\wp(\mathcal{H}-E_0-\hbar\omega)^{-1}(1-\wp)+\wp\frac{\partial\mathcal{H}}{\partial\lambda}G(0)(\mathcal{H}-E_0-\hbar\omega)^{-1}(1-\wp)\\ &\quad-(1-\wp)(\mathcal{H}-E_0-\hbar\omega)^{-1}\frac{\partial(\mathcal{H}-E_0)}{\partial\lambda}(\mathcal{H}-E_0-\hbar\omega)^{-1}(1-\wp)\\ &\quad+(1-\wp)(\mathcal{H}-E_0-\hbar\omega)^{-1}G(0)\frac{\partial\mathcal{H}}{\partial\lambda}\wp+(1-\wp)(\mathcal{H}-E_0-\hbar\omega)^{-1}\wp\frac{\partial\mathcal{H}}{\partial\lambda}G(0).\end{aligned} \tag{B7}$$

Lemma 2 is applied to the first and fifth terms of Equation (B7).

$$\begin{aligned}\frac{\partial G(\omega)}{\partial\lambda} &= \wp\frac{\partial\mathcal{H}}{\partial\lambda}G(0)(\mathcal{H}-E_0-\hbar\omega)^{-1}(1-\wp)\\ &\quad-(1-\wp)\frac{\partial(\mathcal{H}-E_0)}{\partial\lambda}(\mathcal{H}-E_0-\hbar\omega)^{-1}(\mathcal{H}-E_0-\hbar\omega)^{-1}(1-\wp)\\ &\quad+(1-\wp)(\mathcal{H}-E_0-\hbar\omega)^{-1}G(0)\frac{\partial\mathcal{H}}{\partial\lambda}\wp\end{aligned} \tag{B8}$$

Lemma 3 is applied once to the first and third terms and twice to the second term.

$$\begin{aligned}\frac{\partial G(\omega)}{\partial\lambda} &= \wp\frac{\partial\mathcal{H}}{\partial\lambda}G(0)(1-\wp)(\mathcal{H}-E_0-\hbar\omega)^{-1}(1-\wp)\\ &-(1-\wp)(\mathcal{H}-E_0-\hbar\omega)^{-1}(1-\wp)\frac{\partial(\mathcal{H}-E_0)}{\partial\lambda}(1-\wp)(\mathcal{H}-E_0-\hbar\omega)^{-1}(1-\wp)\\ &+(1-\wp)(\mathcal{H}-E_0-\hbar\omega)^{-1}(1-\wp)G(0)\frac{\partial\mathcal{H}}{\partial\lambda}\wp.\end{aligned} \tag{B9}$$

Substituting for the definition of the reduced resolvent yields the result.

$$\frac{\partial G(\omega)}{\partial\lambda} = \wp\frac{\partial\mathcal{H}}{\partial\lambda}G(0)G(\omega) - G(\omega)\frac{\partial(\mathcal{H}-E_0)}{\partial\lambda}G(\omega) + G(\omega)G(0)\frac{\partial\mathcal{H}}{\partial\lambda}\wp. \tag{B10}$$

C. Nuclear coordinate derivative of the Hamiltonian

The nonrelativistic, nonmagnetic Hamiltonian can be written as

$$\mathcal{H}_0 = \frac{-\hbar^2}{2me}\sum_i \nabla_i^2 - \sum_{K=1}^{N}\frac{\hbar^2}{2m^K}\nabla_K^2 - \sum_{K=1}^{N}\int d\bar{r}\frac{\rho(\bar{r})Z^K}{|\bar{r}-\bar{R}^K|} + \int d\bar{r}d\bar{r}'\frac{\rho(\bar{r})\rho(\bar{r}')}{|\bar{r}-\bar{r}'|} + \sum_{K=1}^{N}\sum_{L>K}^{N}\frac{Z^K Z^L}{|\bar{R}^K-\bar{R}^L|} \tag{C1}$$

The terms of the Hamiltonian describe respectively the electronic kinetic energy, the nuclear kinetic energy, the electrostatic potential energy between the electrons and the nuclei, the electrostatic potential energy between the electrons and the electrostatic energy between the nuclei.

Taking the derivative of Equation (C1) with respect to nuclear coordinate $\bar{R}^K$ is straightforward. Only the third and fifth terms of the Hamiltonian have nuclear coordinate dependence.

$$\frac{\partial\mathcal{H}_0}{\partial R_\alpha^K} = -\int d\bar{r}\rho(\bar{r})Z^K\nabla_\alpha^K\frac{1}{|\bar{r}-\bar{R}^K|} - \sum_{J=1}^{N}\sum_{L>J}^{N}Z^J Z^L\nabla_\alpha^J\frac{1}{|\bar{R}^J-\bar{R}^L|}. \tag{C2}$$

In the Born-Oppenheimer approximation, the second term is an additive constant. Since the derivation in the thesis concerns only electronic response, the second term will be ignored. Therefore the nuclear-coordinate derivative of the Hamiltonian to be considered is

$$\frac{\partial \mathcal{H}_0}{\partial R_\alpha^K} = -\int d\bar{r}\rho(\bar{r})\, Z^K \nabla_\alpha^K \frac{1}{\left|\bar{r}-\bar{R}^K\right|}. \tag{C3}$$

The first manipulation is a substitution using the identity $\nabla_\alpha^K \frac{1}{\left|\bar{r}-\bar{R}^K\right|} = -\nabla_\alpha \frac{1}{\left|\bar{r}-\bar{R}^K\right|}$ where ∇_α^K refers to a gradient with respect to the nuclear Cartesian coordinate and ∇_α refers to a gradient with respect to the electronic Cartesian coordinate. Thus Equation (C3) becomes

$$\frac{\partial \mathcal{H}_0}{\partial R_\alpha^K} = \int d\bar{r}\rho(\bar{r})\, Z^K \nabla_\alpha \frac{1}{\left|\bar{r}-\bar{R}^K\right|}. \tag{C4}$$

At this stage an integration by parts is performed to yield the final result. Necessary for the integration by parts is the electrostatic identity $\nabla \cdot P(\bar{r}) = -\rho(\bar{r})$. Considering the form of integration by parts to be $\int u\, dv = uv - \int v\, du$, the integration proceeds as

$$\begin{aligned}
&du = \rho(\bar{r}) = -\nabla \cdot \bar{P}(\bar{r}) \quad \Rightarrow \quad u = -\bar{P}(\bar{r}) \\
&v = \nabla \frac{1}{\left|\bar{r}-\bar{R}^K\right|} \Rightarrow \quad dv = \nabla\nabla \frac{1}{\left|\bar{r}-\bar{R}^K\right|} = T\left(\bar{r}, \bar{R}^K\right) \\
&\frac{\partial \mathcal{H}_0}{\partial R^K} = \bar{P}(\bar{r}) \nabla \frac{1}{\left|\bar{r}-\bar{R}^K\right|} \Big[_{\infty}^{\infty} - \int d\bar{r}\; \bar{P}(\bar{r})\, Z^K \nabla\nabla \frac{1}{\left|\bar{r}-\bar{R}^K\right|}.
\end{aligned} \tag{C5}$$

The boundary term in Equation (C5) is zero since the polarization of a molecule at infinite distances is zero. The definition of the dipole propagator $T(\bar{r},\bar{R}^K) = \nabla\nabla\left(\frac{1}{|\bar{r}-\bar{R}^K|}\right)$ is substituted to yield the result.

$$\frac{\partial H_0}{\partial \bar{R}^K} = -\int d\bar{r}\ \bar{P}(\bar{r}) Z^K T(\bar{r},\bar{R}^K). \tag{C6}$$

APPENDIX B: COMPLETE DERIVATION OF THE HYPERPOLARIZABILITY DERIVATIVE

Introduction

The proof of the result of Chapter 3 begins with the expression for the hyperpolarizability taken from Orr and Ward's article on nonlinear optical polarization.[1] The polarization operators are adapted to be polarization density operators so that the expression becomes a hyperpolarizability density.

$$\begin{aligned}\beta_{\alpha\beta\gamma}(\bar{r},\bar{r}',\bar{r}'';-\omega_\sigma;\omega_1,\omega_2) = \wp_{\beta\gamma}[&\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}^0_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\ &+\langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)\hat{p}^0_\beta(\bar{r}')G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{r})|0\rangle + \langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)\hat{p}^0_\alpha(\bar{r})G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle] \end{aligned} \tag{1}$$

The permutation operator $\wp_{\beta\gamma}$ denotes the sum of permutations of $\hat{p}_\beta(\bar{r}')$ and $\hat{p}_\gamma(\bar{r}')$, simultaneously with their associated frequencies, ω_1 and ω_2, respectively. The frequency ω_σ is defined as $\omega_\sigma = \omega_1 + \omega_2$. Applying the permutation operator, $\wp_{\beta\gamma}$, the hyperpolarizability density is written as

$$\beta_{\alpha\beta\gamma}(\bar{r},\bar{r}',\bar{r}'';-\omega_\sigma;\omega_1,\omega_2) = \left[\begin{array}{l} \langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}^0_\gamma(\bar{r}'')G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\ +\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}^0_\beta(\bar{r}')G(\omega_2)\hat{p}_\gamma(\bar{r}'')|0\rangle \\ +\langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)\hat{p}^0_\beta(\bar{r}')G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{r})|0\rangle \\ +\langle 0|\hat{p}_\beta(\bar{r}')G^*(-\omega_1)\hat{p}^0_\gamma(\bar{r}'')G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{r})|0\rangle \\ +\langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)\hat{p}^0_\alpha(\bar{r})G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\ +\langle 0|\hat{p}_\beta(\bar{r}')G^*(-\omega_1)\hat{p}^0_\alpha(\bar{r})G(\omega_2)\hat{p}_\gamma(\bar{r}'')|0\rangle \end{array}\right]. \tag{2}$$

---

[1] B. J. Orr and J. F. Ward, Molec. Phys. **20,** 513 (1971).

