

Molecular Polarizabilities from Density-Functional Theory: From Small Molecules to Light Harvesting Complexes

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Abstract: We review some recent applications of density-functional theory to molecules and systems of molecules where the role of polarizabilities are particularly relevant. With respect to the implementation of density-functional theory, details related to numerics and basis sets are described. We then describe how self-consistent finite-field calculations may be used to separately extract the electronic polarizability tensor and infrared intensities. We review the relationship between second-harmonic vibrational polarizabilities and molecular infrared intensities. An efficient method for describing the polarization effects in systems of molecules is included and a recent application of this method to a biomimetic light-harvesting complex is discussed.

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1 Introduction

The calculation of molecular polarizabilities [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13] in molecules remains a problem of great interest due to the important role they play in many physical, chemical, and biological processes. In weakly interacting molecular materials, the polarizabilities are responsible for long-range attractions which may be due to either dipole-/monopole- induced dipole interactions or London interactions. In ionic and molecular crystals, the Clausius-Mossotti relation and extensions relates the materials dielectric constant to the polarizabilities of the molecular systems. In biology or biomimetic materials, light-induced charge transfer interactions are often of interest. Molecular polarization impacts such events both directly and indirectly. First, when a charge-transfer excitation occurs on a given molecule or between two neighboring molecules, all of the spectator molecules surrounding the active molecules respond to the change in electric-fields caused by this excitation. Depending upon how quickly the molecular surroundings respond to such an excitation, several different effects could occur. If the absorption and emission were indeed sudden but long-lived, the emission spectrum would be shifted relative to the absorption spectrum.

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At the other limit, where long-range coupling between spectator and active molecules is considered instantaneous, a significant broadening in the absorption and emission spectrum would arise. While the interactions discussed here would often be dominated entirely by electronic polarization effects, dynamical and static coupling between electronic and atomistic degrees of freedom, such as those pioneered by Bishop, complicate the problem further and may be important in some cases. A second, albeit indirect, effect due to molecular polarizability is related to the transition rates that govern the light induced excitations associated with photovoltaic energy conversion. With the possible exception of coherent electron processes, where preparation of an excited electronic configuration is often not considered, the time scale associated with a rattling electron or even an electron-hole pair requires the calculation of transition matrix elements. At the lowest level of approximation, the dipole form of these matrix elements coincides with those requisite for molecular polarizabilities. In this sense, assessing capabilities for calculation of polarizabilities and polarizability derivatives furthers the confidence level in transition rates for excited states.

One method for obtaining information about polarizabilities and polarizability derivatives is the original density-functional theory as well as the various extensions such as time-dependent density functional theory and the hybrid functionals. [14, 15, 16]

In this paper we review some of the recent work in this area that has been primarily accomplished by the NRLMOL suite of density-functional codes. [17, 18, 19, 20] We provide a summary of calculated polarizabilities in many molecules which can will hopefully illustrate general trends.

The paper is organized as follows. Since the methodology utilized here has been developed primarily in the physics and materials-research communities, in Sec. II we briefly discuss the underlying numerical methodologies, the methods for basis-set selection, and provide a few computational benchmarks. In Sec. III we review the calculation of polarizabilities and infrared intensities and discuss how the infrared intensity is related to double-harmonic vibrational polarizabilities. We provide calculated results for several different types of molecules and compare to experimental results as well as other theoretical calculations. In Sec. IV, we review the simple case of an FCC lattice of fullerenes and a simple model for calculating the polarization-induced relaxation associated for a lattice of fullerene molecules. [11] In Sec. V we discuss a problem where all of these capabilities are required. We start by discussing the calculation of the polarizability tensor of a recently proposed light-harvesting molecular triad which is composed of a fullerene molecule, a porphyrin molecule and a carotenoid molecule. [21, 22] The molecule is considered to be interesting because it possesses a charge transfer excited state with a very large dipole moment. We then show that the polarization of surrounding molecules would significantly change the energetics of this excited state compared to excitation in vacuum where charge transfer is not achieved.

2 Computational Methodology

The calculations discussed herein have been performed using the NRLMOL suite of density-functional codes that have been developed by Pederson and collaborators over the last two decades. Except where otherwise noted, we have used the generalized-gradient approximation to exchange-correlation energy [15, 16] for the applications discussed here. For a given molecular geometry, it is necessary to solve a Schroedinger-like equation for each of the electrons. Once the electronic Schroedinger-like equations are self-consistently solved, the forces on each atom are determined from the Hellman-Feynman-Pulay theorem [17]^b and the geometry is relaxed using standard quasi-newtonian approaches such as conjugate gradient.

