

# Hartree-Fock limit values of multipole moments, polarizabilities, and hyperpolarizabilities for atoms and diatomic molecules

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(Received 28 November 2014; published 3 February 2015)

Recently it has been demonstrated that the finite difference Hartree-Fock method can be used to deliver highly accurate values of electric multipole moments together with polarizabilities  $\alpha_{zz}$ ,  $A_{z,zz}$ , and hyperpolarizabilities  $\beta_{zzz}$ ,  $\gamma_{zzz}$ ,  $B_{zz,zz}$ , for the ground states of various atomic and diatomic systems. Since these results can be regarded as *de facto* Hartree-Fock limit values their quality is of the utmost importance. This paper reexamines the use of the finite field method to calculate these electric properties, discusses its accuracy, and presents an updated list of the properties for the following atoms and diatomic molecules:  $H^-$ , He, Li,  $Li^+$ ,  $Li^{2+}$ ,  $Li^-$ ,  $Be^{2+}$ , Be,  $B^+$ ,  $C^{2+}$ , Ne,  $Mg^{2+}$ , Mg,  $Al^+$ ,  $Si^{2+}$ , Ar,  $K^+$ ,  $Ca^{2+}$ ,  $Rb^+$ ,  $Sr^{2+}$ ,  $Zr^{4+}$ ,  $He_2$ ,  $Be_2$ ,  $N_2$ ,  $F_2$ ,  $O_2$ , HeNe,  $LiH^{2+}$ , LiCl, LiBr, BH, CO, FH, NaCl, and KF. The potential energy curves and the dependence of the electric properties on the internuclear distance is also studied for  $He_2$ ,  $LiH^+$ ,  $Be_2$ , and HeNe systems.

DOI: [10.1103/PhysRevA.91.022501](https://doi.org/10.1103/PhysRevA.91.022501)

PACS number(s): 32.10.Dk, 31.15.A-, 31.15.xf, 33.15.Kr

## I. INTRODUCTION

The importance of polarizabilities and hyperpolarizabilities is widely recognized since they are needed in the study of the nonlinear optical properties of atomic and molecular systems (see, e.g., [1–3]. Shelton and Rice reviewed measurements and calculations of hyperpolarizabilities for atoms and small molecules [4]. They point out that in the case of methods that obey the Hellman-Feynman theorem, like the Hartree-Fock (HF), multiconfiguration HF or the full configuration interaction method, the properties can be also calculated as the derivative of the dipole moment with respect to an external field. They stress the difficulty when using the finite field approach since the field strength and the number of points must be well chosen to get numerically stable results. Electric static properties of atoms and molecules can in principle be routinely calculated using any of the available quantum chemistry packages but their sensitivity to the choice of basis set is a well-known fact. Several authors have considered the sensitivity of calculated hyperpolarizabilities to the choice of basis set both within the HF model and beyond [5–10]. In the early 1990s the finite difference HF (FD HF) method for diatomic molecules became available to routinely generate total energies and molecular orbitals together with multipole moments of HF limit accuracy [11,12]. Therefore the quality of finite basis sets employed could not only be checked but new basis sets could be constructed and properly calibrated. That was the rationale for developing the distributed universal even-tempered Gaussian basis sets that proved to be able to reproduce the finite difference orbital and total energies to within submicro-Hartree accuracy together with the dipole (hyper)polarizabilities [13–15] (and references therein). The FD HF method also provided HF limit values for examining convergence patterns of properties calculated using correlation-consistent basis sets within the context of complete basis set models and eventually helped in the development of polarization-consistent basis sets [16–18]. The method was also employed to provide the reference values of spectroscopic constants of several diatomic molecules in order to compare

the convergence patterns of the correlation-consistent and polarization-consistent basis sets towards the complete basis set limit [19].

Halkier and Coriani used the FD HF limit value of the electric quadrupole moment of the hydrogen fluoride to estimate the basis set truncation errors when performing the state-of-the-art calculations to determine the full configuration interaction basis set limit value of this property [20]. This work is an apparent demonstration that when accurate post-HF treatment is at stake then the basis set development must guarantee that the HF values are also accurate. Similarly, Pawłowski *et al.* used the FD HF method to obtain the dipole polarizability and the second hyperpolarizability of the Ne atom to estimate basis set errors present in the calculations using the CCS, CC2, CCSD, and CC3 coupled cluster models and Dunning's correlation-consistent basis sets cc-pVXZ augmented with diffuse functions [21].

Those efforts have established the FD HF approach as a reliable source of the HF limit values of electric properties for diatomic molecules calculated using the finite field method. This method is also well suited to studying the electric properties of atoms and their ions. This is due to the fact that atomic systems placed in an external static electric field are of the same symmetry as diatomic molecules and can be well described in the prolate spheroidal coordinate system employed in the FD HF method. Therefore the method was also applied to a number of atomic systems [22,23] and the calculations were carried out using an improved version of the two-dimensional (2D) finite difference Hartree-Fock program [24].

In this paper the FD HF method has been employed to provide reference values of the dipole and quadrupole moments, dipole polarizabilities, the first and second dipole hyperpolarizabilities, and also dipole-quadrupole polarizabilities and dipole-dipole-quadrupole hyperpolarizabilities for the following atomic and diatomic systems:  $H^-$ , He, Li,  $Li^+$ ,  $Li^{2+}$ ,  $Li^-$ ,  $Be^{2+}$ , Be,  $B^+$ ,  $C^{2+}$ , Ne,  $Mg^{2+}$ , Mg,  $Al^+$ ,  $Si^{2+}$ , Ar,  $K^+$ ,  $Ca^{2+}$ ,  $Rb^+$ ,  $Sr^{2+}$ ,  $Zr^{4+}$ , BH, FH,  $F_2$ , CO,  $N_2$ ,  $O_2$ , LiCl, NaCl, KF, and LiBr. The dependence of the interaction energy, the dipole and quadrupole moments as well as the (hyper)polarizabilities of  $He_2$ ,  $LiH^+$ ,  $Be_2$ , and NeHe on the internuclear distance was also studied.

