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ON ACCURATE HIGH-ORDER NUMERICAL DERIVATIVES COMPUTATIONS FOR QUANTUM CHEMISTRY PURPOSES

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Various molecular parameters in quantum chemistry could be computed as derivatives of energy over different arguments. Unfortunately, it is quite complicated to obtain analytical expression for characteristics that are of interest in the framework of methods that account electron correlation. Especially it relates to the coupled cluster (CC) theory. In such cases, numerical differentiation comes to rescue. This approach, like any other numerical method has empirical parameters and restrictions that require investigation. Current work is called to clarify the details of Finite-Field method usage for high-order derivatives calculation in CC approaches. General approach to the parameter choice and corresponding recommendations about numerical steadiness verification are proposed. As an example of Finite-Field approach implementation characterization of optical properties of fullerene passing process through the aperture of carbon nanotorus is given.

Keywords: energy derivatives, numerical differentiation, finite-field method, coupled cluster theory, hyperpolarizability, DIIS.

Introduction

The bases of Finite-Field method (FF) as an approach for calculations of different molecular parameters (*e.g.* electro-optical properties, shielding constants, *etc.*) were founded in the end of 1960th [1]. Initially FF was used for calculation of polarizabilities of atoms and diatomic molecules for first and second period elements. Its use was restricted by employing the Hartree-Fock method (HF) as a quantum-chemistry approach for in-field system energy calculation. Since then FF is one of the most simple and wide-used methods for energy numerical derivatives computation.

Application of FF for post-HF approximations started at the end of 1970th with appearance of more powerful computation systems. In the first works [2–7] about polarizabilities investigations the configuration interaction (CI) approach was employed. First calculations for di- and triatomic molecules revealed that HF results are in significant divergence with those obtained in more accurate methods. Moreover, the most important circumstance is not only quantitative but qualitative differences. As the result of carried investigations the importance of electron correlation (EC) account became evident.

As computational practice shows [8], account of the EC effects plays essentially important role for π-conjugated systems (especially when high-order susceptibilies are of interest). Usually employed density functional theory (DFT) [9] and second-order many-body perturbation theory (MBPT2) [10] roughly account these effects and for the series of systems are unable to estimate the whole set of desired properties with proper accuracy [8].

It is worth noting that articles devoted to computation of electrical and optical characteristics with FF approach (except several [11]) contain brief information about technical side of the procedure and reliability of presented results. Current work is called to clarify the details of FF implementation and numerical steadiness of proposed derivatives over electric field computation algorithm. As a demonstration the authors' computational complex is employed. Implemented approach uses the PPP (Pariser-Parr-Pople) parameterization for π-electron variant of coupled clusters (CC) singles and doubles (CCSD) method with covalently unbonded ethylene molecules as reference state (cue-CCSD). [12–14]

Derivatives over the electric field strength

Variety of magnitudes in the framework of quantum chemistry could be computed as energy derivatives over corresponding argument. One of the most comprehensive examples is calculation of parameters of system response on external electric field. The change of molecular energy $E\left(\vec{F}\right)$ due to

the action of falling light with significantly large wave-length is described by Buckingham [15] expansion:

$$E\left(\vec{F}\right) = E_0 - \frac{1}{1!}\mu_r F_r - \frac{1}{2!}\alpha_{rs}F_r F_s - \frac{1}{3!}\beta_{rst}F_r F_s F_t - \frac{1}{4!}\gamma_{rstu}F_r F_s F_t F_u - \ldots, \tag{1}$$

where μ_r, α_{rs}, β_{rst} and γ_{rstu} are the components of dipole moment, polarizability, first and second hyperpolarizabilities respectively. Indices $\{r,s,t,u\}$ correspond to axes of Cartesian coordinate system $\{x,y,z\}$. Thus, coefficients (μ_r, α_{rs}, β_{rst}, γ_{rstu}) in equation (1) can be computed as a certain order derivatives of $E\left(\vec{F}\right)$ over the force of applied field F:

$$\mu_r = \frac{\partial E(F)}{\partial F_r}\bigg|_{F=0}, \quad \alpha_{rs} = \frac{\partial^2 E(F)}{\partial F_r \partial F_s}\bigg|_{F=0}, \quad \beta_{rst} = \frac{\partial^3 E(F)}{\partial F_r \partial F_s \partial F_t}\bigg|_{F=0}, \quad \gamma_{rstu} = \frac{\partial^4 E(F)}{\partial F_r \partial F_s \partial F_t \partial F_u}\bigg|_{F=0}. \tag{2}$$

By the analogy with given equations, Brédas et. al. [16,17] proposed an approach that allows to calculate separately every atom contribution to the value of (hyper)polarizabilities. Such method is called Real-Space FF method. Given methodology employs the expansions of dipole moment and charges on atoms in the series by the powers of applied field:

$$\mu_r = \mu_r^0 + \alpha_{rs}F_s + \beta_{rst}F_s F_t + \gamma_{rstu}F_s F_t F_u + \ldots \tag{3}$$

$$q_i = q_i^{(0)} + q_{i,r}^{(\alpha)}F_r + q_{i,rs}^{(\beta)}F_r F_s + q_{i,rst}^{(\gamma)}F_r F_s F_t + \ldots, \tag{4}$$

where for i^{th} atom: $q_i^{(0)}$ – charge in zero field, $q_{i,r}^{(\alpha)}$, $q_{i,rs}^{(\beta)}$ and $q_{i,rst}^{(\gamma)}$ – so-called "hypercharges" that correspond to certain power of F_r. Comparing the equations (3) and (4), it is easy to obtain expression for *e.g. x* component of second hyperpolarizability:

$$\gamma_{xxxx} = \frac{\partial^3 \mu_x}{\partial F_x^3} = \frac{\partial\left(\sum_i q_i x_i\right)}{\partial F_x^3} = \sum_i x_i \frac{\partial^3 q_i}{\partial F_x^3} = \sum_i x_i q_{i,xxx}^{(\gamma)}. \tag{5}$$

It is also worth noting that the elements of reduced density matrix (RDM1) could be computed as energy derivatives [14,18]. It follows from general expression for system energy:

$$E = \sum \rho_{\mu\nu}h_{\nu\mu} + \tfrac{1}{2}\left\langle \rho(12)g(12)\right\rangle \tag{6}$$

thus for atom orbitals (AOs) μ and ν correspondingly:

$$\rho_{\mu\nu} = \frac{1}{2-\delta_{\mu\nu}}\frac{\partial E}{\partial h_{\mu\nu}}, \tag{7}$$

where $h_{\mu\nu}$ is matrix element of core Hamiltonian, $\delta_{\mu\nu}$ – Kronecker delta. Multiplier $1/\left(2-\delta_{\mu\nu}\right)$ presents due to off-diagonal elements contribute twice ($\rho_{\mu\nu} = \rho_{\nu\mu}$) to the system energy. Foregoing scheme is very attractive in π-electron approximation because every atom provides only one AO (p_z–orbital). Also it should be emphasized that in CCSD method the regular linear response theory lead to nonsymmetrical RDM1 matrix ($\rho_{\mu\nu} \neq \rho_{\nu\mu}$ [19,20]). Hence the numerical differentiation (7) is a simple yet physically correct alternative.