To solve the Schroedinger-like equations the wavefunctions are expanded in terms of gaussian basis functions. This reduces the problem to the numerical determination of matrix elements, followed by the solution of a standard algebraic secular equation. While the latter task is accomplished using standard linear-algebra codes, there are a few aspects of the former approach that are

worth mentioning. In order to obtain the matrix elements, it is necessary to calculate terms such as $\langle \phi_i | -\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r}) | \phi_j \rangle$. For gaussian basis functions, the kinetic energy part of this matrix element can be obtained in closed form using standard techniques. However parameterizations of the density functional such as GGA and LDA do not allow the matrix elements for the potential energy to be calculated in closed form. To efficiently and accurately perform the calculation of the potential matrix elements we first determine a variational integration mesh [17]^a that can be used to accurately calculate three-dimensional integrals that are strongly peaked near the positions of nuclei and more slowly decaying in the regions that are far from any atom. This method is based on several different transformations of gaussian quadrature integration strategies and was originally presented in Ref. [17]^a. The general idea is that it is always possible to place a molecule in a parallelepiped that is so large that the basis functions outside the parallelepiped vanish. Then the parallelepiped is iteratively tessalated until one is left with a collection of parallelepipeds that are either empty or have a single atom at the center. The latter case are further reduced to more empty parallelepipeds and an atom at the center of a perfect cube. Three different adaptable and iterative quadrature techniques are then used to develop accurate integration meshes in each of these three regions. Details are given in Ref. [17]^a. Given the integration mesh, it is then only necessary to numerically determine the values of the basis-set pair $[\phi_i(\mathbf{r})\phi_j(\mathbf{r})]$ and the effective potential ($V_{eff}(\mathbf{r})$). Within the generalized-gradient approximation the exchange-correlation potential depends on the spin densities as well as their first and second derivatives. Numerical determination of the electronic Coulomb potential requires one to solve poisson's equation for each pair of basis functions in the problem. Determination of the GGA potential and the Coulomb potential can in fact be done quasi-simultaneously since the latter case requires algebraic reduction of the two-center density matrices to a superposition of single-center gaussian distributions multiplied by polynomials of degree $2L_{max}$ with L the maximum angular-momentum basis function in the problem. It is a fact that this algebraic reduction can then be used to convert the determination of the GGA potential to order-N complexity. Further this strategy is easily parallelized and can be automatically load balanced. A discussion of load balancing is presented in Ref. [18].

In addition to intrinsic numerical accuracy a second issue is related to the choice of gaussian-basis sets. The basis-sets used here have been specifically optimized for GGA calculations [19]. However, initial tests suggest they perform well for HF calculations also. Issues related to basis-set choice are numerous and some of these must be primarily addressed in a brute-force manner by systematically increasing basis-set size until a calculated quantity stops changing. By performing such calculations on smaller systems, reasonably reliable rules of thumb may be deduced which allow high confidence for calculations on larger systems. However, there are several aspects of basis-set selection that can be rigorously addressed in atomic calculations prior to use in molecules and we first ensure that our basis sets satisfy these requirements. With respect to the cusp condition and selection of shortest-range function in the problem, we rely on the a theorem proved in Ref. [19] which we now refer to as the $Z^{10/3}$ theorem. If one requires that the absolute error in energy for a 1s-core electron in a heavy atom be the same as the absolute error in energy for a light atom it can be shown that the ratio of the shortest-range gaussian decay parameters should in fact scale as $(Z_l/Z_h)^{10/3}$ where Z_l and Z_h are the nuclear charges of the lighter and heavier nuclei respectively. We have shown that this condition eliminates the need for counterpoise calculations in systems where basis-set superposition is expected to be an issue. A second issue that can be addressed rigorously at the atomic level is related to the selection of the values of each gaussian decay function. To address this issue we start with a set of N even-tempered decay parameters given by $(\alpha_1, \alpha_2, \alpha_3, \dots, \alpha_N)$ and perform an SCF calculation on a given atom. When self-consistency is achieved one can determine the derivative of the total energy with respect to each decay parameter ($\frac{dE}{d\alpha_i}$) by noting that the Hellman-Feynman theorem tells us that at self-consistency the total derivative is in fact the partial derivative. In conjunction with the conjugate-gradient algorithm and a series of SCF calculations it is then possible to find the best decay parameters within the