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The reported polarizabilities and hyperpolarizabilities were obtained within the finite field method as numerically evaluated derivatives of dipole and quadrupole moments with respect to the external field. Since the FD HF is capable of producing multipole moments with 10–12 significant figure accuracy the high quality of (hyper)polarizability values can be guaranteed. It is claimed that this approach can lead to the  $\alpha_{zz}$  and  $A_{z,zz}$  polarizabilities of 6–8 significant figures accuracy and the  $\beta_{zzz}$  and  $B_{z,zz}$  hyperpolarizabilities can be quoted with 4–6 digits. The second hyperpolarizability is very sensitive to the quality of the solution of the HF equations and its accuracy can vary from 2 to at most 5 significant figures.

The paper is organized as follows. The next section contains a very succinct presentation of the finite fields FD HF method. Afterwards the accuracy of the calculations for atoms and homo- and heteronuclear molecules (in that order) are discussed for selected systems and the results for other species are given. Finally, the potential energy curves and the dependence of the electric properties on the internuclear distance for a number of small molecules are shown.

## II. METHOD

### A. Finite difference Hartree-Fock method

For a closed-shell,  $N$ -electron, atomic or molecular system the Hartree-Fock equations are a set of  $N$  one-particle (integro-differential) equations (Fock equations) [12,24],

$$F\phi_i = \epsilon_i\phi_i, \quad i = 1, \dots, N, \quad (1)$$

where  $\phi_i = \phi_i(x, y, z, \sigma)$  are spin orbitals forming the Slater determinant,

$$\Phi = \frac{1}{\sqrt{N!}} \det |\phi_{i_1}(1), \phi_{i_2}(2), \dots, \phi_{i_N}(N)|$$

being the approximation to the solution of the Schrödinger equation that minimizes the energy functional,

$$\langle \Phi | - \sum_i \frac{1}{2} \nabla_i^2 - \sum_A \sum_i \frac{Z_A}{r_{iA}} + \sum_{i < j} \frac{1}{r_{ij}} + \sum_{A < B} \frac{Z_A Z_B}{R_{AB}} | \Phi \rangle.$$

The Fock equations can be put in the form,

$$-\frac{1}{2} \nabla^2 \phi_i = - \left( - \sum_A \frac{Z_A}{r_A} + \sum_j [V_C^j - V_x^{ij}] - \epsilon_i \right) \phi_i, \quad (2)$$

where

$$\begin{aligned} \nabla^2 V_C^i &= -4\pi \phi_i^* \phi_i, \\ \nabla^2 V_x^{ij} &= -4\pi \phi_i^* \phi_j \end{aligned} \quad (3)$$

are Poisson equations determining the electron-electron Coulomb and exchange potentials via the single particle and the pair densities, respectively [25]. The Fock equations are solved by the self-consistent field (SCF) iterative procedure and therefore the right-hand sides of Eq. (2) can be treated during each iteration as already known functions since they are determined by the orbitals obtained in the previous iteration [and approximate orbital energies obtained via integration of Eq. (1)]. Thus, not only the Coulomb and exchange potentials

but also the orbitals can be obtained by solving Poisson-type equations.

Diatomic molecules can be described in the prolate spheroidal coordinate system,

$$\begin{aligned} \xi &= (r_A + r_B)/R_{AB} & 1 \leq \xi < \infty, \\ \eta &= (r_A - r_B)/R_{AB} & -1 \leq \eta \leq 1, \\ \theta &\text{ azimuth angle} & 0 \leq \theta \leq 2\pi, \end{aligned}$$

where atoms A and B are placed along  $z$  axis at points  $(0, 0, -R_{AB}/2)$  and  $(0, 0, +R_{AB}/2)$ , and  $r_A$  and  $r_B$  are the distances of a given point from these atomic centers. The cylindrical symmetry of the diatomic systems allows for factoring out (and later treating analytically) the angular part and expressing the orbitals and the potentials in the form,

$$\left. \begin{array}{l} \phi_i \\ V_C^i \\ V_x^{ij} \end{array} \right\} = f(\xi, \eta) e^{im\theta} \quad (4)$$

where the parameter  $m$  is equal to  $0, \pm 1, \pm 2, \pm 3$  for  $\sigma, \pi, \delta$ , and  $\varphi$  type of orbitals, respectively.

In the early 1980s Laaksonen, Pyykkö, and Sundholm proposed a fully numerical scheme for solving these two-dimensional Poisson equations by employing high-order finite differences (FD) to transform the Poisson equations into large and sparse systems of linear equations [12,26]. The method has been improved in various ways over the last two decades by the present author and its latest version has recently been published [24].

To allow for a more accurate and easier description of the orbitals and of the potentials in the vicinity of the nuclei, the transformed variables,

$$\begin{aligned} \nu &= \cos^{-1} \eta & 0 \leq \nu \leq \pi, \\ \mu &= \cosh^{-1} \xi & 0 \leq \mu < \infty, \end{aligned}$$

and, consequently, an equidistant two-dimensional grid in  $\nu$  and  $\mu$  variables can be used. [It is a similar approach to that used in the numerical Hartree-Fock method for atoms where the radial variable  $r$  is transformed into  $\rho = \ln(Zr)$  and the differential equations are solved on an equidistant mesh [27,28].] Thus, the HF Eqs (2) and (3) can be cast in the form of the second-order partial differential equations of the elliptic type,

$$\left\{ A(\mu) \frac{\partial^2}{\partial \mu^2} + B(\mu) \frac{\partial}{\partial \mu} + C(\nu) \frac{\partial^2}{\partial \nu^2} + D(\nu) \frac{\partial}{\partial \nu} + E(\nu, \mu) \right\} u(\nu, \mu) = F(\nu, \mu), \quad (5)$$

which have unique solutions within the region, provided the solution is known along its boundary. In practical applications one cannot impose the boundary conditions at the infinity and therefore the solutions are sought on a rectangular domain,

$$(0, \pi) \times (0, \mu_\infty), \quad \cosh(\mu_\infty) = 2r_\infty/R_{AB},$$

where the parameter  $r_\infty$  must be large enough to guarantee proper boundary conditions. Establishing the boundary values

at  $\mu_\infty$  poses no problem since the asymptotic values of the potential functions  $V_C^j$  and  $V_x^{ij}$  can be evaluated from their multipole expansion and the values of orbitals  $\phi_i$  from the asymptotic form of Eq. (2).

