Research paper

Predicting optimal finite field strengths for calculating the first and second hyperpolarizabilities using simple molecular descriptors

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ABSTRACT

The finite field method was used to calculate the static first and second hyperpolarizabilities (β and γ) for organic molecules. The dependence of β and γ on the applied electric field strength was investigated and used to determine the optimal field strength for each individual molecule. For γ, we designed a protocol that uses the maximum atomic distance within the molecule along the direction of the applied field to estimate optimal field strengths. However, β is nearly independent of the descriptors we considered, and largely depends on the composition (e.g., the presence of certain functional groups) of the molecule.

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1. Introduction

The finite field (FF) method is a standard technique in quantum chemistry for calculating electric response properties of molecules like the static dipole polarizabilities (α) and higher order derivatives thereof (e.g., the first and second hyperpolarizabilities, β and γ) [1–4]. The main advantage of the FF method is its low computational cost and ease of implementation, compared to other approaches like the sum over states formalism, coupled-perturbed Hartree-Fock, or response theory (RT) [5,6]. Whereas these methods need additional information such as analytical gradients or excited state information, the FF method simply requires the calculation of the electronic energy in the presence of various external electric fields [7]. As such it is usually the method of choice for newly developed theories, but also for high level ab initio correlated calculations.

However, there are also serious drawbacks of the FF method, the most crucial being the dependence of the result on the initially chosen field strength F. The higher order derivatives, β and γ, are especially sensitive quantities, with a rather narrow range of suitable field strengths. This sensitivity arises because the FF method is effectively a way of numerically differentiating the energy of a

molecule with respect to the magnitude of the electric field, and as such suffers from finite-precision artifacts when the value of F is too small. On the other hand, if one chooses a value of F that is too large the higher-order derivatives become nonnegligible and contaminate the lower-order derivatives of interest. Worse, after a certain critical field strength has been passed, a field-induced state inversion, where an excited state at zero-field becomes lower in energy than the ground state occurs [8]. The first effect can be mitigated using Richardson extrapolation, which combines calculations at several different field strengths in order to reduce the finite difference error [9,10]. This procedure has been successfully applied in the literature [11–13].

In a recent article, we illustrated how to maximize the benefits of such refinement procedures [14]. Using Richardson extrapolation, significant improvements of the precision are obtained when the applied field strengths follow a geometric progression with a common ratio smaller than two [15]. Another finding is that the precision only benefits from the first one or two steps of iterative Richardson refinement. Subsequent Richardson steps lead to an accumulation of numerical noise.

An open question so far is, how an optimal field strength, F_{opt}, which is the field strength that corresponds to the minimum relative error of the calculated FF quantity, should be chosen for a particular molecule. It is clear that molecules of different size and shape react differently to the applied external electric field. Intuitively, one can understand that large and extended molecules are exposed to much higher potential changes when placed in an

external field and thus are expected to have a much smaller F_{opt} than small molecules. Similarly, it is conceivable that molecules of the same size, but different electronic structure (e.g., saturated vs. conjugated hydrocarbon chains) might have very different optimal field strengths. The purpose of this study is to find correlations between the optimal field strength and other molecule-specific descriptors that allow one to make straightforward, *a priori*, predictions for F_{opt}. This is important because it allows one to avoid the (computer) time-consuming search for the optimal field strength.

2. Methodology and computational details

2.1. Finite field method

The energy E of a molecule for a small external homogenous electric field F can be approximated with a McLaurin series,

$$E(F) = E(0) + \left.\frac{\partial E}{\partial F}\right|_0 + \frac{1}{2!}\left.\frac{\partial^2 E}{\partial F^2}\right|_0 F^2 + \frac{1}{3!}\left.\frac{\partial^3 E}{\partial F^3}\right|_0 F^3 + \frac{1}{4!}\left.\frac{\partial^4 E}{\partial F^4}\right|_0 F^4 + \dots \quad (1)$$

$$E(F) = E(0) - \mu F - \frac{1}{2}\alpha F^2 - \frac{1}{6}\beta F^3 - \frac{1}{24}\gamma F^4 + \dots \quad (2)$$

where μ and α denote the dipole moment and the dipole polarizability, respectively. The higher-order nonlinear responses are the first hyperpolarizability (β) and the second hyperpolarizability (γ).

Eq. (2) can be split into even and odd powers of F, which leads to symmetric and antisymmetric combinations of energies at equal positive and negative field strength

$$E_S(F) = \frac{E(F) + E(-F)}{2} = E(0) - \frac{1}{2}\alpha F^2 - \frac{1}{24}\gamma F^4 + O(F^6) \quad (3)$$

$$E_A(F) = \frac{E(F) - E(-F)}{2} = -\mu F - \frac{1}{6}\beta F^3 - \frac{1}{120}\delta F^5 + O(F^7) \quad (4)$$

This allows the polarizabilities and the even-order hyperpolarizabilities to be treated separately from the dipole moment and the odd-order hyperpolarizabilities. By rearranging Eqs. (3) and (4), the dipole moment (μ) and polarizability (α) can be obtained directly as

$$\mu(F) = -\frac{E_A(F)}{F} = \mu + \frac{1}{6}\beta F^2 + \frac{1}{120}\delta F^4 + O(F^6) \quad (5)$$

$$\alpha(F) = 2\frac{E(0) - E_S(F)}{F^2} = \alpha + \frac{1}{12}\gamma F^2 + \frac{1}{360}\varepsilon F^4 + O(F^6) \quad (6)$$

If F is chosen small enough, Eqs. (5) and (6) are good estimate for μ and α, respectively.