constraint of N decay parameters. Finally the total number of decay parameters can be determined by ramping up the value of N until the optimized total energy converges and agrees with a numerical solution to a given accuracy in energy. It was ascertained that the $Z^{10/3}$ scaling law mentioned above is automatically "selected" by the numerical approach discussed above. Also in reference to basis sets, it is worth mentioning that we find it to be computationally advantageous to use a common set of decay parameters for all angular momentum. However the automated use of more conventional quantum-chemistry basis sets is also an option. The final issue that probably can not be addressed systematically pertains to the total number of contracted orbitals necessary to determine an accurate value. With the exception of the total energy most quantities of interest, polarizabilities being one example, are not variational quantities so care must be exercised in assessing the accuracy of such calculations. In this work the default basis sets employed start with a minimal basis set that exactly reproduces the ground state energies. To this basis set we add 3-4 extra single gaussians of s and p character and 2-3 extra single gaussians of d character. Additional detail can be found in Ref. [19].

3 Polarizabilities in Isolated Molecules and Connections Between Vibrational Spectra and Higher Order Derivatives

When a molecule is placed in an external field each of these molecules polarizes in response to the applied fields. As discussed by Bishop and coworkers the total polarizability of a molecule can be analytically broken up into terms due to different types of interactions. Generally the largest response is the electronic polarizability which is commonly designated as α in the literature. This response is associated field-induced relaxations of the electronic density and the formation of induced dipole moments and is of second-order in the electric field.

The next largest response is often the double-harmonic vibrational polarizability [23, 24, 25, 26, 27, 28] that is designated by $([\mu_2]^{0,0})$ in the literature. This response is due to the following physics. At zero field, the equilibrium geometry of a molecule has no net forces. However when an electric field is applied to a molecule, the forces on each atom become nonzero due to the fact that the nuclear charges feel a direct force from the applied field and also an induced force due to the faster rearrangement of electronic density. The molecule then relaxes its geometry slightly to counteract the appearance of the force and lowers its energy further. This effect is also second-order in the electric field. It has been shown that double-harmonic vibrational polarizabilities depend on the same quantities that determine the infrared intensities. [29, 30, 31]

While other higher-order effects are also of interest, the discussion in this paper will concentrate entirely on electronic and infrared calculations because these are often the largest contributions to molecular polarization and because they are of immediate interest to our current studies. Also, these static quantities are indeed ground-state properties and are therefore fully protected by the original formulations of density-functional theory due to Hohenberg, Kohn and Sham. [14] We note that there are many interesting treatises on the more general problem and the interested reader is referred to references at the beginning of the paper.

There are at least two strategies available for calculating the two effects described here. Probably the most general strategy is to determine the ground state of a multiatom system and many of the excited electronic and vibrational states. Given this information, it is possible to develop perturbative expansions of the total energy as a function of applied field and direction and identify the static electronic and double-harmonic vibrational polarizabilities as well as higher-order effects. Such a method also allows for the treatment of dynamical effects. If one is primarily interested in and/or constrained by theoretical formality to look at these two effects, an alternative and conceptually more straightforward approach may be used. The electronic and infrared intensities may be determined directly by mimicing the experimental conditions. In this approach, which is used

in entirety in this work, the calculation of the molecular energy and wavefunctions is performed with a small electric field applied for several different orientations. The various contributions to the polarizabilities are then easily determined by observing the calculated change in energy and dipole moment as a function of applied fields and vibrational displacements. A more mathematical discussion of this approach is outlined below.