Finite Field method

At the present section we provide the details of high-order numerical derivatives computation on the example of (hyper)polarizability calculations. For desired parameters FF method implies following amendment of the unperturbed Hamiltonian $H(0)$:

$$H_{i,j,k} = H(0) + \xi\left(i\hat{X} + j\hat{Y} + k\hat{Z}\right), \tag{8}$$

where $\hat{X}$, $\hat{Y}$ and $\hat{Z}$ – corresponding dipole moment operators; ξ – numerical constant that defines the step of field strength alternation; integers $i,j,k = \ldots \pm 3, \pm 2, \pm 1, 0$ form 3D point grid, where system energy $E_{ijk}^{(xyz)}$ will be calculated. In zero-differential overlap approximation, matrices that represent dipole moment operators are diagonal and contain Cartesian coordinates of atoms.

The points in the 3D grid where system energy to be calculated are defined by the set of desired components and by the symmetry of the molecule under investigation. For example, computation of

geometrical invariant of second hyperpolarizability requires calculation of six derivatives of forth order (among them three cross-components):

$$\langle\gamma\rangle=\frac{1}{5}\left(\gamma_{xxxx}+\gamma_{yyyy}+\gamma_{zzzz}+2\left(\gamma_{xxyy}+\gamma_{xxzz}+\gamma_{yyzz}\right)\right). \tag{9}$$

It means that $3\left(N_p^2-2N_p+1\right)+3\left(N_p-1\right)+1$ points of energy required, where the first summand corresponds to three planes: $E(i,j,0);E(i,0,j);E(0,i,j): i,j\in\left[-N_p,-1\right]\cup\left[1,N_p\right]$, second summand corresponds to three axes: $E(i,0,0);E(0,i,0);E(0,0,i): i\in\left[-N_p,-1\right]\cup\left[1,N_p\right]$ and the last one is zero-field energy. These amount could also be reduced for high symmetric systems. One of the possible approaches for construction of necessary grid is based on calculation of Euclidian distance matrix with atoms and grid points coordinates. Resulting matrix will have following structure (where M – block of molecule atoms and G – block of grid points):

$$D=\begin{pmatrix}MM & MG\\GM & GG\end{pmatrix}. \tag{10}$$

It is known [21] that eigenvector of Euclidian distance matrix that correspond to the biggest absolute eigenvalue contains information about point equivalence. Therefore, analyzing G eigenvector block it is possible to eliminate equal by symmetry grid points.

To obtain numerical energy derivatives there are at least two common approaches: numerical differentiation of Lagrange polynomials (LP) and least squares method (LSM).

For LP interpolating dependence of system energy on the force of applied electrostatic field F is given by the following expression:

$$E(F)=\sum_{i=0}^{N_p}\left[E(i\xi)\cdot\left(\prod_{r=0,r\neq i}^{N_p}\frac{F-i\xi}{i\xi-r\xi}\right)\right], \tag{11}$$

where N_p – number of points in the interpolating polynomial. Differentiation of function (11) in the point $F=0$ gives desired molecular parameters. For example, x components of polarizability α_{xx} and second hyperpolarizability γ_{xxxx} in case $N_p=5\left(\pm2,\pm1,0\right)$ are represented with the following expressions:

$$\alpha_{xx}=\frac{\left[E_x\left(-2\xi\right)-16E_x\left(-\xi\right)+30E(0)-16E_x\left(\xi\right)+E_x\left(2\xi\right)\right]}{12\xi^2}, \tag{12}$$

$$\gamma_{xxxx}=\frac{\left[-E_x\left(-2\xi\right)+4E_x\left(-\xi\right)-6E(0)+4E_x\left(\xi\right)-E_x\left(2\xi\right)\right]}{\xi^4}, \tag{13}$$

where $E_x\left(i\xi\right)$ – system energy in the field applied along x axis with force $i\xi$.

In case of LSM, the problem is reduced to the solution of overdetermined (in general case) linear system of algebraic equations, that characterizes behavior of system energy in fields of different intensity. Metaparameters of the approach are number of averaging points – N_p and maximal polynomial power – N_m:

$$\begin{pmatrix}1 & F_1 & F_1^2 & F_1^3 & F_1^4 & ... & F_1^{N_m}\\1 & F_2 & F_2^2 & F_2^3 & F_2^4 & ... & F_2^{N_m}\\... & ... & ... & ... & ... & ... & ...\\1 & F_{N_p} & F_{N_p}^2 & F_{N_p}^3 & F_{N_p}^4 & ... & F_{N_p}^{N_m}\end{pmatrix}\cdot\begin{pmatrix}E(0)\\\mu/1!\\\alpha/2!\\\beta/3!\\\gamma/4!\\...\\\chi_{N_m}/N_m!\end{pmatrix}=\begin{pmatrix}E(F_1)\\E(F_2)\\...\\E(F_{N_p})\end{pmatrix} \tag{14}$$

or in compact matrix form:

$$A\delta=E. \tag{15}$$

Thus, within selected approach, the solution of FF problem is represented by standard LSM expression:

$$\delta = (A^T A)^{-1} A^T E = GE, \tag{16}$$

where matrix

$$G = (A^T A)^{-1} A^T \tag{17}$$

has order $N_m \times N_p$, at that the numeration of the first dimension is convenient to start with zero, so that for corresponding component of δ vector, i.e. for zero line $G_{0,i}$, the energy of unperturbed system $E(0)$ is given.

It is necessary to mention that characteristic feature of employing LSM for solution of Finite Field problem is possible co-linearity of input data (matrix A). It leads to quasi-degeneration of normal matrix ($A^T A$), and accordingly the standard approaches for its inversion are not applicable.

Within given notation, x components of polarizability α_{xx} and second hyperpolarizability γ_{xxxx} (analogical to (12) and (13) equations) could be represented with following expressions:

$$\alpha_{xx} = (2!) \cdot \sum_{i=1}^{N_p} G_{2,i}^{(x)} E_i^{(x)}, \tag{18}$$

$$\gamma_{xxxx} = (4!) \cdot \sum_{i=1}^{N_p} G_{4,i}^{(x)} E_i^{(x)}. \tag{19}$$

In both cases (LP and LSM) the set of points is taken symmetrical respectively to the unperturbed state:

$$\begin{pmatrix} E(F_1) \\ E(F_2) \\ \cdots \\ E(F_{N_p}) \end{pmatrix} \equiv \begin{pmatrix} E(-N_s \xi) \\ \cdots \\ E(0) \\ \cdots \\ E(N_s \xi) \end{pmatrix}, \tag{20}$$

where $N_s = (N_p + 1)/2$ is shift in the value grid. Such choice is especially reasonable in case of non-symmetric dependence of the energy, i.e. for systems with non-zero dipole moment.