In the above expression, three types of quantities depend on the nuclear coordinate: the ground state wavefunction, $\langle 0|$, the reduced resolvent, $G(\omega_\sigma)$, and the fluctuating polarization operator, $\hat{p}^0_\gamma(\bar{r}'')$. Note that the total polarization operator, $\hat{p}_\alpha(\bar{r})$, has only electronic coordinate dependence. The derivative of the ground state wavefunction for an arbitrary parameter is calculated to be[2]

$$\frac{\partial|0\rangle}{\partial\lambda} = -G(0)\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle . \tag{3}$$

The derivative of the reduced resolvent is[2]

$$\frac{\partial G(\omega)}{\partial\lambda} = -G(\omega)\frac{\partial(\mathcal{H}-E_0)}{\partial\lambda}G(\omega) + \wp_0\frac{\partial\mathcal{H}}{\partial\lambda}G(0)\,G(\omega) + G(\omega)\,G(0)\frac{\partial\mathcal{H}}{\partial\lambda}\wp_0 . \tag{4}$$

The derivative of the fluctuating polarization operator is[2]

$$\frac{\partial\hat{P}^0_\alpha(\bar{r})}{\partial\lambda} = \langle 0|\frac{\partial\mathcal{H}}{\partial\lambda}G(0)\hat{P}_\alpha(\bar{r})|0\rangle + \langle 0|\hat{P}_\alpha(\bar{r})G(0)\frac{\partial\mathcal{H}}{\partial\lambda}|0\rangle . \tag{5}$$

When the arbitrary parameter is specified as the nuclear Cartesian coordinate, i. e. $\lambda = R^K_\delta$, the derivative of the Hamiltonian becomes[2]

$$\frac{\partial\mathcal{H}}{\partial R^K_\delta} = -\int d\bar{\mathbf{r}}'''\, Z^K P_\varepsilon(\bar{\mathbf{r}}''')T_{\varepsilon\delta}(\bar{\mathbf{r}}''',\bar{\mathbf{R}}^K) . \tag{6}$$

Taking the derivative with respect to nuclear coordinate R^K_δ of all six terms of Equation (2) and substituting Equations (3) through (6) yields for the hyperpolarizability derivative, the sixty term expression of Equation (7).

---

[2] Appendix A

$$
\frac{\partial}{\partial R_{\delta}^{K}}\left[\begin{array}{l}
\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{P}_{\gamma}^{0}(\bar{\mathbf{r}}'')G(\omega_{1})\hat{P}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
+\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{P}_{\beta}^{0}(\bar{\mathbf{r}}')G(\omega_{2})\hat{P}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
+\langle 0|\hat{P}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})\hat{P}_{\beta}^{0}(\bar{\mathbf{r}}')G^{*}(-\omega_{\sigma})\hat{P}_{\alpha}(\bar{\mathbf{r}})|0\rangle \\
+\langle 0|\hat{P}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})\hat{P}_{\gamma}^{0}(\bar{\mathbf{r}}'')G^{*}(-\omega_{\sigma})\hat{P}_{\alpha}(\bar{\mathbf{r}})|0\rangle \\
+\langle 0|\hat{P}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})\hat{P}_{\alpha}^{0}(\bar{\mathbf{r}})G(\omega_{1})\hat{P}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
+\langle 0|\hat{P}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})\hat{P}_{\alpha}^{0}(\bar{\mathbf{r}})G(\omega_{2})\hat{P}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle
\end{array}\right]
$$

$$
\begin{aligned}
&\qquad = \int d\bar{\mathbf{r}}'''\, Z^{K}\mathbf{T}_{\varepsilon\delta}\left(\bar{\mathbf{r}}''',\bar{\mathbf{R}}^{K}\right) \\
&\times\{\langle 0|\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{P}_{\gamma}^{0}(\bar{\mathbf{r}}'')G(\omega_{1})\hat{P}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&+\langle 0|\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{P}_{\beta}^{0}(\bar{\mathbf{r}}')G(\omega_{2})\hat{P}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&+\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{P}_{\varepsilon}^{0}(\bar{\mathbf{r}}''')G(\omega_{\sigma})\hat{P}_{\gamma}^{0}(\bar{\mathbf{r}}'')G(\omega_{1})\hat{P}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&+\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{P}_{\varepsilon}^{0}(\bar{\mathbf{r}}''')G(\omega_{\sigma})\hat{P}_{\beta}^{0}(\bar{\mathbf{r}}')G(\omega_{2})\hat{P}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})|0\rangle G(\omega_{\sigma})\hat{P}_{\gamma}^{0}(\bar{\mathbf{r}}'')G(\omega_{1})\hat{P}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})|0\rangle G(\omega_{\sigma})\hat{P}_{\beta}^{0}(\bar{\mathbf{r}}')G(\omega_{2})\hat{P}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})G(0)\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{P}_{\gamma}^{0}(\bar{\mathbf{r}}'')G(\omega_{1})\hat{P}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})G(0)\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{P}_{\beta}^{0}(\bar{\mathbf{r}}')G(\omega_{2})\hat{P}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\hat{P}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})G(\omega_{1})\hat{P}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\hat{P}_{\beta}(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})G(\omega_{2})\hat{P}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{P}_{\gamma}(\bar{\mathbf{r}}'')G(0)\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})G(\omega_{1})\hat{P}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{P}_{\beta}(\bar{\mathbf{r}}')G(0)\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})G(\omega_{2})\hat{P}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&+\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{P}_{\gamma}^{0}(\bar{\mathbf{r}}'')G(\omega_{1})\hat{P}_{\varepsilon}^{0}(\bar{\mathbf{r}}''')G(\omega_{1})\hat{P}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&+\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{P}_{\beta}^{0}(\bar{\mathbf{r}}')G(\omega_{2})\hat{P}_{\varepsilon}^{0}(\bar{\mathbf{r}}''')G(\omega_{2})\hat{P}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{P}_{\gamma}^{0}(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)G(\omega_{1})\hat{P}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{P}_{\beta}^{0}(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)G(\omega_{2})\hat{P}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{P}_{\gamma}^{0}(\bar{\mathbf{r}}'')G(\omega_{1})\langle 0|\hat{P}_{\beta}(\bar{\mathbf{r}}')|0\rangle G(0)\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle \\
&-\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{P}_{\beta}^{0}(\bar{\mathbf{r}}')G(\omega_{2})\langle 0|\hat{P}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle G(0)\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle \\
&+\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{P}_{\gamma}^{0}(\bar{\mathbf{r}}'')G(\omega_{1})\hat{P}_{\beta}(\bar{\mathbf{r}}')G(0)\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle \\
&+\langle 0|\hat{P}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{P}_{\beta}^{0}(\bar{\mathbf{r}}')G(\omega_{2})\hat{P}_{\gamma}(\bar{\mathbf{r}}'')G(0)\hat{P}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle
\end{aligned}
$$

$$
\begin{aligned}
&+\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\,\hat{p}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_2)\hat{p}^{0}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&+\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\,\hat{p}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_1)\hat{p}^{0}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&+\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_2)\hat{p}^{0}_\varepsilon(\bar{\mathbf{r}}''')G^{*}(-\omega_2)\hat{p}^{0}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&+\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_1)\hat{p}^{0}_\varepsilon(\bar{\mathbf{r}}''')G^{*}(-\omega_1)\hat{p}^{0}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&-\langle 0|\hat{p}^{0}_\varepsilon(\bar{\mathbf{r}}''')G(0)\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle G^{*}(-\omega_2)\hat{p}^{0}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&-\langle 0|\hat{p}^{0}_\varepsilon(\bar{\mathbf{r}}''')G(0)\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle G^{*}(-\omega_1)\hat{p}^{0}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&-\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_2)G(0)\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}^{0}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&-\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_1)G(0)\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}^{0}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&-\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\,\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_2)G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&-\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\,\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_1)G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&-\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G(0)\,\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_2)G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&-\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G(0)\,\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_1)G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&+\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_2)\hat{p}^{0}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_\sigma)\hat{p}^{0}_\varepsilon(\bar{\mathbf{r}}''')G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&+\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_1)\hat{p}^{0}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_\sigma)\hat{p}^{0}_\varepsilon(\bar{\mathbf{r}}''')G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&-\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_2)\hat{p}^{0}_\beta(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\,G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&-\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_1)\hat{p}^{0}_\gamma(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\,G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\\
&-\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_2)\hat{p}^{0}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_\sigma)\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle G(0)\,\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\\
&-\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_1)\hat{p}^{0}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_\sigma)\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle G(0)\,\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\\
&+\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_2)\hat{p}^{0}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})G(0)\,\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\\
&+\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^{*}(-\omega_1)\hat{p}^{0}_\gamma(\bar{\mathbf{r}}'')G^{*}(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})G(0)\,\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle
\end{aligned}
\tag{7}
$$

$$
\begin{aligned}
&+\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\,\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_2)\,\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_1)\,\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&+\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\,\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_1)\,\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_2)\,\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&+\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_2)\,\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G^{*}(-\omega_2)\,\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_1)\,\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&+\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_1)\,\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G^{*}(-\omega_1)\,\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_2)\,\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle G^{*}(-\omega_2)\,\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_1)\,\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle G^{*}(-\omega_1)\,\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_2)\,\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_2)G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_1)\,\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_1)G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_2)\,\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\,\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_2)G(\omega_1)\,\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\,\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_1)G(\omega_2)\,\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_2)G(\omega_1)\,\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_1)G(\omega_2)\,\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&+\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_2)\,\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_1)\,\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G(\omega_1)\,\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&+\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_1)\,\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_2)\,\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G(\omega_2)\,\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_2)\,\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)G(\omega_1)\,\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_1)\,\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)G(\omega_2)\,\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_2)\,\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_1)\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle \\
&-\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_1)\,\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_2)\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle \\
&+\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_2)\,\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_1)\,\hat{p}_{\beta}(\bar{\mathbf{r}}')G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle \\
&+\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_1)\,\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_2)\,\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\}.
\end{aligned}
$$