Within the DFT the total energy (E) of a neutral molecule in an electric field \mathbf{G} is given by

$$E = 2 \sum_i \langle \psi_i | -\frac{1}{2} \nabla^2 + V_{nuc} | \psi_i \rangle + \frac{1}{2} \int d^3 r \int d^3 r' \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d^3 r G_{xc}[\rho, \nabla \rho, \dots] + \frac{1}{2} \sum_{\mu \neq \nu} \frac{Z_\mu Z_\nu}{|\mathbf{R}_\mu - \mathbf{R}_\nu|} + \int d^3 r \rho_{tot}(\mathbf{r}) \mathbf{G} \cdot \mathbf{r}. \quad (1)$$

For simplicity the above equation assumes a spin unpolarized molecule. The various contributions to the total energy include the electronic kinetic energy, all the coulomb interactions in the problem, the exchange-correlation energy (represented schematically as G_{xc}) and the interaction between the total charge density and the applied electric field. The total charge density includes the charges of the nuclei and is designated as ρ_{tot} whereas the electronic density $\rho = 2 \sum_i |\psi_i|^2$ appears without a subscript. At the zero-field equilibrium geometry, the change in energy ($\Delta = E - E_0$) to second-order is given by:

$$\Delta = \sum_i \frac{\partial E}{\partial G_i} G_i + \sum_{\nu k i} \frac{\partial^2 E}{\partial G_i \partial R_{\nu k}} G_i X_{\nu k} + \frac{1}{2} \sum_{\mu i, \nu k} \frac{\partial^2 E}{\partial R_{\mu i} \partial R_{\nu k}} X_{\mu i} X_{\nu k} + \frac{1}{2} \sum_{ik} \frac{\partial^2 E}{\partial G_i \partial G_k} G_i G_k. \quad (2)$$

Further we note that

$$\frac{\partial p_i}{\partial R_{\nu, k}} = - \frac{\partial^2 E}{\partial G_i \partial R_{\nu k}} = \frac{\partial F_{\nu, k}}{\partial G_i}. \quad (3)$$

In the above equations, the x-component of the total moment is defined according to $\mathbf{p}_x = \frac{\partial E}{\partial G_x}$. \mathbf{X}_ν is the displacement of the ν^{th} atom. The spring constant matrix is given by $\frac{\partial^2 E}{\partial R_{\mu i} \partial R_{\nu k}} X_{\mu i} X_{\nu k}$. As discussed in Refs. [20], the mixed second derivatives, $\frac{\partial^2 E}{\partial G_i \partial R_{\nu k}}$, when transformed into the space of the normal modes lead to the infrared intensities. Eq. (3) shows that the more conventional representation of this second derivative is in terms of the first derivative of the total dipole moment with respect to an atomic or vibronic displacement. It is both instructive and computationally efficient to notice that the mixed second derivative is also the derivative of the Hellman-Feynman force with respect to applied field. Many authors have noted that this quantity is also responsible for the double-harmonic vibrational polarizability. To see that this is the case, one simply needs to consider the derivative (force) of the above energy with respect to an atomic position:

$$\frac{\partial \Delta}{\partial R_{\nu k}} = \sum_i \frac{\partial^2 E}{\partial G_i \partial R_{\nu k}} G_i + \sum_{\mu i} \frac{\partial^2 E}{\partial R_{\mu i} \partial R_{\nu k}} X_{\mu i} = 0. \quad (4)$$

From the above equation it is clear that inversion of the spring constant matrix (in the space orthogonal to translational and rotational modes) allows one to find the displacements ($X_{\mu i}$) that minimize the energy. It is also clear that such displacements will be linear in the applied field and that the energy difference for these displacements is then quadratic in the applied field. In Ref. [27] a full derivation is presented and the final result is given in terms of spectroscopically measurable quantities (e.g. frequencies and dynamical dipole moments).

In Table I we present recent NRLMOL-based calculations on static polarizabilities. In Table I we compare results as calculated within the local density approximation and the generalized gradient approximation. Experimental values are also included.

Table 1: Calculated polarizability along principle axes for a selection of molecules. All polarizabilities are reported in \AA^3 . Experimental values in parentheses indicate they are average polarizabilities rather than eigenvalues of the polarizability tensor.