It is worth mentioning that in case of $N_m = N_p$ LSM approach is reduced to the interpolation (system is no more overdetermined). Therefore derivative calculation comply with particular expression, so equations (18) and (19) now lead to expressions equivalent to (12) and (13).

Computation of cross-components (e.g. γ_{xxyy}) in LP approach is based on the use of the expression for mixed derivative:

$$\gamma_{xxyy} = \frac{\partial^2}{\partial^2 y} \frac{\partial^2}{\partial^2 x} E(x,y) = \frac{\partial^2}{\partial^2 y} \left[\frac{\partial^2}{\partial^2 x} E(x,y) \right] = \frac{\partial^2}{\partial^2 y} \alpha_{xx}(y). \tag{21}$$

First, one obtains $\alpha_{xx}(y)$ vector from $E(x,y)$ matrix and then desired cross-component is obtained by differentiating of $\alpha_{xx}(y)$. In LP approach despite $\gamma_{xxyy} \equiv \gamma_{yyxx}$, due to round-off errors these two values are different although insignificantly.

In the framework of LSM computation of any derivative along arbitrary axis is represented with simple enough expression:

$$\frac{\partial^{(k+l+m)}}{\partial^k x \partial^l y \partial^m z} E^{(xyz)} = (k! \cdot l! \cdot m!) \cdot \sum_{i=1}^{N_p} \sum_{j=1}^{N_p} \sum_{a=1}^{N_p} G_{ki}^{(x)} G_{lj}^{(y)} G_{ma}^{(z)} E_{ija}^{(xyz)}. \tag{22}$$

Identity $\gamma_{xxyy} \equiv \gamma_{yyxx}$ is guaranteed reasoning from the commutability of multiplication. The value of γ_{xxyy} ($k=2, l=2, m=0$) in given approach is expressed as

$$\gamma_{xxyy} = \frac{\partial^4}{\partial^2 x \partial^2 y} E^{(xyz)} = (2! \cdot 2! \cdot 0!) \cdot \sum_{i=1}^{N_p} \sum_{j=1}^{N_p} \sum_{a=1}^{N_p} G_{2,i}^{(x)} G_{2,j}^{(y)} G_{0,a}^{(z)} E_{ija}^{(xyz)}. \tag{23}$$

Since zero line in G matrix has following form (unity corresponds to the energy of unperturbed along particular axis system)

$$(0 \quad \cdots \quad 0 \quad 1 \quad 0 \quad \cdots \quad 0), \tag{24}$$

equation (23) simplifies into

$$\gamma_{xxyy} = 4 \cdot \sum_{i=1}^{N_p} \sum_{j=1}^{N_p} G_{2,i}^{(x)} G_{2,j}^{(y)} E_{ij0}^{(xyz)}. \tag{25}$$

Coupled cluster singles and doubles

All energy values were obtained using local π-electron variant of CCSD approach. It is well-known that the quality of (hyper)polarizability estimation is in the strong dependence on the level of EC account. CC theory has recommended itself well in various applications including optical and non-linear optical properties calculations. Computational efficiency, elegance and high accuracy of EC estimation made CC theory approximations the methods of choice.

Implementation of CCSD method is well-known and well-described so the following brief description will be given only for better understanding of material below. The wave-function of CCSD method can be represented in the following form (so-called exponential ansatz):

$$\left|\Psi_{CCSD}\right\rangle = e^{\hat{T}_1+\hat{T}_2}\left|0\right\rangle = \left(1+\hat{T}_1+\frac{1}{2!}\hat{T}_1^2+\hat{T}_2+\frac{1}{3!}\hat{T}_1^3+\hat{T}_1\hat{T}_2+\frac{1}{4!}\hat{T}_1^4+\frac{1}{2!}\hat{T}_2^2+\frac{1}{2!}\hat{T}_1^2\hat{T}_2\right)\left|0\right\rangle, \tag{26}$$

where $\left|0\right\rangle$ — reference determinant, operators $\hat{T}_1$ and $\hat{T}_2$ are cluster operators that generate superposition of singly and doubly excited configurations relatively to reference determinant. Employed methodology is based on the use of unitary group generator (UGA) formalism [22]. Working equations are derived projecting Schrödinger equation onto singly and doubly excited configurations:

$$\Delta_i^a = \left\langle 0E_{ia}\left|\hat{H}-E_{CCSD}\right|e^{\hat{T}_1+\hat{T}_2}\left|0\right\rangle\right., \tag{27}$$

$$\Delta_{ij}^{ab} = \left\langle 0E_{ia}E_{jb}\left|\hat{H}-E_{CCSD}\right|e^{\hat{T}_1+\hat{T}_2}\left|0\right\rangle\right.. \tag{28}$$

Action of product $E_{ai}E_{bj}$ onto reference state $\left|0\right\rangle$ leads to doubly excited configuration [22,23]

$$E_{ai}E_{bj}\left|0\right\rangle = \left|\begin{smallmatrix}a_\alpha b_\alpha\\i_\alpha j_\alpha\end{smallmatrix}\right\rangle + \left|\begin{smallmatrix}a_\beta b_\beta\\i_\beta j_\beta\end{smallmatrix}\right\rangle + \left|\begin{smallmatrix}a_\alpha b_\beta\\i_\alpha j_\beta\end{smallmatrix}\right\rangle + \left|\begin{smallmatrix}a_\beta b_\alpha\\i_\beta j_\alpha\end{smallmatrix}\right\rangle. \tag{29}$$

Given function is a linear combination of two orthogonal functions

$$E_{ai}E_{bj}\left|0\right\rangle = \sqrt{3}\left|\begin{smallmatrix}ab\\ij\end{smallmatrix}(1)\right\rangle - \left|\begin{smallmatrix}ab\\ij\end{smallmatrix}(0)\right\rangle. \tag{30}$$

Permutation of indices for occupied and vacant orbitals in (29) leads to new configuration that is neither equal nor orthogonal to the initial one. To avoid the non-orthogonality problem, and as a consequence to increase the speed of iteration procedure, it is possible to build biorthogonal basis. For doubly excited configurations ($E_{ai}E_{bj}\left|0\right\rangle$ and $E_{bi}E_{aj}\left|0\right\rangle$) it is easy to proof that function $\frac{1}{6}\left\langle 0\left(2E_{ia}E_{jb}+E_{ja}E_{ib}\right)\right|$ satisfies required orthogonality condition. Thus, in addition to equation (28) it is possible to write the following projection scheme:

$$\Delta_{ij}^{ab} = \left\langle 0\left(2E_{ia}E_{jb}+E_{ja}E_{ib}\right)\left|\hat{H}-E_{CCSD}\right|e^{\hat{T}_1+\hat{T}_2}\left|0\right\rangle\right.. \tag{31}$$

In our calculations we used π-electron variant of CCSD method and to construct the reference determinant authors' single-electron basis set of Covalently Unbonded molecules of Ethylenes was employed (CUE). [14]

Direct inverse in the iteration subspace

By the definition, derivative is the ratio of infinitesimal function change on infinitesimal argument change, thus the variation of field strength in FF methodology has to be small enough to guarantee that obtained values are actually derivatives. This obviously implies that energy has to be computed with very high accuracy in order to prevent desired values from the distortion due to round-off errors. Such necessity in turn defines the number of iteration steps to be performed.