In the FD HF method, the orbital and the potential functions  $u(v, \mu)$  are discretized on this region using meshes with  $N_v$  and  $N_\mu$  points in the respective variables (such a grid is denoted as  $[N_v \times N_\mu / r_\infty]$ ). The partial differential equations of the HF method in the form of Eq. (5) are discretized using an eighth-order central difference expression and the resulting large and sparse systems of linear equations are solved using the successive overrelaxation method which has proved to be both robust and efficient. Various improvements introduced into the FD HF method in the course of its development have resulted in considerable increase in its efficiency and therefore this method can be applied routinely to small- and medium-size diatomic molecules. Of course, as a result of the constant enhancement in computers' performance the notion of the medium-size molecule refers to the larger and larger systems, a decade ago to the systems containing about 10–15 electrons, nowadays 35–45.

The FD HF method is a truly basis-set-independent approach and if the mesh and  $r_\infty$  are chosen adequately the HF orbitals can be obtained to the required accuracy (within double or quadruple precision arithmetic) [24].

TABLE I. Electric properties of the  $\text{Li}^+$  ion calculated by means of the finite field on  $[343 \times 649/200]$  grid using the data from the upper part of the table.  $\mu_z, \alpha_{zz}$ , etc., denote the  $z$  components of the total dipole moment, polarizability, etc., with respect to the center of mass while  $E_T, \mu_z^e$ , and  $\Theta_{zz}^e$  denote the total energy and electric dipole and quadrupole moments for a given field strength. Entries with  $\Delta$  show the properties modified by their respective relative errors  $1 \times 10^{-13}$ ,  $4 \times 10^{-11}$ , and  $2 \times 10^{-9}$ .

Field strength	$E_T$	$\mu_z^e$	$\Theta_{zz}^e$			
−0.004	$-7.236416717250984 \times 10^0$	$-7.579002451511413 \times 10^{-4}$	$-9.341812447945240 \times 10^{-7}$			
−0.002	$-7.236415580401649 \times 10^0$	$-3.789492129942298 \times 10^{-4}$	$-2.335434197489605 \times 10^{-7}$			
0.0	$-7.236415201452712 \times 10^0$	$-1.393329895904571 \times 10^{-4}$	$-5.228456556594097 \times 10^{-14}$			
+0.002	$-7.236415580401760 \times 10^0$	$-3.789492129784786 \times 10^{-4}$	$-2.335434193569130 \times 10^{-7}$			
+0.004	$-7.236416717250201 \times 10^0$	$-7.579002451544477 \times 10^{-4}$	$-9.341812435628704 \times 10^{-7}$			
$\mu_z$	$7 \times 10^{-11}$	$1 \times 10^{-14}$				
$\mu_z + \Delta$	$2 \times 10^{-10}$	$1 \times 10^{-14}$				
$\alpha_{zz}$	0.1894744	0.18947445489				
$\alpha_{zz} + \Delta$	0.1894747	0.18947445490				
$\beta_{zzz}$	$6 \times 10^{-5}$	$1 \times 10^{-8}$				
$\beta_{zzz} + \Delta$	$4 \times 10^{-5}$	$2 \times 10^{-8}$				
$\gamma_{zzzz}$		0.227398				
$\gamma_{zzzz} + \Delta$		0.227399				
$A_{z,zz}$			$8 \times 10^{-14}$			
$A_{z,zz} + \Delta$			$2 \times 10^{-13}$			
$B_{zz,zz}$			−0.1167713978			
$B_{zz,zz} + \Delta$			−0.1167713979			
$F_z$	$\Delta\mu_z^e/\Delta\Theta_{zz}^e$	$\alpha_{zz}$	$\beta_{zzz}$	$\gamma_{zzzz}$	$A_{z,zz}$	$B_{zz,zz}$
$2 \times 10^{-4}$	$4 \times 10^{-10}/2 \times 10^{-6}$	$1.894744547 \times 10^{-1}$	$1 \times 10^{-6}$	$2.33551 \times 10^{-1}$	$1 \times 10^{-11}$	$-1.1677132 \times 10^{-1}$
$4 \times 10^{-4}$	$1 \times 10^{-10}/2 \times 10^{-7}$	$1.894744549 \times 10^{-1}$	$2 \times 10^{-7}$	$2.27516 \times 10^{-1}$	$4 \times 10^{-12}$	$-1.1677141 \times 10^{-1}$
$8 \times 10^{-4}$	$6 \times 10^{-11}/2 \times 10^{-7}$	$1.894744548 \times 10^{-1}$	$3 \times 10^{-8}$	$2.27455 \times 10^{-1}$	$6 \times 10^{-12}$	$-1.1677140 \times 10^{-1}$
$2 \times 10^{-3}$	$4 \times 10^{-11}/2 \times 10^{-9}$	$1.894744549 \times 10^{-1}$	$1 \times 10^{-8}$	$2.27398 \times 10^{-1}$	$8 \times 10^{-14}$	$-1.1677140 \times 10^{-1}$
$4 \times 10^{-3}$	$6 \times 10^{-11}/1 \times 10^{-9}$	$1.894744549 \times 10^{-1}$	$8 \times 10^{-9}$	$2.27413 \times 10^{-1}$	$2 \times 10^{-13}$	$-1.1677140 \times 10^{-1}$
$2 \times 10^{-3}$	$4 \times 10^{-11}/2 \times 10^{-9}$	$1.89474455 \times 10^{-1}$	$1 \times 10^{-8}$	$2.274 \times 10^{-1}$	$8 \times 10^{-14}$	$-1.1677140 \times 10^{-1}$

## B. Static electric properties

The Hamiltonian of a quantum system in a weak, static electric field can be written as [1]

$$H = H_0 - \sum_{\alpha} \mu_{\alpha} F_{\alpha} - \frac{1}{3} \sum_{\alpha, \beta} \Theta_{\alpha\beta} F_{\alpha} F_{\beta} - \dots (\alpha, \beta, \gamma, \delta = x, y, z), \quad (6)$$

and its energy as

$$E = E_0 - \sum_{\alpha} \mu_{\alpha}(0) F_{\alpha} - \frac{1}{2!} \sum_{\alpha, \beta} \alpha_{\alpha\beta} F_{\alpha} F_{\beta} - \frac{1}{3!} \sum_{\alpha, \beta, \gamma} \beta_{\alpha\beta\gamma} F_{\alpha} F_{\beta} F_{\gamma} - \frac{1}{4!} \sum_{\alpha, \beta, \gamma, \delta} \gamma_{\alpha\beta\gamma\delta} F_{\alpha} F_{\beta} F_{\gamma} F_{\delta} - \dots - \frac{1}{3} \sum_{\alpha, \beta} \Theta_{\alpha\beta}(0) F_{\alpha} F_{\beta} - \frac{1}{3} \sum_{\alpha, \beta, \gamma} A_{\gamma, \alpha\beta} F_{\gamma} F_{\alpha} F_{\beta} - \frac{1}{6} B_{\gamma\delta, \alpha\beta} F_{\gamma} F_{\delta} F_{\alpha} F_{\beta} - \dots \quad (7)$$