Molecule	Method	Ref.	α_1	α_2	α_3
CH ₄	LDA	[20]	2.68	2.68	2.68
	GGA	[20]	2.62	2.62	2.62
	Exp	[34]	2.60	2.60	2.60
C ₂ H ₂	LDA	[20]	4.79	2.98	2.98
	GGA	[20]	4.79	2.89	2.89
	Exp	[34]	5.12	2.43	2.43
C ₂ H ₄	LDA	[20]	5.41	3.99	3.45
	GGA	[20]	5.39	3.91	3.44
	Exp	[34]	5.40	3.85	3.40
C ₂ H ₆	LDA	[20]	4.98	4.35	4.35
	GGA	[20]	4.91	4.24	4.24
C ₆ H ₆	LDA	[11]	12.6	12.6	6.75
	Exp	[35]	(10.3)		
NF ₃	GGA	[27]	3.40	3.40	2.40
	EXP	[31]	(2.81)		
TiCl ₄	GGA	[27]	15.03	15.03	15.03
	Exp	[31]	15.00	15.00	15.00
SF ₆	GGA	[27]	5.15	5.15	5.15
	Exp	[31]	4.49	4.49	4.49
SiF ₄	GGA	[27]	3.72	3.72	3.72
	Exp	[31]	3.32	3.32	3.32
HCN	GGA	[27]	3.42	2.18	2.18
	Exp	[31]	(2.59)		
C ₆₀	LDA	[11]	83.5	83.5	83.5
	GGA	[27]	82.9	82.9	82.9
	EXP	[36]	75-83	75-83	75-83
Na ₂	GGA	[27]	49.8	28.9	28.9
	Exp	[37]	(38.6)		
Na ₈	GGA	[27]	116.2	116.2	116.2
	Exp	[37]	133.5	133.5	133.5
TCNQ C ₆ H ₄ [C(CN) ₂] ₂	GGA	[38]	64.9	27.53	12.5
BEDT [CS ₂ C ₂ S ₂ C ₂ H ₄] ₂	GGA	[38]	75.1	42.4	25.7

In Ref. [27] we have used the second derivatives (Eq. 4) to calculate the second-harmonic vibrational polarizabilities. As is found experimentally [31], the vibrational polarizabilities were found to be relatively large for the halide containing molecules. For example for SiF₄ the (isotropic) vibrational polarizability was found to be 2.09 \AA^3 which is on the same order of the electronic polarizability of 3.72 \AA^3 . For comparison the experimental values for these quantities are 1.75 and 3.32 \AA^3 respectively. In contrast for a nonpolar tetrahedral molecule (CH₄), the vibrational polarizability was found to be very small (0.04 \AA^3) in good agreement with experiment (0.03 \AA^3). Vibrational polarizabilities for many of the molecules shown in Table I may be found in Ref. [27]. One of the possible trends observed in Ref. [27] was that the vibrational polarizability may be less important (percentage wise) for large molecules. An additional recent calculation [?] that might reinforce

this trend is on the TCNQ molecule. This molecule has principal electronic polarizabilities of (61.8, 27.3, 15.9) \AA^3 . However the principal vibrational polarizabilities are only (1.91, 2.49 and 3.12) \AA^3 respectively.

4 Polarization Effects in Systems of Molecules

In principle, calculation of the polarizabilities of a system of molecules may be accomplished using the formalism of the previous section simply by treating the system of molecules as a single macromolecule with space in between. However, this quickly becomes computationally too expensive. Fortunately, many interesting questions related to polarizability of a collection of nearly nonoverlapping molecules may be described efficiently by first calculating the polarizability tensor for each molecule and then determining how long-range interactions between charged or polarized molecules modify the total response of the system. We review a method for determining the response of a collection of molecules as well as some earlier applications of this method to a lattice of fullerene molecules. This method is conceptually analogous to the Clausius-Mossotti method for extracting dielectric constants from molecular polarizabilities. The primary difference is that it allows one to study such effects for finite collections of polarizable molecules and that the constraint of perfect periodicity is not required. In the next section, we discuss applications of a nonisotropic extension of this method to a more complex biomimetic molecule that has a relatively large polarizability.

Suppose we are given a lattice of N nonoverlapping neutral molecules at sites $(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)$ with polarizabilities of $(\alpha_1, \alpha_2, \dots, \alpha_N)$. We then consider modifying the charge distribution on these molecules. For example, we could imagine addition or removal of an electron from a given molecule or removing an electron from one molecule and placing it on a second molecule. As a result of the change in charge distribution, electric fields that are spatially slowly varying in space are produced at each lattice site. This causes each molecule to polarize in response to the new electric field. The change in dipole moment at each molecular site further modifies the electric fields in the system which would further change the dipoles at each site. Providing that the original electric fields are small enough, the dipoles on each site would eventually self-consistently adjust themselves so that the induced dipoles are consistent with the external field due to all other charges, dipoles and external fields in the system. In Ref. [11] Pederson and Quong introduced an energy functional for such a lattice of molecules. It is given by:

$$E = \sum_n \left[\frac{|\mathbf{P}_n^{ind}|^2}{2\alpha_n} - \mathbf{p}_n \cdot \mathbf{G} + \Phi(R_n)q_n + T(q_n) \right] + \sum_{n,m} [U^1(p_n, p_m) + U^2(p_n, q_m) + U^3(q_n, q_m)] \quad (5)$$