In the framework of gradient method, iteration procedure for solution of CC equation can be represented as follows:

$$t^{(k+1)} = t^{(k)} - \alpha^{(k)}\Delta\left(t^{(k)}\right), \tag{32}$$

where k is the number of current iteration, $t^{(k+1)}$ amplitude vector, $\Delta\left(t^{(k)}\right)$ — gradient vector, $\alpha^{(k)}$ — coefficient that defines the "length" of gradient step. In Steepest Descent variation, $\alpha^{(k)}$ value is estimated on every step to reduce the number of iterations taken. However it requires additional calculation of $\Delta\left(\Delta^{(k)}\right)$ that is equal to the cost of iteration. The steepest descent approach is justified only in cases when the acceleration reduces iteration number more than twice. In the simplest approximation $\alpha^{(k)}$ is constant $\alpha^{(k)}=\alpha$. It is manifest that incorrect choice of α will lead either to the divergence (too high α) of iteration procedure or to significant increase (too low α) of calculation duration.

One of the most efficient methods of CCSD solution acceleration is Direct Inverse in the Iterative Subspace (DIIS) [24,25]. Initially this approach was successfully used for SCF problem.

Interpolation DIIS scheme in application to the CCSD method consists in the construction of fixed amplitude vector $\tilde{t}$ that at k^{th} iteration will be expressed through analogical vectors obtained at previous steps

$$\tilde{t}^{(k)} = c_0 t^{(k)} + c_1 t^{(k-1)} + \ldots + c_m t^{(k-m)} \tag{33}$$

with condition

$$\sum_{i=1}^{m} c_i = 1 \cdot \tag{34}$$

In matrix representation, the problem of c_m determination can be written in the form

$$\begin{pmatrix} \langle k|k \rangle & \langle k|k-1 \rangle & \ldots & \langle k|k-m \rangle & 1 \\ \langle k-1|k \rangle & \langle k-1|k-1 \rangle & \ldots & \langle k-1|k-m \rangle & 1 \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ \langle k-m|k \rangle & \langle k-m|k-1 \rangle & \ldots & \langle k-m|k-m \rangle & 1 \\ 1 & 1 & \ldots & 1 & 0 \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \\ \ldots \\ c_m \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \ldots \\ 0 \\ 1 \end{pmatrix}, \tag{35}$$

where matrix elements $\langle k-r|k-s \rangle$ in CCSD method using projection (28) scheme is equal

$$\langle k-r|k-s \rangle = \sum_{ia} \Delta_i^{a(k-r)} \Delta_i^{a(k-s)} + \sum_{(ia)>(jb)} \Delta_{ij}^{ab(k-r)} \Delta_{ij}^{ab(k-s)}, \tag{36}$$

and for (31)

$$\langle k-r|k-s \rangle = \sum_{ia} \Delta_i^{a(k-r)} \Delta_i^{a(k-s)} + \sum_{(ia)>(jb)} \left(2\Delta_{ij}^{ab(k-r)} + \Delta_{ji}^{ab(k-r)} \right) \cdot \left(2\Delta_{ij}^{ab(k-s)} + \Delta_{ji}^{ab(k-s)} \right) \cdot \tag{37}$$

Results and discussion

To estimate efficiency of DIIS procedure it is necessary first to investigate the features of standard approach to CCSD equation solution (eq. 32). For this purpose we will look into dependence of iteration number on the length of iteration step for two systems: polyene $C_{10}H_{12}$ and fulvalene $C_{12}H_{10}$ (Figure 1, A and B respectively). The detailed description of iteration procedure conversion for $C_{10}H_{12}$ in different first order iteration procedures has been investigated in [26]. The hyperpolarizabilities of $C_{10}H_{12}$ and other π-systems in full configuration interaction method were investigated in [27,28,29]. In the present articles we especially interesting in comparison of efficiency for different projection schemes (28) and (31). Also these two systems were selected as representatives of alternant and non-alternant compounds (system B in a contrast to system A has non-zero dipole moment) which as expected will have difference in solution determination.
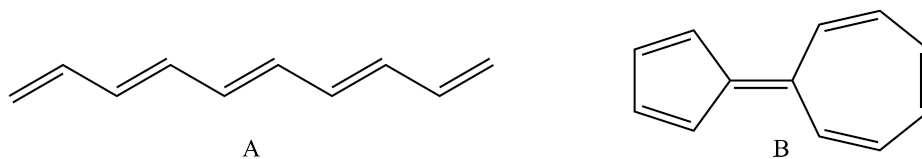

A   B
Figure 1. Systems under consideration.

To figure out the value of the optimal length of iteration step (minimal number of iterations) the series of computations were carried with different α values. Results are presented in Figure 2 for two projection schemes up to the accuracy $\varepsilon = 10^{-13}$ (such strict termination criterion is selected for the maximum correct efficiency estimation).

As seen from the figure, with the increase of α the number of iterations decreases monotonic up to specific value (up to optimum) which rapidly increases after. This growth is connected with oscillation around the minimum of optimizing function. After certain α value divergence is observed.

The Table 1 contains the optimal values for all considered cases. Obtained data shows that every projection scheme is characterized by own values, that generally speaking are close for majority of examined systems. On polyene example established that for eqs. (28) and (31) optimal step length is

0.41 and 0.35 respectively. Projection scheme that employs biorthogonal basis is more efficient in comparison with the standard one.
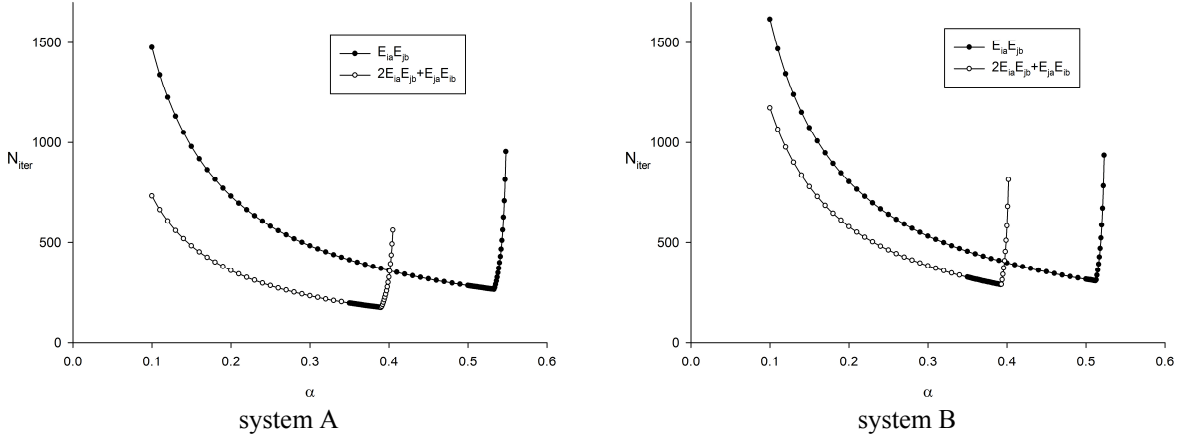

system A   system B

Figure 2. Dependence of iteration number on the length of iteration step within two projection schemes for systems A and B.