Lemma: Proof of fluctuating polarization operator identity

Terms 7, 8, 15, 16, 27, 28, 35, 36, 47, 48, 55 and 56 have matrix elements of the form $\langle 0|\hat{p}_{\alpha}(\bar{r})G(\omega_{\sigma})G(0)\hat{p}_{\varepsilon}(\bar{r}''')|0\rangle\langle 0|\hat{P}^{0}_{\gamma}(\bar{r}'')G(\omega_{1})\hat{p}_{\beta}(\bar{r}')|0\rangle$. The fluctuating polarization operator is changed to a total polarization operator by proving the identity

$$\begin{aligned}&\langle 0|\hat{p}_{\alpha}(\bar{r})G(\omega_{\sigma})G(0)\hat{p}_{\varepsilon}(\bar{r}''')|0\rangle\langle 0|\hat{P}^{0}_{\gamma}(\bar{r}'')G(\omega_{1})\hat{p}_{\beta}(\bar{r}')|0\rangle\\&\quad=\langle 0|\hat{p}_{\alpha}(\bar{r})G(\omega_{\sigma})G(0)\hat{p}_{\varepsilon}(\bar{r}''')|0\rangle\langle 0|\hat{p}_{\gamma}(\bar{r}'')G(\omega_{1})\hat{p}_{\beta}(\bar{r}')|0\rangle.\end{aligned}\tag{8}$$

The proof of the identity (8) begins by substituting the definition of the fluctuating polarization operator, Equation (9) into the left side of identity (8) to yield Equation (10).

$$\hat{p}^{0}_{\gamma}(\bar{r}'')=\hat{p}_{\gamma}(\bar{r}'')-\langle 0|\hat{p}_{\gamma}(\bar{r}'')|0\rangle.\tag{9}$$

$$\begin{aligned}&\langle 0|\hat{p}_{\alpha}(\bar{r})G(\omega_{\sigma})G(0)\hat{p}_{\varepsilon}(\bar{r}''')|0\rangle\langle 0|\hat{P}^{0}_{\gamma}(\bar{r}'')G(\omega_{1})\hat{p}_{\beta}(\bar{r}')|0\rangle\\&\quad=\langle 0|\hat{p}_{\alpha}(\bar{r})G(\omega_{\sigma})G(0)\hat{p}_{\varepsilon}(\bar{r}''')|0\rangle\langle 0|\hat{p}_{\gamma}(\bar{r}'')-\langle 0|\hat{p}_{\gamma}(\bar{r}'')|0\rangle G(\omega_{1})\hat{p}_{\beta}(\bar{r}')|0\rangle\\&\quad=\langle 0|\hat{p}_{\alpha}(\bar{r})G(\omega_{\sigma})G(0)\hat{p}_{\varepsilon}(\bar{r}''')|0\rangle\langle 0|\hat{p}_{\gamma}(\bar{r}'')G(\omega_{1})\hat{p}_{\beta}(\bar{r}')|0\rangle\\&\quad-\langle 0|\hat{p}_{\alpha}(\bar{r})G(\omega_{\sigma})G(0)\hat{p}_{\varepsilon}(\bar{r}''')|0\rangle\langle 0|\langle 0|\hat{p}_{\gamma}(\bar{r}'')|0\rangle G(\omega_{1})\hat{p}_{\beta}(\bar{r}')|0\rangle.\end{aligned}\tag{10}$$

Substituting the sum-over-states definition of the reduced resolvent, Equation (B11), yields Equation (B12) after little manipulation and recalling that $\langle 0|n\rangle=\delta_{0n}$.

$$G(\omega_{1})=\sum_{n}\frac{|n\rangle\langle n|-|0\rangle\langle 0|}{\mathcal{H}-E_{0}-\omega_{1}}=\sum_{n}\frac{|n\rangle\langle n|-|0\rangle\langle 0|}{\Omega_{ng}-\omega_{1}}.\tag{11}$$

$$
\begin{aligned}
&\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\,\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{P}^0_\gamma(\bar{r}'')G(\omega_1)\,\hat{p}_\beta(\bar{r}')|0\rangle \\
&\quad= \langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\,\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(\omega_1)\,\hat{p}_\beta(\bar{r}')|0\rangle \\
&\qquad - \langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\,\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\langle 0|\hat{p}_\gamma(\bar{r}'')|0\rangle \sum_n \frac{|n\rangle\langle n| - |0\rangle\langle 0|}{\Omega_{ng}-\omega_1}\,\hat{p}_\beta(\bar{r}')|0\rangle \\
&\quad= \langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\,\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(\omega_1)\,\hat{p}_\beta(\bar{r}')|0\rangle \\
&\qquad - \langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\,\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')|0\rangle \sum_n \frac{\langle 0|n\rangle\langle n|\hat{p}_\beta(\bar{r}')|0\rangle - \langle 0|0\rangle\langle 0|\hat{p}_\beta(\bar{r}')|0\rangle}{\Omega_{ng}-\omega_1} \\
&\quad= \langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\,\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(\omega_1)\,\hat{p}_\beta(\bar{r}')|0\rangle \\
&\qquad - \langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\,\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')|0\rangle \sum_n \frac{\delta_{n0}\langle n|\hat{p}_\beta(\bar{r}')|0\rangle - 1\langle 0|\hat{p}_\beta(\bar{r}')|0\rangle}{\Omega_{ng}-\omega_1} \\
&\quad= \langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\,\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(\omega_1)\,\hat{p}_\beta(\bar{r}')|0\rangle \\
&\qquad - \langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\,\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')|0\rangle \frac{\langle 0|\hat{p}_\beta(\bar{r}')|0\rangle - \langle 0|\hat{p}_\beta(\bar{r}')|0\rangle}{\Omega_{ng}-\omega_1} \\
&\quad= \langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\,\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(\omega_1)\,\hat{p}_\beta(\bar{r}')|0\rangle \\
&\qquad - \langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\,\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')|0\rangle \times 0 \qquad\qquad (12) \\
&\quad= \langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(0)\,\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G(\omega_1)\,\hat{p}_\beta(\bar{r}')|0\rangle .
\end{aligned}
$$

Thus, the identity is proven.

Continuation of proof

The first and fifth terms in Equation (7) are simplified by applying the definition of the fluctuating polarization operator.

$$
\begin{aligned}
&\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\,\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\,\hat{p}^0_\gamma(\bar{r}'')G(\omega_1)\,\hat{p}_\beta(\bar{r}')|0\rangle \\
&\quad - \langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\langle 0|\hat{p}_\alpha(\bar{r})|0\rangle G(\omega_\sigma)\,\hat{p}^0_\gamma(\bar{r}'')G(\omega_1)\,\hat{p}_\beta(\bar{r}')|0\rangle \qquad (13) \\
&\quad = \langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\,\hat{p}^0_\alpha(\bar{r})G(\omega_\sigma)\,\hat{p}^0_\gamma(\bar{r}'')G(\omega_1)\,\hat{p}_\beta(\bar{r}')|0\rangle
\end{aligned}
$$

Similarly, the following pairs of terms in Equation (7) can be simplified: (2, 6); (19, 17); (20, 18); (21, 25); (22, 26); (39, 37); (40, 38); (41, 45); (42, 46); (59, 57) and (60, 58) to yield Equation (14).

$$
\begin{aligned}
&\frac{\partial\beta_{\alpha\beta\gamma}\left(\bar{r},\bar{r}',\bar{r}'';-\omega_\sigma;\omega_1,\omega_2\right)}{\partial R_\delta^K} = \int d\bar{\mathbf{r}}'''\, Z^K \mathbf{T}_{\varepsilon\delta}\left(\bar{\mathbf{r}}''',\bar{\mathbf{R}}^K\right) \\
&\times\{\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\,\hat{p}_\alpha^0(\bar{\mathbf{r}})G(\omega_\sigma)\hat{p}_\gamma^0(\bar{\mathbf{r}}'')G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle \\
&+\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\,\hat{p}_\alpha^0(\bar{\mathbf{r}})G(\omega_\sigma)\hat{p}_\beta^0(\bar{\mathbf{r}}')G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle \\
&+\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)\hat{p}_\varepsilon^0(\bar{\mathbf{r}}''')G(\omega_\sigma)\hat{p}_\gamma^0(\bar{\mathbf{r}}'')G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle \\
&+\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)\hat{p}_\varepsilon^0(\bar{\mathbf{r}}''')G(\omega_\sigma)\hat{p}_\beta^0(\bar{\mathbf{r}}')G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)G(0)\,\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)G(0)\,\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\,\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\,\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G(0)\,\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G(0)\,\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle \\
&+\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)\hat{p}_\gamma^0(\bar{\mathbf{r}}'')G(\omega_1)\hat{p}_\varepsilon^0(\bar{\mathbf{r}}''')G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle \\
&+\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)\hat{p}_\beta^0(\bar{\mathbf{r}}')G(\omega_2)\hat{p}_\varepsilon^0(\bar{\mathbf{r}}''')G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle \\
&+\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)\hat{p}_\gamma^0(\bar{\mathbf{r}}'')G(\omega_1)\hat{p}_\beta^0(\bar{\mathbf{r}}')G(0)\,\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle \\
&+\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)\hat{p}_\beta^0(\bar{\mathbf{r}}')G(\omega_2)\hat{p}_\gamma^0(\bar{\mathbf{r}}'')G(0)\,\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle \\
&+\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\,\hat{p}_\gamma^0(\bar{\mathbf{r}}'')G^*(-\omega_2)\hat{p}_\beta^0(\bar{\mathbf{r}}')G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle \\
&+\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\,\hat{p}_\beta^0(\bar{\mathbf{r}}')G^*(-\omega_1)\hat{p}_\gamma^0(\bar{\mathbf{r}}'')G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle \\
&+\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)\hat{p}_\varepsilon^0(\bar{\mathbf{r}}''')G^*(-\omega_2)\hat{p}_\beta^0(\bar{\mathbf{r}}')G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle \\
&+\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)\hat{p}_\varepsilon^0(\bar{\mathbf{r}}''')G^*(-\omega_1)\hat{p}_\gamma^0(\bar{\mathbf{r}}'')G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle \\
&-\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)G(0)\,\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle \\
&-\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)G(0)\,\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle \\
&-\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\,\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle \\
&-\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\,\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle
\end{aligned}
$$