For a recent article with a similar point of view and a discussion of many other aspects related to Clausius-Mossotti relations, readers are referred to Ref. [32]. In the above equation, $\mathbf{G} = -\nabla\Phi$ is the electric field that is due to an externally applied potential $\Phi(\mathbf{r})$. $T(q)$ is the energy of the particle as a function of charge state. For example, for $q=1$, $T(q)$ is the ionization energy and for $q=-1$, $T(q)$ is the electron affinity. The electric field interacts with the total dipole moment on each site and the externally applied field interacts with the charge on each site. In addition, the total dipoles and charges interact with one another in terms of the standard dipole-dipole (U^1), dipole-monopole (U^2) and monopole-monopole (U^3) interactions which can be found in any textbook on Electricity and Magnetism. The first term represents the energy penalty associated with forming an induced dipole on a given site. In the limit of a single site, or well-separated sites, with $q_n=0$, it is easily verified that the induced dipole moments that minimize the above energy functional satisfy the expected constraint:

$$\mathbf{p}^{ind} = \alpha \mathbf{G} \quad (6)$$

Since the total energy has terms that are both linear and quadratic in the dipole moments, a self-consistent variational principle can be applied if the ratio of polarizability to molecular volume is small enough. Under these conditions one insists that the total energy should be stationary to small variations in the dipole moments. It can be verified that the condition for minimal energy is satisfied when the electric fields, $\mathbf{G}_{tot}(\mathbf{R}_n)$, due to all other dipoles, charges, and the external field lead to fields at each site that satisfy $\mathbf{p}_{ind}(\mathbf{R}_n) = \alpha \mathbf{G}_{tot}(\mathbf{R}_n)$.

Since this method, with slight improvements, provides the only computationally feasible method for the molecule discussed in the next session, it is worthwhile discussing some early uses of this method to illustrate its accuracy. In Ref. [11] this method was used to calculate the dielectric constant for an FCC lattice of C_{60} molecules and to calculate the screened Hubbard U parameter for the K_3C_{60} superconductor. Overall the agreement between theory and experiment was found to be reasonably good. For example, within LDA, Pederson and Quong calculated the polarizability of a C_{60} molecule to be approximately $80-82 \text{ \AA}^3$ and found a resulting dielectric constant of 3.66 which is in reasonable agreement with experiment (roughly 4.0). [32]. From the same methodology, it is possible to determine the screened hubbard U which was found to be 1.27 eV in Ref. [11]. This is in reasonably good agreement with experimental measurements in the range of 1.4-1.6 eV. See Ref. [33] for further details about the experiments.

A few remarks on the caveat that the polarizability must be small enough may be useful. If the polarizabilities used in Eq. 5 are too large one finds that a self-consistent solution to this equation is not possible. Instead the energy diverges with the dipoles continuing to grow for each iterative cycle. Clearly if the above methodology leads to a total dipole moment significantly larger than a linear dimension of one of the molecules it is indicative that that the lowest-order penalty function is not enough to describe the system and that higher-order refinement of the energy functional may be required. This behavior is related to the Clausius-Mossotti polarization catastrophe. [32]

5 Application to a Light Harvesting Molecule

In this section we illustrate how polarization effects can play an important role in charge transfer processes. In order to do this it is necessary to modify the form of the energy-penalty function to account for an anisotropic polarizability tensor. We have studied a bio-mimetic molecule that converts solar energy into an electric dipole. The molecule contains a chromophore as well as electron-acceptor and an electron-donor components [21, 22]. The chromophore is a diaryl-porphyrin, the acceptor is a pyrrole- C_{60} , and the donor is a carotenoid connected to the porphyrin through an amide (Fig. 1). Absorption of light at 590 nm by the porphyrin prepares the initial excited state and the charge transfer (CT) occurs through a multistep process resulting in the final charge separated (CS) state with the electron on the C_{60} and the hole on the carotenoid. The CS state which is quite long lived, has a large dipole moment of 153 Debye. For the charge separation process, we have considered a limited number of 100 singly excited states in our density functional calculation [22]. Some of the excited states are localized excitations which have smaller dipole moments but the charge separated states with the electron and hole on different components can have large dipole moments. The experiments on such molecular systems are done in solution and it was determined that the solvent polarity is strongly linked to the occurrence of the CT excitation. It was observed that the CS occurs in the polar benzonitrile and in 2-methyltetrahydrofuran solvents but does not occur in the nearly nonpolar toluene solvent.