Table 1. Optimal values for the length of iteration step and corresponding iteration number.

	system A		system B	
	$\alpha^{(opt)}$	$N_{iter}^{(opt)}$	$\alpha^{(opt)}$	$N_{iter}^{(opt)}$
$E_{ia}E_{jb}$	0.533	266	0.512	308
$2E_{ia}E_{jb} + E_{ja}E_{ib}$	0.389	178	0.392	289

DIIS efficiency estimation will be performed in comparison with optimal values (Table 1). Naturally, such approach is idealized and cannot be observed (because for every particular system it is necessary to find $\alpha^{(opt)}$), however it allows to obtain the lower bound.
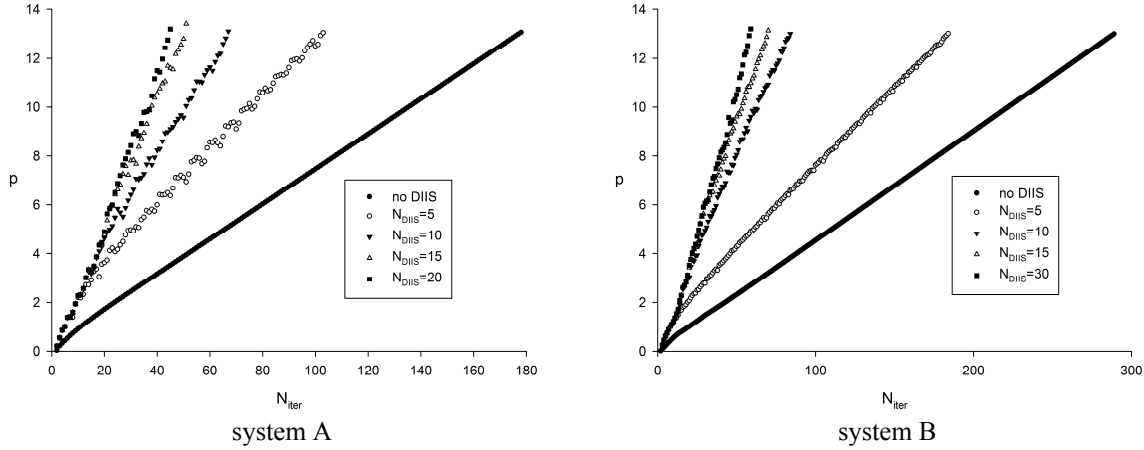

system A   system B

Figure 3. Change of accuracy during CCSD equation solution

First it is necessary to investigate the dependence of the iteration steps number on the quantity of DIIS interpolation points. As an accuracy measure we will use

$$p = -\log_{10} \varepsilon , \qquad (38)$$

where $\varepsilon = \|t\|_2$ is Euclidian norm of the amplitude vector. In Figure 3 the dependence of p on the number of DIIS points is presented (compared to the standard gradient approach – labeled as "no DIIS"). When approximating given dependences with linear function coefficient of the argument

(denoted as v_c) is the velocity of convergence achievement. Then, efficiency can be represented in terms of v_c as the ratio between accelerated with DIIS and standard gradient method:

$$E_v = \frac{v_c^{(DIIS)}}{v_c^{(no\ DIIS)}} . \tag{39}$$

As seen from the Figure 4, for two considered examples (systems A and B) the most efficient interval is from 20 to 30 points. Notably that starting with $N_{DIIS} = 30$ for polyene and with $N_{DIIS} = 40$ for fulvalene the difference between projection schemes vanishes.
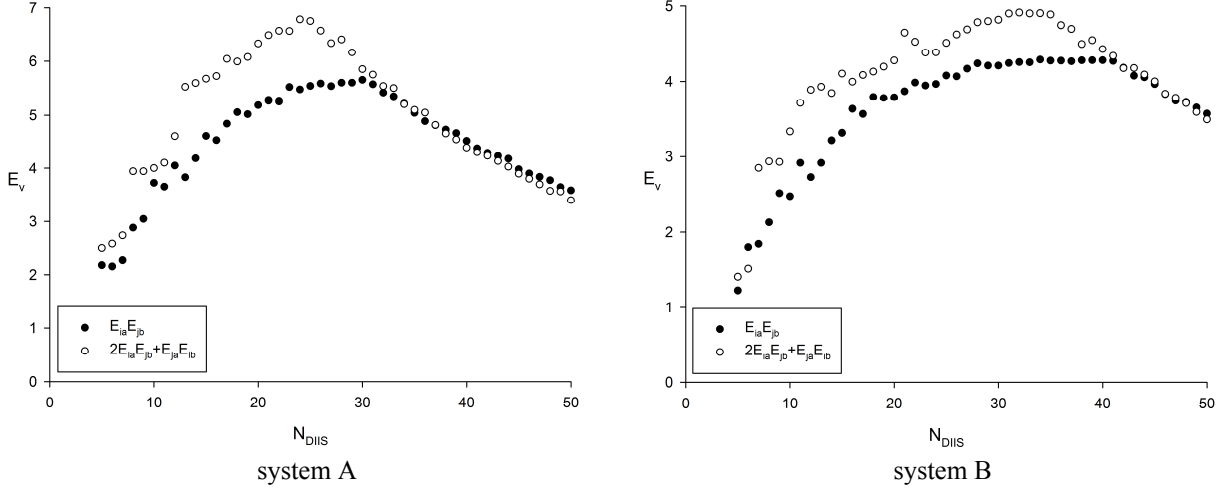

system A   system B

Figure 4. Dependence of DIIS interpolation efficiency E_v on number of DIIS steps N_{DIIS}.

The next objective is ascertainment of the optimal values for FF metaparameters: field step ξ, number of differentiation points N_p and termination criterion p. On the first parameter two intuitive restriction are applied. The first (as mentioned above) – necessity of smallness condition (several hundredths eV/Å). Violating latter restriction leads divergence of observed values with desired magnitudes. Energies obtained in intensive fields are far enough from non-perturbed state (what derivatives are computed for), due to the fact that in standard LSM approach the weights of all points are equal, contribution from high orders increases. Since maximal polynomial power N_m is fixed, it will lead to the overestimation for obtaining coefficients. The second restriction deals with the lower bound of ξ value. In case of small ξ the loss of accuracy and singularity of normal matrix $A^T A$ (due to co-linearity of data) is observed. Limitations of N_p are quite obvious: it can not be less than the maximal derivative order and it should not be too big not to increase computational cost noticeably.