The electric properties, namely the dipole polarizability  $\alpha_{zz}$ , the first and second dipole hyperpolarizabilities  $\beta_{zzz}$  and  $\gamma_{zzzz}$ , the dipole-quadrupole and dipole-dipole-quadrupole polarizabilities  $A_{z,zz}$  and  $B_{zz,zz}$ , can be evaluated by means of the finite field method. Usually, when algebraic,

TABLE II. Electric properties of the Sr<sup>2+</sup> ion calculated by means of the finite field on [1039 × 1987/200] grid using the data from the upper part of the table.  $\mu_z, \alpha_{zz}$ , etc., denote the  $z$  components of the total dipole moment, polarizability, etc., with respect to the center of mass while  $E_T, \mu_z^e$ , and  $\Theta_{zz}^e$  denote the total energy and electric dipole and quadrupole moments for a given field strength. Entries with  $\Delta$  show the properties modified by their respective relative errors  $2 \times 10^{-13}$ ,  $5 \times 10^{-8}$ , and  $2 \times 10^{-6}$ .

Field strength	$E_T$	$\mu_z^e$	$\Theta_{zz}^e$			
-0.0012	$-3.130\,995\,686\,905\,641 \times 10^3$	$-7.061\,227\,300\,986\,449 \times 10^{-3}$	$-1.551\,909\,834\,235\,485 \times 10^{-5}$			
-0.0006	$-3.130\,995\,683\,727\,841 \times 10^3$	$-3.530\,607\,210\,169\,431 \times 10^{-3}$	$-3.879\,769\,625\,820\,077 \times 10^{-6}$			
0.0	$-3.130\,995\,682\,668\,831 \times 10^3$	$-9.387\,699\,944\,733\,510 \times 10^{-11}$	$-2.648\,433\,258\,838\,013 \times 10^{-11}$			
+0.0006	$-3.130\,995\,683\,727\,801 \times 10^3$	$-3.530\,607\,027\,415\,838 \times 10^{-3}$	$-3.879\,762\,220\,242\,375 \times 10^{-6}$			
+0.0012	$-3.130\,995\,686\,905\,472 \times 10^3$	$-7.061\,227\,119\,725\,404 \times 10^{-3}$	$-1.551\,909\,380\,012\,200 \times 10^{-5}$			
$\mu_z$	$2 \times 10^{-8}$	$9 \times 10^{-11}$				
$\mu_z + \Delta$	$6 \times 10^{-7}$	$9 \times 10^{-11}$				
$\alpha_{zz}$	5.883	5.884 341 6				
$\alpha_{zz} + \Delta$	5.885	5.884 341 7				
$\beta_{zzz}$	0.2	$2 \times 10^{-5}$				
$\beta_{zzz} + \Delta$	2.6	$6 \times 10^{-4}$				
$\gamma_{zzzz}$		60.1				
$\gamma_{zzzz} + \Delta$		61.8				
$A_{z,zz}$			$8 \times 10^{-9}$			
$A_{z,zz} + \Delta$			$2 \times 10^{-8}$			
$B_{zz,zz}$			-21.554 07			
$B_{zz,zz} + \Delta$			-21.554 09			
$F_z$	$\Delta\mu_z^e/\Delta\Theta_{zz}^e$	$\alpha_{zz}$	$\beta_{zzz}$	$\gamma_{zzzz}$	$A_{z,zz}$	$B_{zz,zz}$
$2 \times 10^{-4}$	$2 \times 10^{-7}/4 \times 10^{-6}$	$5.884\,341\,6 \times 10^1$	$9 \times 10^{-5}$	$6.00 \times 10^1$	$5 \times 10^{-9}$	$-2.155\,409 \times 10^1$
$3 \times 10^{-4}$	$1 \times 10^{-7}/5 \times 10^{-5}$	$5.884\,341\,5 \times 10^1$	$2 \times 10^{-4}$	$6.11 \times 10^1$	$8 \times 10^{-8}$	$-2.155\,415 \times 10^1$
$6 \times 10^{-4}$	$5 \times 10^{-8}/2 \times 10^{-6}$	$5.884\,341\,6 \times 10^1$	$1 \times 10^{-5}$	$6.01 \times 10^1$	$9 \times 10^{-9}$	$-2.155\,406 \times 10^1$
$8 \times 10^{-4}$	$3 \times 10^{-8}/8 \times 10^{-6}$	$5.884\,341\,6 \times 10^1$	$1 \times 10^{-4}$	$6.01 \times 10^1$	$3 \times 10^{-8}$	$-2.155\,414 \times 10^1$
$1 \times 10^{-3}$	$3 \times 10^{-6}/8 \times 10^{-6}$	$5.884\,341\,6 \times 10^1$	$3 \times 10^{-4}$	$6.01 \times 10^1$	$4 \times 10^{-10}$	$-2.155\,406 \times 10^1$
$2 \times 10^{-3}$	$5 \times 10^{-7}/5 \times 10^{-4}$	$5.884\,349\,9 \times 10^1$	$2 \times 10^{-3}$	$5.78 \times 10^1$	$6 \times 10^{-6}$	$-2.155\,266 \times 10^1$
$6 \times 10^{-4}$	$5 \times 10^{-8}/2 \times 10^{-6}$	$5.884\,342 \times 10^0$	$6 \times 10^{-4}$	$6.0 \times 10^1$	$1 \times 10^{-8}$	$-2.155\,41 \times 10^1$

basis-set-dependent methods are used to solve the HF equations for atoms and molecules the total energy is more accurately determined than the wave function and therefore the  $E(F_z)$  function (in fact, its discrete representation) is used to evaluate the properties. On the contrary, in the FD HF method the accuracy of the total energy and the corresponding wave function match each other (for a detailed discussion see [24]). Therefore one can get these properties using the following equations:

$$\mu_z(F_z) = \mu_z(0) + \alpha_{zz}F_z + \frac{1}{2}\beta_{zzz}F_z^2 + \frac{1}{6}\gamma_{zzzz}F_z^3 + \dots, \quad (8)$$

$$\Theta_{zz}(F_z) = \Theta_{zz}(0) + A_{z,zz}F_z + \frac{1}{2}B_{zz,zz}F_z^2 + \dots, \quad (9)$$

$$\alpha_{zz} = \left(\frac{d\mu_z}{dF_z}\right)_{F_z=0} \quad \beta_{zzz} = \left(\frac{d^2\mu_z}{dF_z^2}\right)_{F_z=0}$$

$$\gamma_{zzzz} = \left(\frac{d^3\mu_z}{dF_z^3}\right)_{F_z=0}, \quad (10)$$

$$A_{z,zz} = \left(\frac{d\Theta_{zz}}{dF_z}\right)_{F_z=0} \quad B_{zz,zz} = \left(\frac{d^2\Theta_{zz}}{dF_z^2}\right)_{F_z=0}. \quad (11)$$