$$
\begin{aligned}
&-\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})G^{*}(-\omega_{\sigma})\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle\\
&-\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})G^{*}(-\omega_{\sigma})\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle\\
&+\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})\hat{p}^{0}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{\sigma})\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G^{*}(-\omega_{\sigma})\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle\\
&+\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})\hat{p}^{0}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{\sigma})\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G^{*}(-\omega_{\sigma})\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle\\
&-\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\,G^{*}(-\omega_{\sigma})\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle\\
&-\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\,G^{*}(-\omega_{\sigma})\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle\\
&+\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})\hat{p}^{0}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{\sigma})\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\\
&+\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})\hat{p}^{0}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{\sigma})\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\\
&+\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\,\hat{p}^{0}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle\\
&+\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\,\hat{p}^{0}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle\\
&+\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G^{*}(-\omega_{2})\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle\\
&+\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G^{*}(-\omega_{1})\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle\\
&-\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle\\
&-\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle\\
&-\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\,\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle\\
&-\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\,\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle\\
&-\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle\\
&-\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle\\
&+\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_{1})\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle\\
&+\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_{2})\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle\\
&-\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle\\
&-\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle\\
&+\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_{1})\hat{p}^{0}_{\beta}(\bar{\mathbf{r}}')G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\\
&+\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_{2})\hat{p}^{0}_{\gamma}(\bar{\mathbf{r}}'')G(0)\,\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\}
\end{aligned}
\tag{14}
$$

The expression within the {} brackets in Equation (14) is compared to the expression for the second hyperpolarizability density adapted from Orr and Ward.[1]

$$
\begin{aligned}
&\gamma_{\alpha\beta\gamma\varepsilon}\left(\bar{r},\bar{r}',\bar{r}'',\bar{r}''';-\omega_{\sigma};\omega_{1},\omega_{2},0\right)= \\
&\quad\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G(\omega_{\sigma})\hat{p}^{0}_{\gamma}(\bar{\mathbf{r}}'')G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&+\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{p}^{0}_{\beta}(\bar{\mathbf{r}}')G(\omega_{2})\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&+\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{p}^{0}_{\gamma}(\bar{\mathbf{r}}'')G(\omega_{1})\hat{p}^{0}_{\beta}(\bar{\mathbf{r}}')G(0)\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle \\
&+\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G(\omega_{\sigma})\hat{p}^{0}_{\beta}(\bar{\mathbf{r}}')G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&+\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{p}^{0}_{\gamma}(\bar{\mathbf{r}}'')G(\omega_{1})\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&+\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{p}^{0}_{\beta}(\bar{\mathbf{r}}')G(\omega_{2})\hat{p}^{0}_{\gamma}(\bar{\mathbf{r}}'')G(0)\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle \\
&+\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{p}^{0}_{\gamma}(\bar{\mathbf{r}}'')G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&+\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})\hat{p}^{0}_{\beta}(\bar{\mathbf{r}}')G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})G(0)\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle \\
&-\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G(0)\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})G(0)\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle \\
&-\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G(0)\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{\sigma})G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}_{\alpha}(\bar{\mathbf{r}})G(\omega_{2})\hat{p}_{\gamma}(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)G(\omega_{1})\hat{p}_{\beta}(\bar{\mathbf{r}}')|0\rangle \\
&+\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})\hat{p}^{0}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{\sigma})\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(0)\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle \\
&+\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})\hat{p}^{0}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{\sigma})\hat{p}^{0}_{\alpha}(\bar{\mathbf{r}})G(0)\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')|0\rangle \\
&+\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})\hat{p}^{0}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{\sigma})\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G^{*}(-\omega_{\sigma})\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle \\
&+\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G^{*}(-\omega_{2})\hat{p}^{0}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{\sigma})\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle \\
&+\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\hat{p}^{0}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})\hat{p}^{0}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{\sigma})\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle \\
&+\langle 0|\hat{p}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})\hat{p}^{0}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{\sigma})\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G^{*}(-\omega_{\sigma})\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle \\
&+\langle 0|\hat{p}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{1})\hat{p}^{0}_{\varepsilon}(\bar{\mathbf{r}}''')G^{*}(-\omega_{1})\hat{p}^{0}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{\sigma})\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle \\
&+\langle 0|\hat{p}_{\varepsilon}(\bar{\mathbf{r}}''')G(0)\hat{p}^{0}_{\gamma}(\bar{\mathbf{r}}'')G^{*}(-\omega_{2})\hat{p}^{0}_{\beta}(\bar{\mathbf{r}}')G^{*}(-\omega_{\sigma})\hat{p}_{\alpha}(\bar{\mathbf{r}})|0\rangle
\end{aligned}
$$

$$\begin{gathered}
-\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle \\
-\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle \\
-\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle \\
-\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle \\
-\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle \\
-\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle \\
-\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)G(0)\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle \\
-\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)G(0)\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle \\
+\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)\hat{p}^0_\alpha(\bar{\mathbf{r}})G(\omega_2)\hat{p}^0_\varepsilon(\bar{\mathbf{r}}''')G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle \\
+\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)\hat{p}^0_\alpha(\bar{\mathbf{r}})G(\omega_1)\hat{p}^0_\beta(\bar{\mathbf{r}}')G(0)\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle \\
+\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)\hat{p}^0_\alpha(\bar{\mathbf{r}})G(\omega_1)\hat{p}^0_\varepsilon(\bar{\mathbf{r}}''')G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle \\
+\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)\hat{p}^0_\alpha(\bar{\mathbf{r}})G(\omega_2)\hat{p}^0_\gamma(\bar{\mathbf{r}}'')G(0)\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle \\
+\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)\hat{p}^0_\varepsilon(\bar{\mathbf{r}}''')G^*(-\omega_2)\hat{p}^0_\alpha(\bar{\mathbf{r}})G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle \\
+\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\hat{p}^0_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)\hat{p}^0_\alpha(\bar{\mathbf{r}})G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle \\
+\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)\hat{p}^0_\varepsilon(\bar{\mathbf{r}}''')G^*(-\omega_1)\hat{p}^0_\alpha(\bar{\mathbf{r}})G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle \\
+\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\hat{p}^0_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)\hat{p}^0_\alpha(\bar{\mathbf{r}})G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle \\
-\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(0)\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle \\
-\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(0)\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle \\
-\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)G(0)\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle \\
-\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)G(0)\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle \\
-\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle \\
-\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle \\
-\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle \\
-\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle
\end{gathered} \tag{15}$$

Proof of a sum-over-states identity

The expression in the brackets {} of Equation (14) is equal to Equation (15) if term by term they are equal. Forty of the terms are equal to each other; however, eight terms are not. The following convention is adopted for an ordered pair: (nth term of (14), mth term of (15)). In this convention the following terms are similar but not equal: (7, 10); (8, 13); (13, 16); (14, 15); (21, 31); (22, 32); (25, 29) and (26, 26). The equality is found once the terms are grouped into two distinct sums and the sum-over-states definition is substituted for the reduced resolvent. The substitution for the reduced resolvent is needed since the equality is proven by manipulating the energy denominators. The algebraic manipulations below will show that the sum of terms 7, 14, 21 and 26 of Equation (14) (labeled S_1) equals the sum of terms 10, 15, 26 and 31 of Equation (15) (labeled S_2). Similarly, the sum of terms 8, 13, 22 and 25 of Equation (14) (labeled S'_1) equals the sum of terms 13, 16, 29, 32 of Equation (15) (labeled S'_2).

$$\begin{aligned}
S_1 = &-\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\hat{p}_\gamma(\bar{r}'')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
&-\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)G(\omega_2)\hat{p}_\gamma(\bar{r}'')|0\rangle \\
&-\langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{r}')G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{r})|0\rangle \\
&-\langle 0|\hat{p}_\gamma(\bar{r}'')G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{r}')G^*(-\omega_1)G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{r})|0\rangle .
\end{aligned} \tag{16}$$

$$\begin{aligned}
S_1 = &-\sum_m{}'\sum_n{}' \frac{\langle 0|\hat{p}_\varepsilon(\bar{r}''')|m\rangle\langle m|\hat{p}_\gamma(\bar{r}'')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})|n\rangle\langle n|\hat{p}_\beta(\bar{r}')|0\rangle}{\Omega_{mg}(\Omega_{ng}-\omega_\sigma)(\Omega_{ng}-\omega_1)} \\
&-\sum_m{}'\sum_n{}' \frac{\langle 0|\hat{p}_\alpha(\bar{r})|m\rangle\langle m|\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')|n\rangle\langle n|\hat{p}_\gamma(\bar{r}'')|0\rangle}{(\Omega_{mg}-\omega_\sigma)\Omega_{ng}(\Omega_{ng}-\omega_2)} \\
&-\sum_m{}'\sum_n{}' \frac{\langle 0|\hat{p}_\gamma(\bar{r}'')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{r}')|n\rangle\langle n|\hat{p}_\alpha(\bar{r})|0\rangle}{(\Omega^*_{mg}+\omega_2)\Omega_{mg}(\Omega^*_{ng}+\omega_\sigma)} \\
&-\frac{\sum_m{}'\sum_n{}'\langle 0|\hat{p}_\gamma(\bar{r}'')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{r}')|n\rangle\langle n|\hat{p}_\alpha(\bar{r})|0\rangle}{\Omega_{mg}(\Omega^*_{ng}+\omega_1)(\Omega^*_{ng}+\omega_\sigma)} .
\end{aligned} \tag{17}$$