The polarizability of the triad is calculated using the finite field method described above and we find that the polarizability of the triad is quite large - the diagonal components of the polarizability

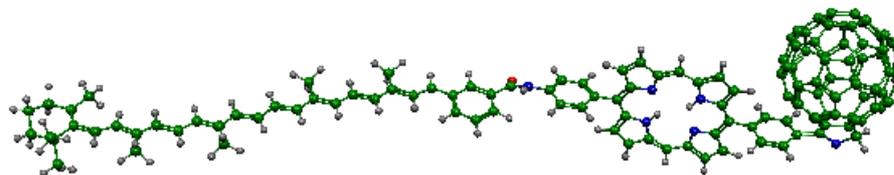


Figure 1: The geometry of the molecular triad shown in the color scheme C=green, H=grey, O=red, N= blue.

tensor are 878, 220, and 199 \AA^3 . The largest value is along the molecular axis. The polarization effects become important when we consider a solution or a crystal. For simplicity, if we consider an assembly of the molecule as a 3-dimensional lattice, then when one of the molecule transits to a CS state with a large dipole moment, it will induce dipole moments on other molecules. The field due to the induced dipoles in turn lowers the energy of the CS state. This stabilization energy is larger for excited states with large dipole moments and also depends on the molecular volume. For large molecular volume, the stabilization energy is small while it increases for small volumes. As the volume decreases, it reaches the Clausius-Mossotti dipole catastrophe discussed in the previous section. The stabilization energy as a function of dipole moments and at different volumes is shown in Fig. 2. This stabilization effect has an important consequence in case of the molecular triad. The energies of the CS states in *vacuo* are higher than that of the initial porphyrin excited state. Now, due to the polarization induced lowering of energy of the large dipole states, it also brings the energies of CS states below the porphyrin excited state thus bringing the calculated levels into good agreement with experiment. These results indicate the important role that polarization can play in photo-induced charge transfer reactions.

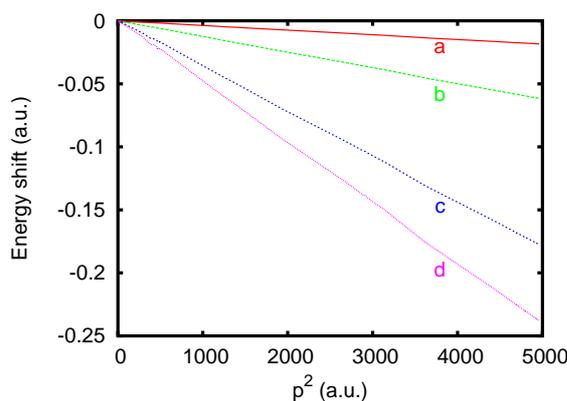


Figure 2: The shift in energy of the excited states as a function of square of dipole moment p and also as a function of molecular volume [$a = 120 \times 42 \times 42$, $b = 105 \times 36.75 \times 36.75$, $c = 100 \times 31.5 \times 31.5$, $d = 100 \times 31 \times 31$ (a.u.).]

6 Summary

In this work we have presented density-functional-based calculations on polarizabilities of several molecules. The results have been generated using reasonably large basis sets using the GGA and LDA versions of DFT. The agreement with experiment is generally good for the systems presented. In addition we have discussed a methodology for using calculated (or measured) molecular polarizabilities to understand the polarization phenomena in collections of weakly interacting and nearly nonoverlapping molecules. The results in this case, while limited, suggest that polarization phenomena in such systems may be reasonably well accounted for. As a very large scale example we have discussed recent calculations on a light-harvesting organic photovoltaic. [22] Our results show that polarization effects in such charge-transfer systems can be large enough to change the ordering of excited states. While improvements of this method could and will be achieved without significantly increasing the computational burden, the results clearly show that such simplified polarization models allow for reliable computational investigations.

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