As a result these equations allow one to calculate the properties in a more numerically stable manner and thus also more accurately.

TABLE III. Dependence of the electric properties of the H<sup>-</sup> ion on the finite field strength (in a.u.).

$F_z$	$\Delta\mu_z^e/\Delta\Theta_{zz}^e$	$\alpha_{zz}$	$\beta_{zzz}$	$\gamma_{zzzz}$	$A_{z,zz}$	$B_{zz,zz}$
$2.5 \times 10^{-5}$	$5 \times 10^{-9}/1 \times 10^{-8}$	$9.140\,589\,7 \times 10^1$	$6 \times 10^{-5}$	$5.9769 \times 10^6$	$6 \times 10^{-9}$	$-7.670\,234 \times 10^4$
$5 \times 10^{-5}$	$3 \times 10^{-9}/4 \times 10^{-9}$	$9.140\,589\,6 \times 10^1$	$2 \times 10^{-4}$	$5.9805 \times 10^6$	$6 \times 10^{-9}$	$-7.670\,232 \times 10^4$
$7.5 \times 10^{-5}$	$2 \times 10^{-9}/1 \times 10^{-9}$	$9.140\,588\,9 \times 10^1$	$4 \times 10^{-6}$	$5.9862 \times 10^6$	$2 \times 10^{-9}$	$-7.670\,226 \times 10^4$
$1 \times 10^{-4}$	$1 \times 10^{-9}/1 \times 10^{-9}$	$9.140\,587\,2 \times 10^1$	$4 \times 10^{-7}$	$5.9944 \times 10^6$	$2 \times 10^{-9}$	$-7.670\,210 \times 10^4$
$7.5 \times 10^{-5}$	$2 \times 10^{-9}/1 \times 10^{-9}$	$9.140\,589 \times 10^1$	$4 \times 10^{-6}$	$5.99 \times 10^6$	$2 \times 10^{-9}$	$-7.670\,23 \times 10^4$

TABLE IV. Polarizabilities and hyperpolarizabilities (in a.u.) of selected atoms and ions obtained by means of the finite field method. Each atomic systems is treated as a diatomic molecule with the B nucleus having zero charge and the internuclear distance set to 2 a.u. In the case of the  $\text{Li}^-$  ion the calculations were also carried out in quadruple precision (QP). The first column lists the systems studied together with the electric field strength,  $F_z$  (in a.u.), and the grid used denoted as  $[N_v \times N_\mu/R_\infty]$ . The rows with a single dipole polarizability value show results of the numerical RHF finite field calculations of Koch and Andrae [29].

