CHAPTER 7

Future work and the conclusions

Abstract:

This chapter focuses mainly on the future scope of the NIA-CPKS method. The methodology and the implementation of the NIA-CPKS, discussed so far were limited to the closed shell molecules only. The newer implementation of the NIA-CPKS in SCP formalism facilitates further development of the method for open shell molecules. This implementation will make the NIA-CPKS more inclusive for calculation of static response properties. Further the derivative of dipole-dipole polarizabilities, dipole-quadrupole polarizabilities and electric–magnetic dipole polarizability with respect to normal coordinates can be calculated within deMon2k. In this chapter we discuss the methodology for implementation of polarizabilities derivatives. We finally conclude the work presented in this thesis.
7.1 NIA-CPKS for open shell systems

The open shell systems can be studied within DFT either with unrestricted Kohn-Sham (UKS) or with restricted open shell Kohn-Sham (ROKS) approach. For UKS the total electronic density is represented as a sum of $\alpha$ spin density and $\beta$ spin density.

$$\rho(r) = \rho^\alpha(r) + \rho^\beta(r)$$  \hspace{1cm} (7.1)

Both UKS and ROKS had been implemented in dMon2k. We mainly discuss here the way ROKS and UKS have been implemented in deMon2k. As discussed in chapter 1, within ADFT the auxiliary functions are used to fit the charge density. The auxiliary density is also separated into two spin densities contributions as above and from equation (1.36) of auxiliary density we get the following equation,

$$\tilde{\rho}(r) = \tilde{\rho}^\alpha(r) + \tilde{\rho}^\beta(r) = \sum_k (x_k^\alpha + x_k^\beta) \tilde{k}(r)$$  \hspace{1cm} (7.2)

Here $x_k^\alpha$ and $x_k^\beta$ are spin polarized fitting coefficients which are obtained from separate fitting equations for $\alpha$ and $\beta$ densities. The spin polarized KS matrix is given as,

$$K_{\mu\nu}^{\sigma} = H_{\mu\nu} + \sum_k \langle \mu\nu | k \rangle \left( x_k^\alpha + x_k^\beta + z_k^\sigma \right)$$  \hspace{1cm} (7.3)

The symbol $\sigma$ represents the spin, either $\alpha$ or $\beta$. In UKS, the two decoupled sets of KS equations are solved similar to unrestricted HF (UHF) method [1]. The $\alpha$ and $\beta$ Fock matrices are individually diagonalized and the solutions iterated until self-consistency is achieved.

For calculation of response properties within SCP theory for open shell case, the response of the spin polarized density matrix has to be calculated [2-8]. The spin polarised perturbed density is given as:

$$(P^\sigma)^\lambda = \sum_{i,a} \frac{(\mathcal{K}^\sigma)_{i\alpha}^\lambda}{\varepsilon_i^\sigma - \varepsilon_a^\sigma} (c_i^\sigma c_a^{\sigma\dagger} + c_a^\sigma c_i^{\sigma\dagger})$$  \hspace{1cm} (7.4)

The perturbed KS matrix $(\mathcal{K}^\sigma)_{i\alpha}^{(\lambda)}$ is given in the molecular orbital representation as,
\[ K^{\sigma(\lambda)}_{\mu\nu} = \frac{K^{\sigma}_{\mu\nu}(+\Delta F_{\lambda}) - K^{\sigma}_{\mu\nu}(-\Delta F_{\lambda})}{2\Delta F} \]  

(7.6)

Within NIA-CPKS for UKS the perturbed KS matrix for each spin is calculated by finite difference method. Under this approximation the perturbed KS matrix in atomic orbitals is given as,

\[ K^{\sigma(\lambda)}_{\mu\nu} = K^{\mu\nu}_{\mu\nu} + \Delta F \lambda - K^{\mu\nu}_{\mu\nu} \frac{\Delta F_{\lambda}}{2} \]  

(7.5)

This perturbed KS matrix calculated from eq. (7.6) can be substituted in eq. (7.5) to calculate the corresponding perturbed densities. The final perturbed density is obtained by adding corresponding perturbed densities of \( \alpha \) and \( \beta \) spin. Once the total perturbed density matrix is calculated the dipole-dipole polarizability and dipole quadrupole polarizability components can be obtained from the trace of product of perturbed density matrix and respective moment integrals as shown in formula (3.4) and (3.5).