Recalling that the summation labels m and n are arbitrary, we exchange m and n in the second summation and sum like terms together over a common denominator.

$$
\begin{aligned}
S_1 = &-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|m\rangle\langle m|\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})|n\rangle\langle n|\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle}{\Omega_{mg}(\Omega_{ng}-\omega_\sigma)(\Omega_{ng}-\omega_1)} \\
&-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})|n\rangle\langle n|\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|m\rangle\langle m|\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle}{(\Omega_{ng}-\omega_\sigma)\Omega_{mg}(\Omega_{mg}-\omega_2)} \\
&-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')|n\rangle\langle n|\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle}{(\Omega^*_{mg}+\omega_2)\Omega_{mg}(\Omega^*_{ng}+\omega_\sigma)} \\
&-\frac{\sum_m{}'\sum_n{}'\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')|n\rangle\langle n|\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle}{\Omega_{mg}(\Omega^*_{ng}+\omega_1)(\Omega^*_{ng}+\omega_\sigma)}.
\end{aligned}
\tag{18}
$$

$$
\begin{aligned}
S_1 = &-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|m\rangle\langle m|\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})|n\rangle\langle n|\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle\left[(\Omega_{mg}-\omega_2)+(\Omega_{ng}-\omega_1)\right]}{\Omega_{mg}(\Omega_{ng}-\omega_\sigma)(\Omega_{ng}-\omega_1)(\Omega_{mg}-\omega_2)} \\
&-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')|n\rangle\langle n|\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\left[(\Omega^*_{ng}+\omega_1)+(\Omega^*_{mg}+\omega_2)\right]}{(\Omega^*_{mg}+\omega_2)\Omega_{mg}(\Omega^*_{ng}+\omega_1)(\Omega^*_{ng}+\omega_\sigma)} \\
= &-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|m\rangle\langle m|\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})|n\rangle\langle n|\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle(\Omega_{mg}+\Omega_{ng}-\omega_1-\omega_2)}{\Omega_{mg}(\Omega_{ng}-\omega_\sigma)(\Omega_{ng}-\omega_1)(\Omega_{mg}-\omega_2)} \\
&-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')|n\rangle\langle n|\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle(\Omega^*_{mg}+\Omega^*_{ng}+\omega_1+\omega_2)}{(\Omega^*_{mg}+\omega_2)\Omega_{mg}(\Omega^*_{ng}+\omega_1)(\Omega^*_{ng}+\omega_\sigma)}.
\end{aligned}
\tag{19}
$$

The same manipulations are performed on the sum, S_2

$$
\begin{aligned}
S_2 = &-\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_\sigma)G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle \\
&-\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')G(0)G(\omega_2)\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle \\
&-\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle \\
&-\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')G^*(-\omega_1)\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')G^*(-\omega_2)G(0)\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle.
\end{aligned}
\tag{20}
$$

$$
\begin{aligned}
S_2 = &-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|m\rangle\langle m|\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})|n\rangle\langle n|\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle}{(\Omega_{mg}-\omega_2)(\Omega_{ng}-\omega_\sigma)(\Omega_{ng}-\omega_1)} \\
&-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})|m\rangle\langle m|\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|n\rangle\langle n|\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle}{(\Omega_{mg}-\omega_1)\Omega_{ng}(\Omega_{ng}-\omega_2)} \\
&-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')|n\rangle\langle n|\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle}{(\Omega^*_{mg}+\omega_2)(\Omega^*_{ng}+\omega_1)(\Omega^*_{ng}+\omega_\sigma)} \\
&-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')|m\rangle\langle m|\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')|n\rangle\langle n|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle}{(\Omega^*_{mg}+\omega_1)(\Omega^*_{ng}+\omega_2)\Omega_{ng}}.
\end{aligned}
\tag{21}
$$

Next the summation labels, m and n are exchanged in the second and fourth summations.

$$
\begin{aligned}
S_2 = &-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\varepsilon(\bar{r}''')|m\rangle\langle m|\hat{p}_\gamma(\bar{r}'')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})|n\rangle\langle n|\hat{p}_\beta(\bar{r}')|0\rangle}{(\Omega_{mg}-\omega_2)(\Omega_{ng}-\omega_\sigma)(\Omega_{ng}-\omega_1)} \\
&-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\alpha(\bar{r})|n\rangle\langle n|\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')|m\rangle\langle m|\hat{p}_\gamma(\bar{r}'')|0\rangle}{(\Omega_{ng}-\omega_1)\Omega_{mg}(\Omega_{mg}-\omega_2)} \\
&-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\gamma(\bar{r}'')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{r}')|n\rangle\langle n|\hat{p}_\alpha(\bar{r})|0\rangle}{(\Omega^{*}_{mg}+\omega_2)(\Omega^{*}_{ng}+\omega_1)(\Omega^{*}_{ng}+\omega_\sigma)} \\
&-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\beta(\bar{r}')|n\rangle\langle n|\hat{p}_\alpha(\bar{r})|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{r}''')|0\rangle}{(\Omega^{*}_{ng}+\omega_1)(\Omega^{*}_{mg}+\omega_2)\Omega_{mg}}.
\end{aligned}
\tag{22}
$$

$$
\begin{aligned}
S_2 = &-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\varepsilon(\bar{r}''')|m\rangle\langle m|\hat{p}_\gamma(\bar{r}'')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})|n\rangle\langle n|\hat{p}_\beta(\bar{r}')|0\rangle\left[(\Omega_{mg})+(\Omega_{ng}-\omega_\sigma)\right]}{(\Omega_{mg}-\omega_2)(\Omega_{ng}-\omega_\sigma)(\Omega_{ng}-\omega_1)\Omega_{mg}} \\
&-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\gamma(\bar{r}'')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{r}')|n\rangle\langle n|\hat{p}_\alpha(\bar{r})|0\rangle\left[(\Omega_{mg})+(\Omega^{*}_{ng}+\omega_\sigma)\right]}{(\Omega^{*}_{mg}+\omega_2)(\Omega^{*}_{ng}+\omega_1)(\Omega^{*}_{ng}+\omega_\sigma)\Omega_{mg}} \\
= &-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\varepsilon(\bar{r}''')|m\rangle\langle m|\hat{p}_\gamma(\bar{r}'')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})|n\rangle\langle n|\hat{p}_\beta(\bar{r}')|0\rangle(\Omega_{mg}+\Omega_{ng}-\omega_1-\omega_2)}{(\Omega_{mg}-\omega_2)(\Omega_{ng}-\omega_\sigma)(\Omega_{ng}-\omega_1)\Omega_{mg}} \\
&-\sum_m{}'\sum_n{}'\frac{\langle 0|\hat{p}_\gamma(\bar{r}'')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\beta(\bar{r}')|n\rangle\langle n|\hat{p}_\alpha(\bar{r})|0\rangle(\Omega_{mg}+\Omega^{*}_{ng}+\omega_1+\omega_2)}{(\Omega^{*}_{mg}+\omega_2)(\Omega^{*}_{ng}+\omega_1)(\Omega^{*}_{ng}+\omega_\sigma)\Omega_{mg}}.
\end{aligned}
\tag{23}
$$

At this point, the only difference between S_1 and S_2 is the frequency Ω^{*}_{mg} in the second summation of S_1 and Ω_{mg} in the second summation of S_2. The frequency Ω_{mg} is defined as $\Omega_{mg} = \Omega_m - \Omega_g$. Spontaneous decay of the state Ω_m is introduced via the inverse radiative lifetime Γ_m such that $\Omega_m = \omega_m - i\Gamma_m/2$. Spontaneous decay is neglected in this treatment; therefore, $\Omega^{*}_{mg} = \Omega_{mg}$. Thus $S_1 = S_2$. At this point, 44 terms of Equation (14) are equal to 44 terms of Equation (15). The manipulations below show that $S'_1 = S'_2$.

$$\begin{aligned}
S'_1 = &-\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)G(\omega_2)\hat{p}_\gamma(\bar{r}'')|0\rangle \\
&-\langle 0|\hat{p}_\alpha(\bar{r})G(\omega_\sigma)\hat{p}_\gamma(\bar{r}'')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')G(0)G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle \\
&-\langle 0|\hat{p}_\beta(\bar{r}')G^*(-\omega_1)G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{r})|0\rangle \\
&-\langle 0|\hat{p}_\beta(\bar{r}')G(0)\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')G^*(-\omega_2)G^*(-\omega_\sigma)\hat{p}_\alpha(\bar{r})|0\rangle.
\end{aligned} \tag{24}$$

$$\begin{aligned}
S'_1 = &-\sum_{m}'\sum_{n}'\frac{\langle 0|\hat{p}_\varepsilon(\bar{r}''')|m\rangle\langle m|\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})|n\rangle\langle n|\hat{p}_\gamma(\bar{r}'')|0\rangle}{\Omega_{mg}(\Omega_{ng}-\omega_\sigma)(\Omega_{ng}-\omega_2)} \\
&-\sum_{m}'\sum_{n}'\frac{\langle 0|\hat{p}_\alpha(\bar{r})|m\rangle\langle m|\hat{p}_\gamma(\bar{r}'')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')|n\rangle\langle n|\hat{p}_\beta(\bar{r}')|0\rangle}{(\Omega_{mg}-\omega_\sigma)\Omega_{ng}(\Omega_{ng}-\omega_1)} \\
&-\sum_{m}'\sum_{n}'\frac{\langle 0|\hat{p}_\beta(\bar{r}')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')|n\rangle\langle n|\hat{p}_\alpha(\bar{r})|0\rangle}{(\Omega^*_{mg}+\omega_1)\Omega_{mg}(\Omega^*_{ng}+\omega_\sigma)} \\
&-\sum_{m}'\sum_{n}'\frac{\langle 0|\hat{p}_\beta(\bar{r}')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')|n\rangle\langle n|\hat{p}_\alpha(\bar{r})|0\rangle}{\Omega_{mg}(\Omega^*_{ng}+\omega_2)(\Omega^*_{ng}+\omega_\sigma)}.
\end{aligned} \tag{25}$$