System/grid/ $F_z$	$\alpha_{zz}$	$\beta_{zzz}$	$\gamma_{zzzz}$	$A_{z,zz}$	$B_{zz,zz}$
$\text{H}^-$ [649 × 1231/200] $7.5 \times 10^{-5}$	$9.140\,589 \times 10^1$ $9.140\,59 \times 10^1$	$2 \times 10^{-3}$	$5.99 \times 10^6$	$2 \times 10^{-9}$	$-7.670\,2 \times 10^4$
$\text{He}$ [349 × 661/200] $1 \times 10^{-3}$	$1.322\,233\,73 \times 10^0$ $1.322\,23 \times 10^0$	$2 \times 10^{-6}$	$3.604 \times 10^1$	$6 \times 10^{-12}$	$-6.579\,796\,8 \times 10^0$
$\text{Li}$ [445 × 883/250] $1.25 \times 10^{-4}$	$1.701\,201\,9 \times 10^2$	$3 \times 10^{-4}$	$-5.7 \times 10^4$	$1 \times 10^{-7}$	$-5.809\,54 \times 10^4$
$\text{Li}^+$ [343 × 649/200] $2 \times 10^{-3}$	$1.894\,744\,55 \times 10^{-1}$ $1.894\,74 \times 10^{-1}$	$1 \times 10^{-8}$	$2.274 \times 10^{-1}$	$1 \times 10^{-13}$	$-1.167\,714\,0 \times 10^{-1}$
$\text{Li}^{2+}$ [349 × 661/200] $4 \times 10^{-3}$	$5.555\,555\,6 \times 10^{-2}$	$2 \times 10^{-10}$	$2.257\,7 \times 10^{-2}$	$6 \times 10^{-14}$	$-1.623\,228\,2 \times 10^{-2}$
$\text{Li}^-$ [445 × 883/250] $1 \times 10^{-5}$ $1 \times 10^{-5}$ QP	$1.199\,134 \times 10^3$ $1.199\,133\,6 \times 10^3$ $1.199\,13 \times 10^3$	$5.4 \times 10^1$ $2 \times 10^{-7}$	$2.28 \times 10^9$ $2.28 \times 10^9$	$7 \times 10^{-4}$ $5 \times 10^{-12}$	$-1.043\,4 \times 10^7$ $-1.043\,44 \times 10^7$
$\text{Be}^{2+}$ [349 × 643/200] $8 \times 10^{-3}$	$5.185\,735\,6 \times 10^{-2}$ $5.185\,74 \times 10^{-2}$	$3 \times 10^{-9}$	$8.191 \times 10^{-3}$	$1 \times 10^{-13}$	$-8.226\,611 \times 10^{-3}$
$\text{Be}$ [445 × 853/200] $2 \times 10^{-4}$	$4.561\,638\,1 \times 10^1$ $4.561\,64 \times 10^1$	$2 \times 10^{-3}$	$3.912 \times 10^4$	$3 \times 10^{-9}$	$-3.315\,156\,1 \times 10^3$
$\text{B}^+$ [349 × 661/200] $8 \times 10^{-4}$	$1.137\,900\,81 \times 10^1$ $1.137\,90 \times 10^1$	$7 \times 10^{-5}$	$3.501 \times 10^2$	$2 \times 10^{-10}$	$-1.384\,317\,7 \times 10^2$
$\text{C}^{2+}$ [349 × 661/200] $1 \times 10^{-3}$	$4.508\,404\,0 \times 10^0$ $4.508\,40 \times 10^0$	$3 \times 10^{-5}$	$-5 \times 10^{-1}$	$2 \times 10^{-11}$	$-1.738\,099\,57 \times 10^1$
$\text{Ne}$ [349 × 661/200] $2 \times 10^{-3}$	$2.376\,746\,66 \times 10^0$ $2.376\,75 \times 10^0$	$4 \times 10^{-5}$	$6.884 \times 10^2$	$3 \times 10^{-12}$	$-1.303\,830\,86 \times 10^1$
$\text{Mg}^{2+}$ [349 × 661/200] $1 \times 10^{-3}$	$4.700\,407\,0 \times 10^{-1}$ $4.700\,41 \times 10^{-1}$	$3 \times 10^{-6}$	$5.2 \times 10^{-1}$	$1 \times 10^{-11}$	$3.107\,60 \times 10^{-1}$
$\text{Mg}$ [349 × 661/200] $2.5 \times 10^{-4}$	$8.159\,373\,0 \times 10^1$ $8.159\,37 \times 10^1$	$5 \times 10^{-5}$	$1.501 \times 10^5$	$1 \times 10^{-8}$	$-1.074\,371\,2 \times 10^4$
$\text{Al}^+$ [445 × 853/200] $7.5 \times 10^{-4}$	$2.644\,310\,21 \times 10^1$ $2.644\,31 \times 10^1$	$5 \times 10^{-4}$	$2.941 \times 10^3$	$2 \times 10^{-9}$	$-8.071\,986\,9 \times 10^2$
$\text{Si}^{2+}$ [445 × 853/200] $1 \times 10^{-3}$	$1.259\,460\,46 \times 10^1$ $1.259\,46 \times 10^1$	$2 \times 10^{-4}$	$1.154 \times 10^2$	$9 \times 10^{-10}$	$-1.544\,828\,35 \times 10^2$
$\text{Ar}$ [451 × 859/200] $1 \times 10^{-3}$	$1.075\,800\,16 \times 10^1$ $1.075\,80 \times 10^1$	$1 \times 10^{-4}$	$9.603 \times 10^2$	$2 \times 10^{-10}$	$-1.397\,828\,4 \times 10^2$
$\text{K}^+$ [445 × 853/200] $1 \times 10^{-3}$	$5.460\,454\,17 \times 10^0$ $5.460\,45 \times 10^1$	$1 \times 10^{-4}$	$9.35 \times 10^1$	$6 \times 10^{-10}$	$-2.516\,412\,7 \times 10^1$
$\text{Ca}^{2+}$ [451 × 859/200.0] $2 \times 10^{-3}$	$3.260\,676\,9 \times 10^0$ $3.260\,68 \times 10^0$	$1 \times 10^{-5}$	$1.665 \times 10^1$	$4 \times 10^{-10}$	$-6.999\,720\,4 \times 10^0$

TABLE IV. (Continued.)

System/grid/ $F_z$	$\alpha_{zz}$	$\beta_{zzz}$	$\gamma_{zzzz}$	$A_{z,zz}$	$B_{zz,zz}$
Rb <sup>+</sup> [1039 × 1987/200] 1 × 10 <sup>-3</sup>	9.143 821 × 10 <sup>0</sup> 9.143 82 × 10 <sup>0</sup>	4 × 10 <sup>-3</sup>	2.76 × 10 <sup>2</sup>	5 × 10 <sup>-9</sup>	-6.532 556 × 10 <sup>1</sup>
Sr <sup>2+</sup> [103 9 × 1987/200] 6 × 10 <sup>-4</sup>	5.884 341 6 × 10 <sup>0</sup> 5.884 34 × 10 <sup>0</sup>	6 × 10 <sup>-4</sup>	6.0 × 10 <sup>1</sup>	1 × 10 <sup>-8</sup>	-2.155 41 × 10 <sup>1</sup>
Zr <sup>4+</sup> [103 9 × 1987/200] 1 × 10 <sup>-3</sup>	3.036 933 9 × 10 <sup>0</sup> 3.036 93 × 10 <sup>0</sup>	1 × 10 <sup>-4</sup>	6.3 × 10 <sup>0</sup>	1 × 10 <sup>-9</sup>	-4.204 097 × 10 <sup>0</sup>

III. RESULTS

The finite difference HF method together with the finite field method applied along the  $z$  axis have been used to obtain the dipole (hyper)polarizabilities of selected atomic and diatomic systems. The quality of (hyper)polarizability values is directly dependent on the field strength used to produce the raw data, i.e., the dipole and quadrupole moments calculated for the following five field strengths: 0,  $\pm F_z$  and  $\pm 2F_z$ . The first, second, and third derivatives are calculated using the corresponding central difference five-point formulas. The problem is that the field strength has to be small enough to make the Taylor expansion satisfactory and large enough to perform the numerical differentiations to a desired accuracy, i.e., without losing too many significant figures. Moreover, if

too large a field strength is used the HF method may fail to converge.

Let's begin with the analysis of the raw data obtained for the small ionic system Li<sup>+</sup> (cf. Table I) for which highly accurate finite difference solutions of the 2D HF equations are possible. Due to the inversion symmetry of the system the accuracy of the total energy and the electric dipole and quadrupole moments can be estimated by looking at the respective values obtained independently for  $\pm F_z$  field strengths. The relative errors of the total energy are about 10<sup>-13</sup> and they are directly related to the accuracy of the 1 $\sigma$  orbital. The quality of the orbital can be also assessed by accuracy of the  $\mu_z^e$  and  $\Theta_{zz}^e$  values which for  $F_z = 0$  come out 10<sup>-14</sup> and 5 × 10<sup>-15</sup>, respectively. For the nonzero values of the external electric

TABLE V. Electric properties of the homonuclear N<sub>2</sub> molecule ( $R = 2.068$  a.u.) calculated by means of the finite field on [445 × 841/200] grid using the data from the upper part of the table.  $\mu_z, \alpha_{zz}$ , etc., denote the  $z$  components of the total dipole moment, polarizability, etc., with respect to the center of mass while  $E_T, \mu_z^e$ , and  $\Theta_{zz}^e$  denote the total energy and electric dipole and quadrupole moments for a given field strength. Entries with  $\Delta$  show the properties modified by their respective relative errors 2 × 10<sup>-13</sup>, 3 × 10<sup>-11</sup>, and 2 × 10<sup>-12</sup>.