The other method to deal with open shell systems is ROKS [6, 9, 10]. This is a DFT analogue of Roothaan's open-shell method for Hartree-Fock theory [11]. For ROKS implementation in deMon2k the \( \alpha \) and \( \beta \) density matrices (and densities) are used as in the case of UKS case. However, these are built from only one set of MO coefficients. Thus the differences of these two matrices arise solely from the different occupation numbers. As a result, \( \alpha \) and \( \beta \) Coulomb and exchange-correlation fitting coefficients are calculated as for UKS. However, in contrast to UKS, only one KS matrix is diagonalized. This KS matrix is built from the \( \alpha \) and \( \beta \) Kohn-Sham matrices which are both generated in ROKS [12]. Thus only one set of coefficients is generated using this KS matrix. These coefficients are used to build the density matrix (and density) as described above. Thus for electric properties calculation only one perturbed KS matrix can be generated by finite-field method and thereby the perturbed density can be built for calculation of polarizabilities. The polarizabilities are calculated as per the trace formula. We can follow the same perturbation branch for NIA-CPKS scheme in which the ADPT [8] has been implemented for open-shell case except that the KS matrix is calculated directly by finite-field method.
7.2 Implementation and simulation of VROA in deMon2k

The vibrational Raman optical activity is an important field of research due to its application in determination of the absolute configuration of chiral molecules and the enantiomeric excess of stereoisomer in a given enantiomeric mixture [13-20]. Experimentally, the presence of enantiomer and enantiomeric excess in a mixture can be identified with optical rotation and circular dichroism [21]. These conventional techniques have practical difficulties and time consuming. Thus ROA has gained attention among all other spectroscopic techniques of studying the structural characteristics of molecule. Compared to NMR, ROA has a significant advantage in structural studies of biomolecules as the much shorter time scale is accessible here due to which short-lived conformers can also be investigated. In contrast to crystallographic methods, it is possible to study the molecules in an aqueous environment with the ROA technique. The first evidence of the scattering mechanism responsible for ROA was observed by Atkins and Barron [22]. In 1971, Barron and Buckingham presented the theoretical background for ROA phenomenon [23]. They defined the dimensionless circular intensity difference (CIDi) to describe the effect of scattering in VROA, which is given as

\[
\Delta = \frac{I^R - I^L}{I^R + I^L} \tag{7.11}
\]

where \(I^R\) and \(I^L\) are the scattered intensities in right- and left-circularly polarized incident light respectively. For a sample of randomly oriented molecules, the expressions for CIDi of forward and backward Rayleigh (elastic) scattering are

\[
\Delta(0^\circ) = \frac{4[45\alpha G' + \beta(G')^2 - \beta(A)^2]}{c[45\alpha^2 + 7\beta(\alpha)^2]} \tag{7.12}
\]

And

\[
\Delta(180^\circ) = \frac{24\left[\beta(G')^2 + \frac{1}{3}\beta(A)^2\right]}{c[45\alpha^2 + 7\beta(\alpha)^2]} \tag{7.13}
\]

The isotropic and anisotropic invariants defined in above equations are given as,

\[
\alpha = \frac{1}{3} \alpha_{\alpha\alpha} \quad \text{and} \quad G' = \frac{1}{3} G'_{\alpha\alpha} \tag{7.14}
\]
\[
\beta(\alpha)^2 = \frac{1}{2} \left( 3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta} \right) \quad (7.15)
\]

\[
\beta(G')^2 = \frac{1}{2} \left( 3\alpha_{\alpha\beta}\alpha'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta} \right), \quad (7.16)
\]

\[
\beta(A)^2 = \frac{1}{2} \omega \alpha_{\alpha\beta} \epsilon_{\alpha\gamma\delta} A_{\gamma\delta \beta} \quad (7.17)
\]

where \( \epsilon_{\alpha\gamma\delta} \) is the Levi–Civita tensor (the unit third-rank antisymmetric tensor). In the above equations, \( \alpha \) is the electric dipole–dipole polarizability, \( G' \) is the linear polarization of the electric dipole moment by the magnetic field component of the incident light (the electric dipole–magnetic dipole polarizability), and \( A \) is the electric dipole–quadrupole polarizability. The definition and the formula to evaluate \( \alpha \) and \( A \) have been already specified in earlier chapters of this thesis. The elements of the electric dipole–magnetic dipole polarizability tensor can be defined either with respect to the electric dipole moment or the magnetic dipole moment as [24],

\[
G'_{i,j}(-\omega, \omega) = \frac{\partial \mu_i}{\partial B_j(\omega)} \quad (7.18)
\]

\[
= \frac{\partial m_i}{\partial F_j(\omega)} \quad (7.19)
\]