$$\begin{aligned}
S'_1 = &-\sum_{m}'\sum_{n}'\frac{\langle 0|\hat{p}_\varepsilon(\bar{r}''')|m\rangle\langle m|\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})|n\rangle\langle n|\hat{p}_\gamma(\bar{r}'')|0\rangle\left[(\Omega_{mg}-\omega_1)+(\Omega_{ng}-\omega_2)\right]}{\Omega_{mg}(\Omega_{ng}-\omega_\sigma)(\Omega_{ng}-\omega_2)(\Omega_{mg}-\omega_1)} \\
&-\sum_{m}'\sum_{n}'\frac{\langle 0|\hat{p}_\beta(\bar{r}')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')|n\rangle\langle n|\hat{p}_\alpha(\bar{r})|0\rangle\left[(\Omega^*_{ng}+\omega_2)+(\Omega^*_{mg}+\omega_1)\right]}{(\Omega^*_{mg}+\omega_1)\Omega_{mg}(\Omega^*_{ng}+\omega_\sigma)(\Omega^*_{ng}+\omega_2)} \\
= &-\sum_{m}'\sum_{n}'\frac{\langle 0|\hat{p}_\varepsilon(\bar{r}''')|m\rangle\langle m|\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})|n\rangle\langle n|\hat{p}_\gamma(\bar{r}'')|0\rangle(\Omega_{mg}+\Omega_{ng}-\omega_1-\omega_2)}{\Omega_{mg}(\Omega_{ng}-\omega_\sigma)(\Omega_{ng}-\omega_2)(\Omega_{mg}-\omega_1)} \\
&-\sum_{m}'\sum_{n}'\frac{\langle 0|\hat{p}_\beta(\bar{r}')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')|n\rangle\langle n|\hat{p}_\alpha(\bar{r})|0\rangle(\Omega^*_{mg}+\Omega^*_{ng}+\omega_1+\omega_2)}{(\Omega^*_{mg}+\omega_1)\Omega_{mg}(\Omega^*_{ng}+\omega_\sigma)(\Omega^*_{ng}+\omega_2)}.
\end{aligned} \tag{26}$$

Next the S'_2 sum is manipulated.

$$\begin{aligned}
S'_2 = &-\sum_{m}'\sum_{n}'\frac{\langle 0|\hat{p}_\varepsilon(\bar{r}''')|m\rangle\langle m|G(\omega_1)\hat{p}_\beta(\bar{r}')|0\rangle\langle 0|\hat{p}_\alpha(\bar{r})|n\rangle\langle n|\hat{p}_\gamma(\bar{r}'')|0\rangle}{(\Omega_{mg}-\omega_1)(\Omega_{ng}-\omega_\sigma)(\Omega_{ng}-\omega_2)} \\
&-\sum_{m}'\sum_{n}'\frac{\langle 0|\hat{p}_\alpha(\bar{r})|m\rangle\langle m|\hat{p}_\gamma(\bar{r}'')|0\rangle\langle 0|\hat{p}_\varepsilon(\bar{r}''')|n\rangle\langle n|\hat{p}_\beta(\bar{r}')|0\rangle}{(\Omega_{mg}-\omega_2)\Omega_{ng}(\Omega_{ng}-\omega_1)} \\
&-\sum_{m}'\sum_{n}'\frac{\langle 0|\hat{p}_\beta(\bar{r}')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{r}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{r}'')|n\rangle\langle n|\hat{p}_\alpha(\bar{r})|0\rangle}{(\Omega^*_{mg}+\omega_1)(\Omega^*_{ng}+\omega_2)(\Omega^*_{ng}+\omega_\sigma)} \\
&-\sum_{m}'\sum_{n}'\frac{\langle 0|\hat{p}_\gamma(\bar{r}'')|m\rangle\langle m|\hat{p}_\alpha(\bar{r})|0\rangle\langle 0|\hat{p}_\beta(\bar{r}')|n\rangle\langle n|\hat{p}_\varepsilon(\bar{r}''')|0\rangle}{(\Omega^*_{mg}+\omega_2)(\Omega^*_{ng}+\omega_1)\Omega_{ng}}.
\end{aligned} \tag{27}$$

$$
\begin{aligned}
S'_2 = &-\sum_m{}' \sum_n{}' \frac{\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|m\rangle\langle m|G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})|n\rangle\langle n|\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle\left[\Omega_{mg} + \left(\Omega_{ng} - \omega_\sigma\right)\right]}{\left(\Omega_{mg} - \omega_1\right)\left(\Omega_{ng} - \omega_\sigma\right)\left(\Omega_{ng} - \omega_2\right)\Omega_{mg}} \\
&-\sum_m{}' \sum_n{}' \frac{\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')|n\rangle\langle n|\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\left[\Omega_{mg} + \left(\Omega^{*}_{ng} + \omega_\sigma\right)\right]}{\left(\Omega^{*}_{mg} + \omega_1\right)\left(\Omega^{*}_{ng} + \omega_2\right)\left(\Omega^{*}_{ng} + \omega_\sigma\right)\Omega_{mg}} \\
= &-\sum_m{}' \sum_n{}' \frac{\langle 0|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|m\rangle\langle m|G(\omega_1)\hat{p}_\beta(\bar{\mathbf{r}}')|0\rangle\langle 0|\hat{p}_\alpha(\bar{\mathbf{r}})|n\rangle\langle n|\hat{p}_\gamma(\bar{\mathbf{r}}'')|0\rangle\left(\Omega_{mg} + \Omega_{ng} - \omega_1 - \omega_2\right)}{\left(\Omega_{mg} - \omega_1\right)\left(\Omega_{ng} - \omega_\sigma\right)\left(\Omega_{ng} - \omega_2\right)\Omega_{mg}} \\
&-\sum_m{}' \sum_n{}' \frac{\langle 0|\hat{p}_\beta(\bar{\mathbf{r}}')|m\rangle\langle m|\hat{p}_\varepsilon(\bar{\mathbf{r}}''')|0\rangle\langle 0|\hat{p}_\gamma(\bar{\mathbf{r}}'')|n\rangle\langle n|\hat{p}_\alpha(\bar{\mathbf{r}})|0\rangle\left(\Omega_{mg} + \Omega^{*}_{ng} + \omega_1 + \omega_2\right)}{\left(\Omega^{*}_{mg} + \omega_1\right)\left(\Omega^{*}_{ng} + \omega_2\right)\left(\Omega^{*}_{ng} + \omega_\sigma\right)\Omega_{mg}}
\end{aligned}
\tag{28}
$$

Result

The preceding work has shown that the 48 terms inside the {} brackets of Equation (14) are equal to the 48 terms of the second hyperpolarizability density of Equation (15). Thus, substituting the second hyperpolarizability density into the brackets of Equation (14) yields the result:

$$
\begin{aligned}
&\frac{\partial\beta_{\alpha\beta\gamma}\left(\bar{r},\bar{r}',\bar{r}'';-\omega_\sigma;\omega_1,\omega_2\right)}{\partial R^K_\delta} \\
&\quad = \int d\bar{\mathbf{r}}'''\, Z^K \gamma_{\alpha\beta\gamma\varepsilon}\left(\bar{r},\bar{r}',\bar{r}'',\bar{r}''';-\omega_\sigma;\omega_1,\omega_2,0\right)\mathbf{T}_{\varepsilon\delta}\left(\bar{\mathbf{r}}''',\bar{\mathbf{R}}^K\right).
\end{aligned}
\tag{29}
$$

APPENDIX C: EFFECT OF CREATION AND ANNIHILATION OPERATORS ON MULTI-ELECTRON WAVEFUNCTIONS

Multi-electron wavefunctions can be represented as Slater determinants or as occupation number wavefunctions. When an occupation number wavefunction is used, the single-electron states that comprise the multi-electron wavefunction are placed in a conventional order. In this work, the ordering of the single electron states will be in terms of energy. The occupation number wavefunction can be written as a product of creation operators acting on the vacuum state. The creation operator product also is placed in a conventional order.

$$\left|n_{1s\alpha}\, n_{1s\beta} \cdots n_{nlm\beta}\right\rangle = \left(a^{\dagger}(1s_{\alpha})\right)^{n_{1s\alpha}} \left(a^{\dagger}(1s_{\beta})\right)^{n_{1s\beta}} \cdots \left(a^{\dagger}(nlm_{\beta})\right)^{n_{nlm\beta}} \left|\varnothing\right\rangle \tag{1}$$

The wavefunction is written in terms of n with the understanding that n is either 0 or 1. Thus, Equation (1) can be rewritten neglecting creation operators raised to the zeroth power.

$$\left|n_{1s\alpha}\, n_{1s\beta} \cdots n_{nlm\beta}\right\rangle = a^{\dagger}(1s_{\alpha})\, a^{\dagger}(1s_{\beta}) \cdots a^{\dagger}(nlm_{\beta}) \left|\varnothing\right\rangle \tag{2}$$

The electrons in the multi-electron wavefunction must be indistinguishable. Therefore, when the electrons are placed in a different order into a multi-electron state, the differently ordered state is still a valid wavefunction, though the sign of the function may change depending on how and how many electrons were exchanged. The anticommutation rules for electron operators allow for the proper accounting of the sign of the multi-electron state when electrons are exchanged.

$$\begin{aligned}\left\{a_m^\dagger, a_n^\dagger\right\} &= a_m^\dagger a_n^\dagger + a_n^\dagger a_m^\dagger = 0\\ \left\{a_m, a_n\right\} &= a_m a_n + a_n a_m = 0\\ \left\{a_m^\dagger, a_n\right\} &= a_m^\dagger a_n + a_n a_m^\dagger = \delta_{mn}\end{aligned} \tag{3}$$

Specific examination of the anticommutation relations for the creation operators yields the proper sign of the wavefunction under electron exchange.

$$a_m^\dagger a_n^\dagger = -a_n^\dagger a_m^\dagger \tag{4}$$

Therefore, in the occupation number formalism, the relationship becomes

$$a_m^\dagger a_n^\dagger|\varnothing\rangle = -a_n^\dagger a_m^\dagger|\varnothing\rangle \Rightarrow |n_m n_n\rangle = -|n_n n_m\rangle\,. \tag{5}$$

Thus every time the order of a pair of creation operators is reversed, a sign change results.