$F_z$	$E_T$	$\mu_z^e$	$\Theta_{zz}^e$
-1.2 × 10 <sup>-3</sup>	-1.089 938 447 722 347 × 10 <sup>2</sup>	-2.392 248 703 020 261 × 10 <sup>-2</sup>	-9.401 253 994 444 838 × 10 <sup>-1</sup>
-0.6 × 10 <sup>-3</sup>	-1.089 938 304 188 615 × 10 <sup>2</sup>	-1.196 104 010 930 643 × 10 <sup>-2</sup>	-9.399 567 475 222 500 × 10 <sup>-1</sup>
-0.0 × 10 <sup>0</sup>	-1.089 938 256 344 605 × 10 <sup>2</sup>	-3.463 895 836 830 488 × 10 <sup>-14</sup>	-9.399 005 371 198 514 × 10 <sup>-1</sup>
+0.6 × 10 <sup>-3</sup>	-1.089 938 304 188 612 × 10 <sup>2</sup>	-1.196 104 010 889 165 × 10 <sup>-2</sup>	-9.399 567 475 231 024 × 10 <sup>-1</sup>
+1.2 × 10 <sup>-3</sup>	-1.089 938 447 722 242 × 10 <sup>2</sup>	-2.392 248 702 996 902 × 10 <sup>-2</sup>	-9.401 253 994 455 708 × 10 <sup>-1</sup>
$\mu_z$	8 × 10 <sup>-10</sup>	3 × 10 <sup>-14</sup>	
$\mu_z + \Delta$	1 × 10 <sup>-8</sup>	3 × 10 <sup>-14</sup>	
$\alpha_{zz}$	1.495 121 × 10 <sup>1</sup>	1.495 121 538 39 × 10 <sup>1</sup>	
$\alpha_{zz} + \Delta$	1.495 125 × 10 <sup>1</sup>	1.495 121 538 42 × 10 <sup>1</sup>	
$\beta_{zzz}$	1 × 10 <sup>-2</sup>	7 × 10 <sup>-7</sup>	
$\beta_{zzz} + \Delta$	3 × 10 <sup>-2</sup>	1 × 10 <sup>-6</sup>	
$\gamma_{zzzz}$		7.945 54 × 10 <sup>2</sup>	
$\gamma_{zzzz} + \Delta$		7.945 56 × 10 <sup>2</sup>	
$A_{z,zz}$			6 × 10 <sup>-10</sup>
$A_{z,zz} + \Delta$			7 × 10 <sup>-10</sup>
$B_{zz,zz}$			-1.756 521 15 × 10 <sup>2</sup>
$B_{zz,zz} + \Delta$			-1.756 521 18 × 10 <sup>2</sup>

  

$F_z$	$\Delta\mu_z^e/\Delta\Theta_{zz}^e$	$\alpha_{zz}$	$\beta_{zzz}$	$\gamma_{zzzz}$	$A_{z,zz}$	$B_{zz,zz}$
4 × 10 <sup>-4</sup>	4 × 10 <sup>-11</sup> /2 × 10 <sup>-12</sup>	1.495 121 539 7 × 10 <sup>1</sup>	3 × 10 <sup>-6</sup>	7.943 × 10 <sup>2</sup>	3 × 10 <sup>-90</sup>	-1.756 521 3 × 10 <sup>2</sup>
5 × 10 <sup>-4</sup>	2 × 10 <sup>-11</sup> /2 × 10 <sup>-12</sup>	1.495 121 539 5 × 10 <sup>1</sup>	2 × 10 <sup>-6</sup>	7.944 60 × 10 <sup>2</sup>	3 × 10 <sup>-90</sup>	-1.756 521 2 × 10 <sup>2</sup>
8 × 10 <sup>-4</sup>	4 × 10 <sup>-11</sup> /2 × 10 <sup>-12</sup>	1.495 121 538 4 × 10 <sup>1</sup>	1 × 10 <sup>-6</sup>	7.945 54 × 10 <sup>2</sup>	6 × 10 <sup>-10</sup>	-1.756 521 15 × 10 <sup>2</sup>
1 × 10 <sup>-3</sup>	3 × 10 <sup>-12</sup> /2 × 10 <sup>-12</sup>	1.495 121 536 5 × 10 <sup>1</sup>	5 × 10 <sup>-8</sup>	7.946 43 × 10 <sup>2</sup>	2 × 10 <sup>-90</sup>	-1.756 521 11 × 10 <sup>2</sup>
8 × 10 <sup>-4</sup>	4 × 10 <sup>-11</sup> /2 × 10 <sup>-12</sup>	1.495 121 54 × 10 <sup>1</sup>	1 × 10 <sup>-6</sup>	7.94622 × 10 <sup>2</sup>	7 × 10 <sup>-10</sup>	-1.756 521 × 10 <sup>2</sup>

TABLE VI. Polarizabilities and hyperpolarizabilities (in a.u.) of selected diatomic homonuclear molecules obtained by means of the finite field method. The first column lists the systems studied together with the internuclear distance in parentheses (a.u.), the grid ( $[N_v \times N_\mu/R_\infty]$ ), and the electric field strength  $F_z$  (in a.u.) used. The second set of the values was obtained using the nonlinear least-squares Marquardt-Levenberg algorithm. The  $\alpha_{zz}$ ,  $\beta_{zzz}$ , and  $\gamma_{zzzz}$  parameters were obtained by fitting a third degree polynomial to five dipole moment values while  $A_{z,zz}$  and  $B_{zz,zz}$  to a polynomial of the second degree and five quadrupole moments.