And it can be calculated by the trace formula,

\[
G'_{i,j}(-\omega, \omega) = -Tr \left[ P'^{(\lambda)}_i(-\omega) \cdot \mathbf{m}_j \right] \quad (7.20)
\]

\[
G'_{i,j}(-\omega, \omega) = -Tr \left[ \mathbf{\mu}_i \cdot P'^{(\kappa)}_j(\omega) \right] \quad (7.21)
\]

where \( P'^{(\lambda)}_i \) and \( P'^{(\kappa)}_j \) is the first order derivative of the density matrix with respect to electric field and magnetic field respectively. \( \mathbf{m}_j \) represents the component of magnetic dipole moment integrals and electric \( \mathbf{\mu}_i \) the electric dipole moment integrals.

The CIDi mentioned in equation (7.12-7.16) account for the Rayleigh scattering of the incident light. The CIDi arising from the Raman scattering, are determined by the vibrational transition moments. These transition moments are generated due to the interaction of scattered light with molecular vibrations, inducing excitations or de-excitations in the different vibrational modes of the molecule. The transition moments can be represented as follows,
\[
\langle \nu_0 | \alpha_\alpha \beta | \nu_1 p \rangle \langle \nu_1 p | \alpha_\alpha \beta | \nu_0 p \rangle = \frac{1}{2 \omega_p} \left( \frac{\partial \alpha_\alpha \beta}{\partial Q_p} \right) \left( \frac{\partial \alpha_\alpha \beta}{\partial Q_p} \right) \tag{7.22}
\]

\[
\langle \nu_0 | \alpha_\alpha \beta | \nu_1 p \rangle \langle \nu_1 p | \gamma_\alpha \beta' | \nu_0 p \rangle = \frac{1}{2 \omega_p} \left( \frac{\partial \alpha_\alpha \beta}{\partial Q_p} \right) \left( \frac{\partial \gamma_\alpha \beta'}{\partial Q_p} \right) \tag{7.23}
\]

\[
\langle \nu_0 | \alpha_\alpha \beta | \nu_1 p \rangle \langle \nu_1 p | \epsilon_\alpha \gamma \delta A_\gamma \delta \beta | \nu_0 p \rangle = \frac{1}{2 \omega_p} \left( \frac{\partial \alpha_\alpha \beta}{\partial Q_p} \right) \epsilon_\alpha \gamma \delta \left( \frac{\partial A_\gamma \delta \beta}{\partial Q_p} \right) \tag{7.24}
\]

Where, \( \nu_0 \) and \( \nu_1 \) are the vibrational ground and excited-state wave functions respectively, for mode \( p \) and the corresponding normal coordinate \( Q_p \). \( \omega_p \) is the harmonic frequency. Thus the transition moments can be calculated from the geometric derivatives of the three tensors \( \alpha, A \) and \( G' \). \[25, 26\].

The above discussion highlights the importance of the electric dipole-dipole and dipole-quadrupole polarizabilities for the study of VROA spectra. In recent years, attempts are made to investigate VROA with \textit{ab initio} techniques. The first HF level calculations of molecular tensors significant in determining ROA intensities were carried out by Amos \textit{et.al.} \[27\]. Using the static approximation of Amos \textit{et al.} CIDis observed in ROA spectra were reported by Polavarapu \[28\]. This was the first complete theoretical study of ROA. Some studies have reported results calculated with correlated methods such as MCSCF wave functions \[29\]. An analytical method for evaluating the derivatives of polarizabilities at TDHF level was presented by Quinet and Champagne \[30\]. The methods have also been developed using TDDFT for calculation of ROA intensities for some small molecules \[31, 32\]. The theoretical simulation of VROA spectra is time consuming and the calculations demand reasonable accuracy. Thus there is a need for efficient methodology for calculation of ROA CIDs for realistic molecules which overcome the practical difficulties of experimental methods. The main challenge in simulation of the VROA spectra is efficient and accurate calculation of polarizabilities and their geometric derivatives. We have already discussed the implementation NIA-CPKS method for calculation of static dipole-dipole polarizabilities and dipole-quadrupole polarizabilities. It has been observed that the method is reasonably accurate and efficient and hence can be applied for large molecules. However, calculation of
VROA spectra requires the dynamic polarizabilities, which can be calculated with ADPT method. Thus the VROA spectra can be calculated by implementing the methodology to calculate the geometric derivatives of these polarizabilities within deMon2k. The components of the dipole-dipole and dipole-quadrupole polarizabilities can be calculated with ADPT method at given experimental frequency. Similarly, it is possible to calculate the electric dipole–magnetic dipole polarizability using equation (7.20). The first order perturbed density matrix is generated for calculation of dipole-dipole and dipole quadrupole polarizabilities and magnetic dipole integrals are available in deMon2k. Hence, it is easy to implement electric–magnetic dipole polarizability with ADPT. For calculation of geometric derivatives of these polarizabilities, it is more convenient to calculate the derivatives with respect to Cartesian coordinates first and then transform them into normal coordinates. The derivative of $\alpha, A$ and $G'$ with respect to atomic Cartesian coordinate $a$ is given as,