It is evident, that the most sensible to the value of ξ are derivatives of high orders. Thus, the influence of ξ on the computation accuracy will be examined on the values of average second hyperpolarizability $\langle \gamma \rangle$.

For adequate investigation strict iteration procedure termination criterion is selected ($p = 13$). The results are presented in Figure 5. After elapsing unstable area in the region of small fields (up to $5 \cdot 10^{-3}$ eV/Å), $\langle \gamma \rangle$ values ceases changing and the result keeps stable up to the 0.1 eV/Å (deviation is near 5%). According to obtained results, as optimal value of ξ is selected $2 \cdot 10^{-2}$ eV/Å. For this field strength the influence of termination criterion size will be examined varying $p \in [6,13]$. As can be seen from the graph given in Figure 6, the stable region starts from $p = 10$, thus reliable is $p \geq 11$.

Aforesaid argumentation about the optimal/reliable parameters intervals are based on the stability of selected magnitude on the particular range, however the question how close computed derivatives are to the true values of second hyperpolarizability remains unanswered. To get unambiguous proof of particular numerical approach applicability it is necessary to build model function with predefined

coefficients and compare them with calculated ones. In case of system energy dependence on the strength of applied electrostatic field, model function has to expressed as follows

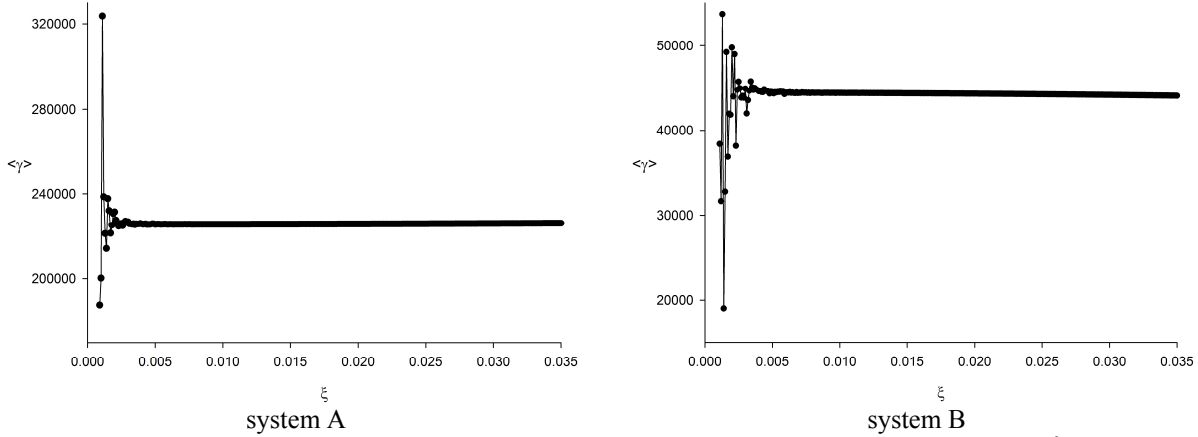$$M(x) = -a_0 + a_1 x - a_2 x^2 + a_3 x^3 - a_4 x^4 + \dots . \tag{40}$$

Figure 5. Dependence of average second hyperpolarizability $\langle \gamma \rangle$ (a.u.) on the ξ (eV/Å)

In addition to the components that correspond to system energy (a_0), dipole moment (a_1), polarizability (a_2), first (a_3) and second (a_4) hyperpolarizabilities, model function has to contain terms of higher orders. Besides, it is obvious that function for systems A and B will have principal differences, since system A has zero dipole moment. It means that coefficients that belong to the odd power of x vanish. Constructed model functions for both systems are presented in the Table 2.
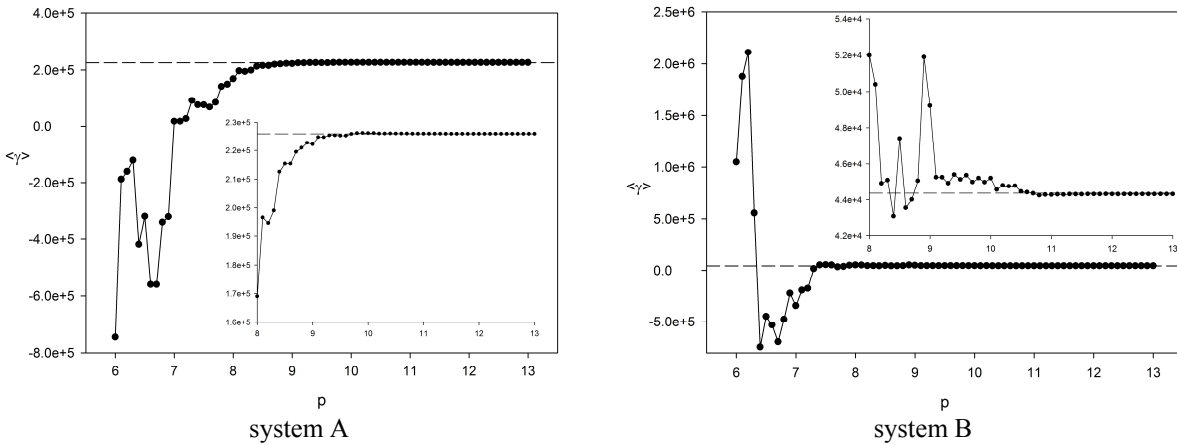

Figure 6. Average second hyperpolarizability as a function of termination criterion p

Table 2. Model function of energy expansion by the power of applied field strength

	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
model A	100	0	1	0	0.1	0	0.1	0	0.05
model B	100	1	1	0.2	0.02	0.1	0.05	0.01	0.03

The numerical steadiness of LSM solution is easy to estimate controlling condition number of normal matrix $A^T A$. For such matrices, condition number is equal to the ratio of the biggest eigenvalue to the smallest one. There is an empiric rule, which according to the number of significant digits lost during the inversion of matrix with condition number κ is equal $L = \log_{10} \kappa$ [30]. Table 3 contains values of L parameter for different combination of numerical differentiation metaparameters.

Table 3. A prior estimation of significant digits quantity lost (L) due to the bad conditionality of $A^T A$ matrix.

ξ (eV/Å)	Number of differentiation points			
	5	7	9	11
0.002	21.3	19.8	18.8	18.0
0.010	15.8	14.3	13.3	12.5
0.020	13.3	11.8	10.8	10.0
0.050	10.3	8.6	7.6	6.8
0.100	7.8	6.3	5.3	4.5

Table 3 data shows that employing standard "float64" type (16 significant digits) is meaningless for strength of applied field less than $1 \cdot 10^{-2}$ eV/Å, due to almost all digits will be lost during $A^T A$ matrix inversions through round-off errors.