When a creation operator operates on a multi-electron wavefunction, the number of particle exchanges required to place the operator in standard order must be determined so that the correct sign of the function can be found. Consider the operator $a_r^\dagger$ operating on the wavefunction $|n_m n_n\rangle$. (In the examples, standard order is alphabetical order.)

$$a_r^\dagger|n_m n_n\rangle = a_r^\dagger a_m^\dagger a_n^\dagger|\varnothing\rangle = (-1)a_m^\dagger a_r^\dagger a_n^\dagger|\varnothing\rangle = (-1)(-1)a_m^\dagger a_n^\dagger a_r^\dagger|\varnothing\rangle = |n_m n_n n_r\rangle \tag{6}$$

The $a_r^\dagger$ operator needed to be exchanged twice to place it in conventional order. Thus, a factor of $(-1)^2$ is included in the final wavefunction. The two following examples further illustrate the concept.

$$\begin{aligned}a_s^\dagger|n_m n_n n_r\rangle &= a_s^\dagger a_m^\dagger a_n^\dagger a_r^\dagger|\varnothing\rangle = (-1)^3 a_m^\dagger a_n^\dagger a_r^\dagger a_s^\dagger|\varnothing\rangle = -|n_m n_n n_r n_s\rangle\\ a_p^\dagger|n_m n_n n_r\rangle &= a_p^\dagger a_m^\dagger a_n^\dagger a_r^\dagger|\varnothing\rangle = (-1)^2 a_m^\dagger a_n^\dagger a_p^\dagger a_r^\dagger|\varnothing\rangle = |n_m n_n n_p n_r\rangle\end{aligned} \tag{7}$$

The factor of -1 can be written using the notation $(-1)^{S_p}$ where S_p indicates the number of operator exchanges, i. e. particle exchanges, needed to put the operator $a_p^\dagger$ into conventional order.

A similar situation arises when an annihilation operator is applied to a multi-electron state. The anticommutation relations yield

$$\begin{aligned} a_n a_m^\dagger &= -a_m^\dagger a_n \quad && m \neq n \\ a_n a_n^\dagger &= 1 - a_n^\dagger a_n \quad && m = n \end{aligned} \tag{8}$$

Consider the effect of the annihilation operator a_r on the examples in Equation (7),

$$\begin{aligned} a_r|n_m n_n n_r n_s\rangle &= a_r a_m^\dagger a_n^\dagger a_r^\dagger a_s^\dagger|\varnothing\rangle = (-1) a_m^\dagger a_r a_n^\dagger a_r^\dagger a_s^\dagger|\varnothing\rangle = (-1)^2 a_m^\dagger a_n^\dagger a_r a_r^\dagger a_s^\dagger|\varnothing\rangle \\ &= (-1)^2 a_m^\dagger a_n^\dagger \left(1 - a_r^\dagger a_r\right) a_s^\dagger|\varnothing\rangle = a_m^\dagger a_n^\dagger a_s^\dagger|\varnothing\rangle + (-1)^3 a_m^\dagger a_n^\dagger a_r^\dagger a_r a_s^\dagger|\varnothing\rangle \\ &= a_m^\dagger a_n^\dagger a_s^\dagger|\varnothing\rangle + (-1)^4 a_m^\dagger a_n^\dagger a_r^\dagger a_s^\dagger a_r|\varnothing\rangle = a_m^\dagger a_n^\dagger a_s^\dagger|\varnothing\rangle + 0 = |n_m n_n n_s\rangle \end{aligned} \tag{9}$$

$$\begin{aligned} a_r|n_m n_n n_p n_r\rangle &= a_r a_m^\dagger a_n^\dagger a_p^\dagger a_r^\dagger|\varnothing\rangle = (-1) a_m^\dagger a_r a_n^\dagger a_p^\dagger a_r^\dagger|\varnothing\rangle = (-1)^2 a_m^\dagger a_n^\dagger a_r a_p^\dagger a_r^\dagger|\varnothing\rangle \\ &= (-1)^3 a_m^\dagger a_n^\dagger a_p^\dagger a_r a_r^\dagger|\varnothing\rangle = (-1)^3 a_m^\dagger a_n^\dagger a_p^\dagger \left(1 - a_r^\dagger a_r\right)|\varnothing\rangle \\ &= -a_m^\dagger a_n^\dagger a_p^\dagger|\varnothing\rangle + 0 = -|n_m n_n n_p\rangle \end{aligned} \tag{10}$$

where $a_r|\varnothing\rangle = 0$. Therefore, the same set of operator exchanges is needed when determining the sign of the multi-electron wavefunction when an annihilation operator is applied. The effect of a creation operator upon an arbitrary occupation number wavefunction can be written as

$$a_\lambda^\dagger|n_1 n_2 \cdots n_\lambda \cdots\rangle = (-1)^{S_\lambda}|n_1 n_2 \cdots n_\lambda + 1 \cdots\rangle \quad n_\lambda = 0 \tag{11}$$

The restriction on the occupation number $n_\lambda = 0$ should be noted since the application of the operator gives zero when $n_\lambda = 1$, i. e., the complete destruction of the multi-electron state. The effect of an annihilation operator upon an arbitrary occupation number wavefunction can be written as

$$a_\kappa|n_1 n_2 \cdots n_\kappa \cdots\rangle = (-1)^{S_\kappa}|n_1 n_2 \cdots n_\kappa - 1 \cdots\rangle \quad n_\kappa = 1 \tag{12}$$

Similarly when $n_\kappa = 0$, the annihilation operator gives zero.

The matrix element of an arbitrary single-electron number-conserving operator can be calculated using Equations (11) and (12).

$$\begin{aligned}
&\langle n'_1 n'_2 \cdots n'_\kappa \cdots n'_\lambda \cdots | a_\lambda^\dagger a_\kappa | n_1 n_2 \cdots n_\kappa \cdots n_\lambda \cdots \rangle \\
&= (-1)^{S_\lambda + S_\kappa} \langle n'_1 n'_2 \cdots n'_\kappa \cdots n'_\lambda \cdots | n_1 n_2 \cdots n_\kappa - 1 \cdots n_\lambda + 1 \cdots \rangle \\
&= (-1)^{S_\lambda - S_\kappa} \delta_{n'_1, n_1} \delta_{n'_2, n_2} \cdots \delta_{n'_\kappa, n_\kappa - 1} \cdots \delta_{n'_\lambda, n_\lambda + 1} \cdots
\end{aligned} \tag{13}$$

Note that $(-1)^{S_\lambda + S_\kappa}$ in Equation (13) has been written identically as $(-1)^{S_\lambda - S_\kappa}$.

APPENDIX D: RELATION OF POLARIZATION PROPAGATOR DERIVATIVE TO POLARIZABILITY DENSITY DERIVATIVE

The derivation relating the derivative of the polarization propagator to the first-order nonlinear polarization propagator is suggested by the relationship found by Hunt *et al.*[1,2] between the nuclear-coordinate derivative of the polarizability and the hyperpolarizability density,

$$\partial\alpha_{\alpha\beta}(\bar{r};\bar{r}',\omega)/\partial R_{\gamma}^{K} = \int d\bar{r}''\,\beta_{\alpha\beta\delta}(\bar{r};\bar{r}',\omega,\bar{r}'',0)Z^{K}\mathbf{T}_{\delta\gamma}(\bar{r}'',\bar{R}^{K})\,. \tag{1}$$

The hyperpolarizability density can be expressed in terms of the quadratic polarization propagator.

$$\beta_{\alpha\beta\gamma}(\bar{r},\bar{r}',\bar{r}'';\omega',\omega'') = \left[p(\bar{r})_{\alpha}\right]_{\lambda}^{\kappa}\left[p(\bar{r}')_{\beta}\right]_{\lambda'}^{\kappa'}\left[p(\bar{r}'')_{\gamma}\right]_{\lambda''}^{\kappa''}\Pi_{\kappa,\kappa',\kappa''}^{\lambda,\lambda',\lambda''}(\omega',\omega''). \tag{2}$$

There are no linear polarization propagators in Equation (2). The purpose of this appendix is to demonstrate that the linear polarization propagators that arise from taking the derivative of the polarizability density cancel each other to yield an expression with only the quadratic polarization propagator.