To evaluate β and γ, μ and α have to be eliminated from Eqs. (5) and (6), respectively. This can be achieved if the energy is known at two different field strengths, e.g., F and $2F$, besides the energy at zero field

$$\beta(F) = 2\frac{\mu(2F) - \mu(F)}{F^2} = \frac{2E_A(F) - E_A(2F)}{F^3} = \beta + \frac{1}{4}\delta F^2 + O(F^4) \quad (7)$$

$$\gamma(F) = 4\frac{\alpha(2F) - \alpha(F)}{F^2} = \frac{-2E_S(2F) + 8E_S(F) - 6E(0)}{F^4}$$
$$= \gamma + \frac{1}{6}\varepsilon F^2 + O(F^4) \quad (8)$$

More generally, for any two values of field strengths (say F and xF), Eqs. (7) and (8) can be generalized to

$$\beta(F) = \frac{6}{x^2 - 1} \cdot \frac{\mu(xF) - \mu(F)}{F^2} = \frac{6}{F^3 x} \cdot \frac{xE_A(F) - E_A(xF)}{x^2 - 1} \quad (9)$$

$$\gamma(F) = \frac{12}{x^2 - 1} \cdot \frac{\alpha(xF) - \alpha(F)}{F^2}$$
$$= \frac{24}{F^4 x^2}\left(\frac{x^2 E_S(F) - E_S(xF)}{x^2 - 1} - E(0)\right) \quad (10)$$

The common practice to work with field strengths F and $2F$ corresponds to the choice $x = 2$ in Eq. (10) [16,17]. However, in a recent study we showed that using $x < 2$ improves the accuracy of FF calculations because it allows for more points lying in the acceptable region of field strengths [14]. Motivated by the results of that study, we always use $x = \sqrt{2}$ in our calculations of γ. Eq. (10) then simplifies to

$$\gamma(F) = \frac{12}{F^4}\left(-E_S(\sqrt{2}F) + 2E_S(F) - E(0)\right) \quad (11)$$

For β, we use $x = \sqrt[4]{2}$. Eq. (9) becomes

$$\beta(F) = \frac{6}{F^3\sqrt[4]{2}} \cdot \frac{\sqrt[4]{2}E_A(F) - E_A(\sqrt[4]{2}F)}{\sqrt{2} - 1} \quad (12)$$

2.2. Error reduction

The scaling of the error in Eqs. (7) and (8) can be lifted to a higher order by Richardson extrapolation [9]. This method is widely applied to improve the precision of FF quantities by reducing the error from truncating the Taylor expansion, and it is known to improve the precision of the higher order derivatives β and γ in the first few iterations. A detailed description of the recursive Richardson extrapolation can be found in Ref. [14]. Based on these results, we use at most two iterations of refinement ($m = 0, 1, 2$). Eq. (11) corresponds to the unrefined $\gamma_{m=0}$ case. Combining two or three instances of $\gamma_{m=0}$ with adjusted fields, we obtain

$$\gamma_{m=1}(F) = \frac{3}{F^4}\left(E_S(2F) - 10E_S(\sqrt{2}F) + 16E_S(F) - 7E(0)\right) \quad (13)$$

and

$$\gamma_{m=2}(F) = \frac{1}{4F^4}\left(\begin{array}{l}-E_S(2^{3/2}F) + 26E_S(2F) - 176E_S(\sqrt{2}F) \\ +256E_S(F) - 105E(0)\end{array}\right) \quad (14)$$

For β, we use only one step of Richardson extrapolation and $x = \sqrt[4]{2}$

$$\beta_{m=1}(F) = \frac{3}{F^3(\sqrt{2} - 1)^2}(E_A(\sqrt{2}F) - 3\sqrt[4]{2}E_A(\sqrt[4]{2}F) + 2\sqrt{2}E_A(F)) \quad (15)$$

2.3. Electronic structure calculations

For each molecule a geometry optimization was performed using the Gaussian 09 program [18], using the long-range corrected hybrid density functional CAM-B3LYP [19–24], which was proven to produce accurate molecular geometries [25,26], with a 6-31G(d) basis set [27–30].

All calculations of the response and finite field properties were done with the DALTON quantum chemistry program using the aforementioned optimized geometries [31]. The level of theory was HF/6-31G(d), which is known to supersede DFT polarizabilities in some respects [12,16,17]. We used the natural population analysis method to calculate atomic charges using HF/6-31G(d). As our primary interest is developing *methods* for FF calculations, rather than actually computing accurate hyperpolarizabilities, the level of theory is relatively unimportant to our study. It is more important that (a) reference hyperpolarizabilities are available from response theory and (b) the method is fast enough to allow us to thoroughly explore different FF approaches. The