Data presented in the Table 4 shows that LP approach for $N_p \geq 7$ shows absolute match of coefficients for model function. Starting with $\xi = 5 \cdot 10^{-2}$ eV/Å LSM demonstrates significant errors relatively to model coefficients. Probably, it is connected with the fact when maximal polynomial power is fixed it is impossible to account high-order terms ($a_5 - a_8$). In the fields of high intensity these contributions will be included in coefficients ($a_0 - a_4$). Exact matching of results for LP and LSM for case of 5 points (except field 0.002 eV/Å, where round-off errors are determining) is the proof of above mentioned consideration about LSM case for non-overdetermined system of equations.

Table 4. Relative errors (%) in model function coefficients determination

ξ (eV/Å)	LP				LSM			
	5	7	9	11	5	7	9	11
	model A, a_4							
0.002	0.07	0.09	0.10	0.10	0.14	-0.01	0.01	0.01
0.010	0.05	0.00	0.00	0.00	0.05	-0.13	0.24	0.38
0.020	0.20	0.00	0.00	0.00	0.20	0.53	0.97	1.52
0.050	1.26	-0.02	0.00	0.00	1.26	3.34	6.16	9.78
0.100	5.11	-0.25	0.00	0.00	5.11	13.86	26.35	43.30
	model B, a_4							
0.002	-0.45	-0.76	-0.96	-1.11	0.08	-0.03	0.07	0.02
0.010	0.12	0.00	0.00	0.00	0.12	0.33	0.60	0.94
0.020	0.50	0.00	0.00	0.00	0.50	1.32	2.42	3.80
0.050	3.14	-0.05	0.00	0.00	3.14	8.37	15.48	24.62
0.100	12.82	-0.74	0.00	0.00	12.82	34.99	67.02	111.02
	model B, a_3							
0.002	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
0.010	0.03	0.00	0.00	0.00	0.03	0.06	0.10	0.16
0.020	0.10	0.00	0.00	0.00	0.10	0.23	0.41	0.63
0.050	0.63	0.00	0.00	0.00	0.63	1.46	2.58	3.99
0.100	2.51	-0.02	0.00	0.00	2.51	5.89	10.46	16.26

Numerical illustrations

To illustrate the use of all mentioned above considerations we have modeled the process of fullerene C_{60} penetration through the aperture of carbon nanotorus. Carbon nanotorus represents the structure of looped single-wall carbon nanotube. In our case we considered tore built of topology (5,0) nanotube with 10 unit cells. Structure on investigated system is given in Figure 7.

Computation was carried with cue$_{(2)}$-CCSD method (see for details [14]) and following FF parameters: $\xi = 2 \cdot 10^{-2}$ eV/Å, $N_p = 7$, $p = 12$. Average iteration step number for every point is near 51 (for $N_{DIIS} = 20$), with the size of optimizing amplitude vector over 1.5 million parameters. Because of high

symmetry, number of energy calculations in different field was reduced from 127 to 76 grid points. Comparison of most significant components obtained for the moment of passing fullerene through nanotorus aperture, i.e. distance between centers $r_{t \leftrightarrow f} = 0$, is presented in the Table 5 (components $\alpha_{xx} = \alpha_{yy}$ and $\gamma_{xxxx} = \gamma_{yyyy}$ due to high symmetry of the system under investigation).
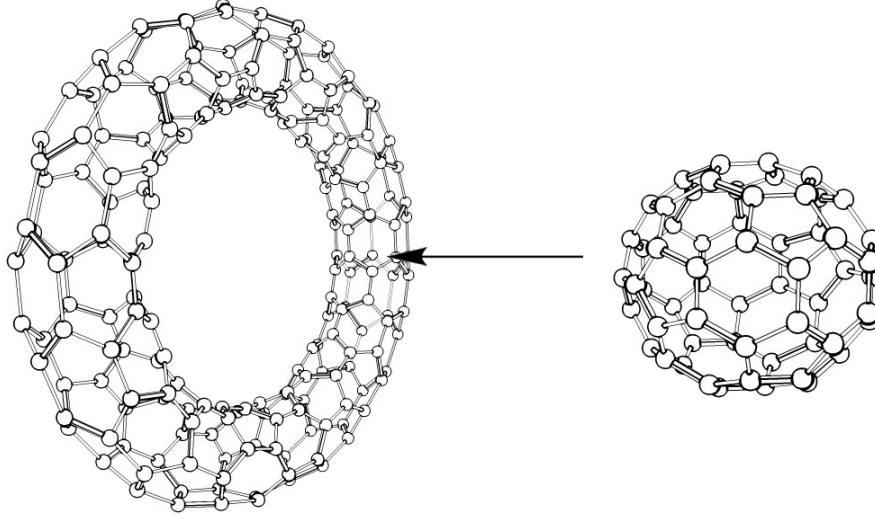

Figure 7. Penetration of fullerene C_{60} through the structure of carbon nanotorus built from carbon nanotube of (5,0) topology with 10 unit cells.

Table 5. Calculated values of polarizability and second hyperpolarizability (a.u.) for $r_{t \leftrightarrow f} = 0$

	N_p		
	$N_p = 5$ (LP/LSM)	$N_p = 7$ LP	$N_p = 7$ LSM
α_{xx}	704.4306	704.4307	704.4300
γ_{xxxx}	$1.2767 \cdot 10^8$	$1.2760 \cdot 10^8$	$1.2778 \cdot 10^8$
γ_{xxyy}	$4.2533 \cdot 10^7$	$4.2530 \cdot 10^7$	$4.2532 \cdot 10^7$

The difference in given values is insignificant that argues for stable solution obtained, therefore results are reliable and following investigation as for differentiation is trustworthy.

To estimate the interaction between fullerene and tore it is convenient to carry using corresponding magnitudes:

$$\eta^{(\alpha)} = 100\% \frac{\langle \alpha \rangle^r}{\langle \alpha \rangle^\Sigma} \tag{41}$$

$$\eta^{(\gamma)} = 100\% \frac{\langle \gamma \rangle^r}{\langle \gamma \rangle^\Sigma} \tag{42}$$

where $\langle \alpha \rangle^r$ and $\langle \gamma \rangle^r$ – average polarizability and second hyperpolarizability on current distance $r_{t \leftrightarrow f}$ between centers; $\langle \alpha \rangle^\Sigma$ and $\langle \gamma \rangle^\Sigma$ are sums of non-interacting molecules that are equal to $5.307 \cdot 10^3$ and $7.658 \cdot 10^7$ atom units respectively. Dependence of values (41), (42) and γ_{zzzz} are presented in Figure 8 and Figure 9 respectively.