$$\alpha_{ij}^a(-\omega, \omega) = \frac{\partial \alpha_{ij}(-\omega, \omega)}{\partial a}$$

$$A_{ij}^a(-\omega, \omega) = \frac{\partial A_{ijk}(-\omega, \omega)}{\partial a}$$

$$G'^a_{ij}(-\omega, \omega) = \frac{\partial G'^a_{ijk}(-\omega, \omega)}{\partial a}$$

The geometric derivative of these polarizabilities can be calculated numerically by small geometric distortion. The central difference formula with suitable step size can be used for derivative calculation of each component of polarizability.

$$\alpha_{ij}^a(-\omega, \omega) = \frac{\alpha_{ij}(+\Delta a) - \alpha_{ij}(-\Delta a)}{2 \Delta a}$$

The values $+\Delta a$ and $-\Delta a$ in the parentheses denote the symmetrically chosen coordinate value and $\Delta a$ is the magnitude of the geometric displacement. Other two derivatives given in equation (7.26) and (7.27) can be obtained using same formula. Similarly, the derivatives of static polarizabilities obtained from NIA-CPKS can be calculated. The static polarizability derivatives calculated from NIA-CPKS and ADPT can be compared to test the exactness of the implementation. The method can be validated by the assessment of these results with higher level results. Thus progressively we can develop a methodology for simulation of VROA spectra.
7.3 Conclusions

In this thesis we discussed the electric repose properties in detail. We presented here the new method for efficient calculation of dipole-dipole and dipole-quadrupole polarizabilities. This approach can be further extended for calculation of non-linear response properties such as hyperpolarizability. Our method can be applied to larger systems; hence, it is possible to study the NLO properties of some experimentally important molecules. The results of polarizabilities presented here have validated our method for calculation of reasonably accurate values. In first chapter we defined the electric response properties and a brief overview of the literature have been presented. We have also discussed various electronic structure methods available for calculation of various properties. In chapter 1, we have focussed on the methods which have been used for this work. In our discussion we have emphasised mainly on DFT. The structure of the deMon2k program and the LC-GTO approach has been argued in detail. The earlier implementation of NIA-CPKS and ADPT formalism for calculation of electric response properties have been presented in this chapter. The chapter ends with the short discussion on MD simulation and property calculation within MD. In chapter 2 we have reported dipole-polarizabilities for azoarene molecule and its di-substituted derivatives. The aim of this chapter is to validate our implementation and compare the NIA-CPKS and ADPT method. We have successfully produced the trend of the polarizabilities supposed to be observed for these push-pull systems, hence both the methods have been validated. Chapter 3 is more technical chapter where the newer implementation of the NIA-CPKS version of SCP for calculation of dipole-dipole and dipole-quadrupole polarizabilities has been given described. The newer implementation of the NIA-CPKS has been validated by calculation of dipole-quadrupole polarizabilities of tetrahedral molecules, these results are reported in chapter 4. In Chapter 5, we have studied the temperature and frequency effects on dipole-quadrupole polarizabilities of the P4 and adamantane molecule. The effect of temperature for accurate calculation of dipole-quadrupole polarizability of adamantane molecule has been highlighted by our calculation. Chapter 6, we have studied the dipole-dipole polarizabilities and dipole-quadrupole polarizabilities at distorted geometries calculated using various functionals. We have argued here the need of better functional or the new methodology such as MR-DFT to take into
account the static correlation for calculation of electric response properties of the molecules at distorted geometries. In present chapter we have discussed the methodology for extending our NIA-CPKS implementation for open-shell molecules. The implementation of polarizability derivatives using ADPT method will facilitate the simulation of VROA spectra within deMon2k.
References