The polarizability density written in terms of the polarization propagator is.

$$\alpha_{\alpha\beta}(\bar{r},\bar{r}';\omega) = -\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi_{\kappa,\kappa'}^{\lambda,\lambda'}(\omega) \tag{3}$$

The derivative of the polarizability density with respect to any arbitrary parameter is

$$\begin{aligned}&\frac{\partial\alpha_{\alpha\beta}(\bar{r},\bar{r}';\omega)}{\partial\eta}\\&=-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\left(\begin{array}{l}\frac{\partial\langle\lambda|}{\partial\eta}p(\bar{r})_\alpha|\kappa\rangle\langle\lambda'|p(\bar{r}')_\beta|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)+\langle\lambda|p(\bar{r})_\alpha\frac{\partial|\kappa\rangle}{\partial\eta}\langle\lambda'|p(\bar{r}')_\beta|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\\+\langle\lambda|p(\bar{r})_\alpha|\kappa\rangle\frac{\partial\langle\lambda'|}{\partial\eta}p(\bar{r}')_\beta|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)+\langle\lambda|p(\bar{r})_\alpha|\kappa\rangle\langle\lambda'|p(\bar{r}')_\beta\frac{\partial|\kappa'\rangle}{\partial\eta}\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\\+\langle\lambda|p(\bar{r})_\alpha|\kappa\rangle\langle\lambda'|p(\bar{r}')_\beta|\kappa'\rangle\frac{\partial\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)}{\partial\eta}\end{array}\right)\end{aligned}\tag{4}$$

Upon substitution of the polarization propagator derivative, the polarizability density becomes

$$\begin{aligned}&\frac{\partial\alpha_{\alpha\beta}(\bar{r},\bar{r}';\omega)}{\partial\eta}\\&=-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\{\frac{\partial\langle\lambda|}{\partial\eta}p(\bar{r})_\alpha|\kappa\rangle\langle\lambda'|p(\bar{r}')_\beta|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)+\langle\lambda|p(\bar{r})_\alpha\frac{\partial|\kappa\rangle}{\partial\eta}\langle\lambda'|p(\bar{r}')_\beta|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\\&\quad+\langle\lambda|p(\bar{r})_\alpha|\kappa\rangle\frac{\partial\langle\lambda'|}{\partial\eta}p(\bar{r}')_\beta|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)+\langle\lambda|p(\bar{r})_\alpha|\kappa\rangle\langle\lambda'|p(\bar{r}')_\beta\frac{\partial|\kappa'\rangle}{\partial\eta}\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\}\\&-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\langle\lambda|p(\bar{r})_\alpha|\kappa\rangle\langle\lambda'|p(\bar{r}')_\beta|\kappa'\rangle\\&\quad\times\left[\begin{array}{r}\sum_{\lambda'',\kappa''}\left[\frac{\partial h_0}{\partial\eta}\right]^{\kappa''}_{\lambda''}\Pi^{\lambda,\lambda',\lambda''}_{\kappa,\kappa',\kappa''}(\omega,0)+\sum_{m\neq\lambda}C_{\lambda m}\Pi^{m,\lambda'}_{\kappa,\kappa'}(\omega)+\sum_{m\neq\lambda'}C_{\lambda' m}\Pi^{\lambda,m}_{\kappa,\kappa'}(\omega)\\+\sum_{k\neq\kappa'}C^{*}_{\kappa' k}\Pi^{\lambda,\lambda'}_{\kappa,k}(\omega)+\sum_{k\neq\kappa}C^{*}_{\kappa k}\Pi^{\lambda,\lambda'}_{k,\kappa'}(\omega)\end{array}\right].\end{aligned}\tag{5}$$

The derivative of the single electron wavefunctions in Equation (5) can be expressed as a sum-over-states.

$$\frac{\partial|k\rangle}{\partial\eta}=\sum_{m\neq k}C_{km}|m\rangle\tag{6}$$

Substitution of Equation (6) into Equation (5) yields

$$
\begin{aligned}
\frac{\partial \alpha_{\alpha\beta}(\bar{r},\bar{r}';\omega)}{\partial \eta}
&= -\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}
\begin{bmatrix}
\sum\limits_{m\neq\lambda} C^{*}_{\lambda m}\langle m|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle \\
+\sum\limits_{m\neq\kappa} C_{\kappa m}\langle\lambda|p(\bar{r})_{\alpha}|m\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle \\
+\sum\limits_{m\neq\lambda'} C^{*}_{\lambda' m}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle m|p(\bar{r}')_{\beta}|\kappa'\rangle \\
+\sum\limits_{m\neq\kappa'} C_{\kappa' m}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|m\rangle
\end{bmatrix}
\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega) \\
&\quad -\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\times
\left\{
\begin{array}{l}
\sum\limits_{\lambda'',\kappa''}\left[\dfrac{\partial h_0}{\partial \eta}\right]^{\kappa''}_{\lambda''}\Pi^{\lambda,\lambda',\lambda''}_{\kappa,\kappa',\kappa''}(\omega,0) \\
+\sum\limits_{m\neq\lambda} C_{\lambda m}\Pi^{m,\lambda'}_{\kappa,\kappa'}(\omega)+\sum\limits_{m\neq\lambda'} C_{\lambda' m}\Pi^{\lambda,m}_{\kappa,\kappa'}(\omega) \\
+\sum\limits_{k\neq\kappa'} C^{*}_{\kappa' k}\Pi^{\lambda,\lambda'}_{\kappa,k}(\omega)+\sum\limits_{k\neq\kappa} C^{*}_{\kappa k}\Pi^{\lambda,\lambda'}_{k,\kappa'}(\omega)
\end{array}
\right\}.
\end{aligned}
\tag{7}
$$

After simple rearrangements of coefficients and summations, Equation (7) becomes

$$
\begin{aligned}
\frac{\partial \alpha_{\alpha\beta}(\bar{r},\bar{r}';\omega)}{\partial \eta}
&= -\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\lambda} C^{*}_{\lambda m}\langle m|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega) \\
&\quad -\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\kappa} C_{\kappa m}\langle\lambda|p(\bar{r})_{\alpha}|m\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega) \\
&\quad -\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\lambda'} C^{*}_{\lambda' m}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle m|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega) \\
&\quad -\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\kappa'} C_{\kappa' m}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|m\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega) \\
&\quad -\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{\lambda'',\kappa''}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\left[\frac{\partial h_0}{\partial \eta}\right]^{\kappa''}_{\lambda''}\Pi^{\lambda,\lambda',\lambda''}_{\kappa,\kappa',\kappa''}(\omega,0) \qquad (8) \\
&\quad -\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\lambda} C_{\lambda m}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{m,\lambda'}_{\kappa,\kappa'}(\omega) \\
&\quad -\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\lambda'} C_{\lambda' m}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,m}_{\kappa,\kappa'}(\omega) \\
&\quad -\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{k\neq\kappa'} C^{*}_{\kappa' k}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,k}(\omega) \\
&\quad -\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{k\neq\kappa} C^{*}_{\kappa k}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,\lambda'}_{k,\kappa'}(\omega).
\end{aligned}
$$

Since λ, λ′, κ, κ′, m and k are dummy indices, they can be reassigned different labels. In the sixth term, let m be interchanged with λ (m ↔ λ). In the seventh term, m ↔ λ′. In the eighth term, k → κ′ and κ′ → m. In the ninth term, k → κ and κ → m.

$$
\begin{aligned}
\frac{\partial \alpha_{\alpha\beta}(\bar{r},\bar{r}';\omega)}{\partial \eta} = &-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\lambda} C^{*}_{\lambda m}\langle m|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\\
&-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\kappa} C_{\kappa m}\langle\lambda|p(\bar{r})_{\alpha}|m\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\\
&-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\lambda'} C^{*}_{\lambda' m}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle m|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\\
&-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\kappa'} C_{\kappa' m}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|m\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\\
&-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{\lambda'',\kappa''}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\left[\frac{\partial h_0}{\partial \eta}\right]^{\kappa''}_{\lambda''}\Pi^{\lambda,\lambda',\lambda''}_{\kappa,\kappa',\kappa''}(\omega,0)\\
&-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\lambda} C_{m\lambda}\langle m|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\\
&-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\lambda'} C_{m\lambda'}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle m|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\\
&-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{k\neq\kappa'} C^{*}_{m\kappa'}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|m\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\\
&-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{k\neq\kappa} C^{*}_{m\kappa}\langle\lambda|p(\bar{r})_{\alpha}|m\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega).
\end{aligned}
\tag{9}
$$

Common quantities can be factored from terms (1 and 6), (2 and 9), (3 and 7) and (4 and 8) in Equation (9).

$$
\begin{aligned}
\frac{\partial \alpha_{\alpha\beta}(\bar{r},\bar{r}';\omega)}{\partial \eta} = &-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\lambda}\left[C^{*}_{\lambda m}+C_{m\lambda}\right]\langle m|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\\
&-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\kappa}\left[C_{\kappa m}+C^{*}_{m\kappa}\right]\langle\lambda|p(\bar{r})_{\alpha}|m\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\\
&-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\lambda'}\left[C^{*}_{\lambda' m}+C_{m\lambda'}\right]\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle m|p(\bar{r}')_{\beta}|\kappa'\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\\
&-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{m\neq\kappa'}\left[C_{\kappa' m}+C^{*}_{m\kappa'}\right]\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|m\rangle\Pi^{\lambda,\lambda'}_{\kappa,\kappa'}(\omega)\\
&-\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{\lambda'',\kappa''}\langle\lambda|p(\bar{r})_{\alpha}|\kappa\rangle\langle\lambda'|p(\bar{r}')_{\beta}|\kappa'\rangle\left[\frac{\partial h_0}{\partial \eta}\right]^{\kappa''}_{\lambda''}\Pi^{\lambda,\lambda',\lambda''}_{\kappa,\kappa',\kappa''}(\omega,0).
\end{aligned}
\tag{10}
$$

Because of the orthonormality condition placed upon the perturbed wavefunctions $C_{\lambda m} + C^{*}_{m\lambda} = 0$, the sum of coefficients in the [] brackets is zero.[3] Therefore,

$$\frac{\partial \alpha_{\alpha\beta}(\bar{r},\bar{r}';\omega)}{\partial \eta} = -\sum_{\lambda,\lambda'}\sum_{\kappa,\kappa'}\sum_{\lambda'',\kappa''} \langle \lambda | p(\bar{r})_{\alpha} | \kappa \rangle \langle \lambda' | p(\bar{r}')_{\beta} | \kappa' \rangle \left[\frac{\partial h_0}{\partial \eta} \right]_{\lambda''}^{\kappa''} \Pi_{\kappa,\kappa',\kappa''}^{\lambda,\lambda',\lambda''}(\omega,0). \quad (11)$$

Thus, the derivative of the polarizability has no dependence on linear polarization propagators.

---

[1] K. L. C. Hunt, J. Chem. Phys. **90,** 4909 (1989).

[2] K. L. C. Hunt, Y. Q. Liang, R. Nimalakirthi, and R. A. Harris, J. Chem. Phys. **91,** 5251 (1989).

[3] Chapter 2, pg. 32.