In the moment when fullerene is passing through the aperture of tore, the distance between surfaces of molecules is equal 3.5 Å. It satisfies the condition of maximal interaction, decrease of average polarizability is of 4%, while average second hyperpolarizability is slightly more sensitive – 7%. Interaction decays slowly: at distance $r_{t \leftrightarrow f}$ of 40 Å decrease of $\langle \gamma \rangle^r$ is still near 0.5%. It is worth noting (Figure 9) the dependence of γ_{zzzz} (z axis coincides with the direction of fullerene movement) has extremums near $r_{t \leftrightarrow f} = 11$ Å. The reason of it requires posterior investigations.

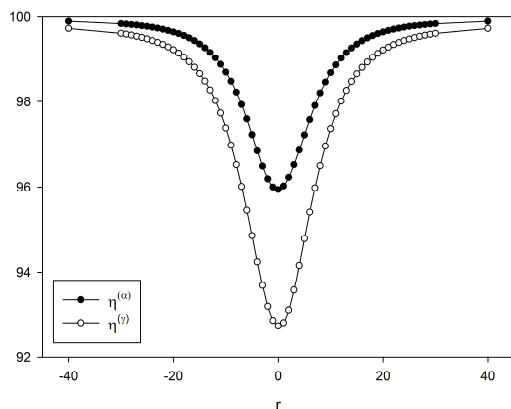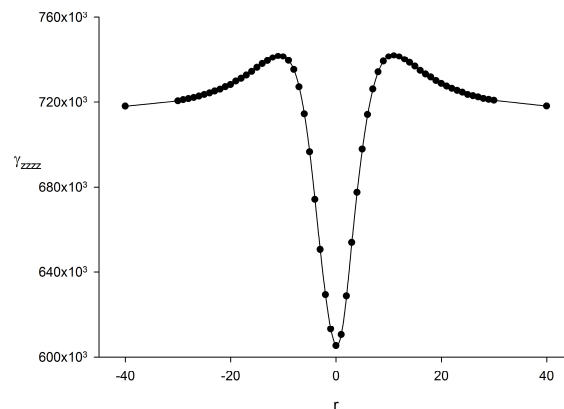**Figure 8.** Dependence of $\eta^{(\alpha)}$ and $\eta^{(\gamma)}$ on the distance between molecules

Figure 9. Dependence of γ_{zzzz} on the distance between molecules

Conclusions

The universal recipe for reliable numerical computation of high-order derivatives is the use of several approaches and comparing their results. In case obtained values are noticeably different, solution is unstable and it is necessary to change metaparameters.

LP does not require derivation of interpolation function for every calculation, corresponding expressions for proper number of points has integer coefficients. For LSM it is also possible not to calculate G matrix equation (27) every time. Since computation of G requires "float128" type one should carry one computation for certain combination of $N_p - \xi$ and to store resulting G values and then use them for derivatives calculation.

The use of LP gives results (as can be concluded from Table 4) that are closer to the desired coefficients of model polynomial so it is preferable to employ LP as numerical approach for high-order derivatives calculation.

Investigated interaction between fullerene and carbon nanotorus fragments revealed that second hyperpolarizability is the most sensitive, so the impact remains up to the distance equal 40 Å. In the limit $r \rightarrow \infty$ values of $\langle \alpha \rangle^r$ and $\langle \gamma \rangle^r$ correctly approaches to $\langle \alpha \rangle^\Sigma$ and $\langle \gamma \rangle^\Sigma$ due to the size-extensivity of coupled cluster energy. However, despite interaction between given fragments has purely dispersion nature, cue$_{(2)}$–CCSD method gives for the state of maximal interaction (3.5 Å) the change of $\langle \gamma \rangle^r$ near 7%.

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А.Б. Захаров, В.В. Иванов. О точных расчетах численных производных высших порядков для нужд квантовой химии.

Различные молекулярные параметры в квантовой химии могут быть рассчитаны как производные от энергии по различным аргументам. К сожалению, получить аналитические выражения для интересующих характеристик в рамках методов, которые учитывают эффекты электронной корреляции не так легко. В особенности это касается теории связанных кластеров (Coupled Cluster, CC). В подобных случаях, на помощь приходит метод численного дифференцирования. Подобный подход, как и любые другие численные методы имеет ряд эмпирических оптимизируемых параметров и ряд ограничений, требующих изучения. Данная работа призвана прояснить детали использования метода конечного поля для расчета производных высших порядков теории CC. Предложен общий подход к выбору параметров и соответствующие рекомендации по оценке численной устойчивости. В качестве примера реализации метода конечного поля выбраны оптические свойства процесса пролета фуллерена сквозь структуру углеродного нанотора.

Ключевые слова: производные от энергии, численное дифференцирование, метод конечного поля, теория связанных кластеров, гиперполяризуемости, DIIS.

А.Б. Захаров, В.В. Іванов. Про точні розрахунки чисельних похідних вищих порядків для потреб квантової хімії.

Різноманітні параметри в квантовій хімії можуть бути розраховані як похідні від енергії по різним аргументам. Як відомо з літературних даних та розрахункового досвіду, якість оцінки оптичних та нелінійно-оптичних параметрів, які можуть бути розраховані як похідні від енергії системи по напруженості зовнішнього електростатичного поля, є у дуже тісному зв'язку із точністю урахування ефектів електронної кореляції. Нажаль, отримати аналітичні вирази для характеристик що цікавлять в рамках таких методів не легко. В особливості це стосується теорії звязаних кластерів (Coupled Cluster, CC). Тому треба прибігати до варіацій методу чисельного диференціювання. Цей підхід, як і більшість чисельних методів має ряд емпіричних параметрів, що оптимізуються та ряд обмежень, які потребують детального вивчення. Дана робота поклкана прояснити особливості використання методу скінченого поля для розрахунків похідних вищих порядків в теорії СС. Запропоновано загальний підхід до вибору параметрів та відповідні рекомендації до оцінки чисельної стійкості. Визначено оптимальний інтервал кроку варіювання напруженості електричного поля та критерію закінчення ітераційної процедури для надійного розрахунку шуканих похідних. Прояснено застосування методу прямого обертання в ітераційному підпросторі для прискорення рішення рівнянь методів теорії зв'язаних кластерів. Розглянуто особливості реалізації альтернативної проекційної схеми та її ефективність у порівнянні із стандартною. На прикладі модельного поліному встановлено, що приоритетним підходом із двох розглянутих є метод інтерполяції за допомогою поліномів Лагранжа. У якості прикладу реалізації методу скінченого поля обрано оптичні властивості фулерену в процесі його проходження крізь вуглецевий нанотор. Встановлено, що найбільший відгук у цьому процесі спостерігається для другої гіперполяризовності та чутливість між двома фрагментами залишається на відстані більше 40 ангстрем.

Ключові слова: похідні від енергії, чисельне диференціювання, метод скінченого поля, теорія зв'язаних кластерів, гіперполяризовності, DIIS.