System/grid/ $F_z$	$\alpha_{zz}$	$\beta_{zzz}$	$\gamma_{zzzz}$	$A_{z,zz}$	$B_{zz,zz}$
He <sub>2</sub> (2.9750) [343 × 607/200]					
$1.5 \times 10^{-3}$	$2.617\,432\,0 \times 10^0$	$-6 \times 10^{-8}$	$-7.864 \times 10^1$	$-5 \times 10^{-12}$	$-1.957\,977 \times 10^1$
	$2.617\,432\,0 \times 10^0$	$-2 \times 10^{-8}$	$-7.864 \times 10^1$	$-1 \times 10^{-11}$	$-1.958\,342 \times 10^1$
Be <sub>2</sub> (3.750) [343 × 583/200]					
$1 \times 10^{-4}$	$2.163\,362\,0 \times 10^2$	$-3 \times 10^{-4}$	$-3.553 \times 10^5$	$-3 \times 10^{-8}$	$-2.860\,762 \times 10^4$
	$2.163\,362\,0 \times 10^2$	$-3 \times 10^{-6}$	$-3.553 \times 10^5$	$-2 \times 10^{-9}$	$-2.860\,988 \times 10^4$
N <sub>2</sub> (2.068) [445 × 841/200]					
$8 \times 10^{-4}$	$1.495\,121\,54 \times 10^1$	$-1 \times 10^{-6}$	$-7.946 \times 10^2$	$-7 \times 10^{-10}$	$-1.756\,521 \times 10^2$
	$1.495\,121\,54 \times 10^1$	$-1 \times 10^{-7}$	$-7.946 \times 10^2$	$-1 \times 10^{-9}$	$-1.756\,727 \times 10^2$
N <sub>2</sub> (2.07432) [445 × 841/200]					
$8 \times 10^{-4}$	$1.503\,043\,81 \times 10^1$	$-7 \times 10^{-7}$	$-8.001 \times 10^2$	$-2 \times 10^{-9}$	$-1.764\,957 \times 10^2$
	$1.503\,043\,81 \times 10^1$	$-2 \times 10^{-7}$	$-8.001 \times 10^2$	$-1 \times 10^{-9}$	$-1.765\,165 \times 10^2$
O <sub>2</sub> (2.28188) [445 × 829/200]					
$8 \times 10^{-4}$	$2.080\,161 \times 10^1$	$-8 \times 10^{-6}$	$-3.680 \times 10^3$	$-2 \times 10^{-10}$	$-1.410\,816 \times 10^2$
	$2.080\,162 \times 10^1$	$-1 \times 10^{-6}$	$-3.680 \times 10^3$	$-1 \times 10^{-9}$	$-1.410\,926 \times 10^2$
F <sub>2</sub> (2.66816) [445 × 805/200]					
$1 \times 10^{-3}$	$1.464\,222\,34 \times 10^1$	$-8 \times 10^{-7}$	$-2.016 \times 10^2$	$-5 \times 10^{-10}$	$-9.006\,44 \times 10^1$
	$1.464\,222\,34 \times 10^1$	$-1 \times 10^{-7}$	$-2.016 \times 10^2$	$-1 \times 10^{-9}$	$-9.007\,56 \times 10^1$

field such accurate orbitals lead to the relative errors of the dipole and quadrupole moments equal to  $4 \times 10^{-11}$  and  $2 \times 10^{-9}$ . Of course, if the dipole moment is calculated as the first derivative of the energy via the five-point finite difference formula its accuracy is lower by 3–4 orders of magnitude. Taking the second and third derivatives lead to the  $\alpha_{zz}$  and  $\beta_{zzz}$  values with only about 6 and 4 significant figures. When, however, the values of the dipole moment are used to calculate the polarizabilities we get the results having 10 and 8 significant figures. The accuracy of the dipole moment is high enough that even the  $\gamma_{zzzz}$  value can be quoted with 5 significant figures. Similarly, the good quality of the quadrupole moments lead to the very accurate values of  $A_{z,zz}$  and  $B_{zz,zz}$ .

The lower part of Table I shows dependence of the polarizabilities and hyperpolarizabilities on the external electric field. Usually four to five different field strengths can be selected that lead to numerically stable values of the properties which can be quoted with 9, 4, and 8 significant figures in case of  $\alpha_{zz}$ ,  $\gamma_{zzzz}$ , and  $B_{zz,zz}$  values, respectively.

Similar analysis can be carried out for the Sr<sup>2+</sup> ion with 36 electrons (cf. Table II). The relative errors of the total energy are about the same as for the Li<sup>+</sup> system, namely,  $2 \times 10^{-13}$  but are larger for the dipole and quadrupole moments ( $5 \times 10^{-8}$  and  $2 \times 10^{-6}$ , respectively). Consequently, for each nonzero field strength the  $\alpha_{zz}$ ,  $\gamma_{zzzz}$ , and  $B_{zz,zz}$  values can be calculated with 8, 3, and 6 significant figures of accuracy. When their dependence on the field is taken into account these properties can be given with 7, 2, and 6 figures.

In case of the Li<sup>+</sup> and Sr<sup>2+</sup> systems the strength of the electric field varied between  $2 \times 10^{-3}$  and  $2 \times 10^{-4}$ . In the case of anions the highest electron is very weakly bound and therefore evaluation of the electric properties by the finite

field method requires an order of magnitude smaller external electric fields. But still the properties can be evaluated in a numerically stable manner and the relative accuracy of the properties is retained as the results for the H<sup>-</sup> ion in Table III show.

Similar calculations and analyses of the electric properties have been carried out for various small- and medium-sized atoms and ions with up to 38 electrons and are collected in Table IV. For such systems the  $\alpha_{zz}$  values have been calculated with 6-digit accuracy by an alternative numerical method by Koch and Andrae [29] and are also included in the table to show the perfect agreement of the one-dimensional and 2D numerical HF methods. When examining these results a few remarks are in place.  $\alpha_{zz}$  is calculated with 7–9 significant figures and the accuracy is not directly dependent on the number of electrons although positively charged ions are usually more accurate than the corresponding neutral species. Anions are most difficult to deal with since the ground-state energy is very small and it is difficult to obtain a well-converged solution when the external electric field is switched on. In the case of the Li<sup>-</sup> ion, the calculations have to be performed in quadruple precision in order to obtain meaningful results. Although the  $\beta_{zzz}$  and  $A_{z,zz}$  values for atoms and ions should be zero by symmetry they are shown in the table as the accuracy indicators of the dipole and quadrupole moments. In fact, their relative errors may serve as a good measure of the number of significant figures at our disposal.

For homonuclear molecules the  $\pm F$  symmetry still holds and therefore the same accuracy analysis can be applied. For example, let's examine the N<sub>2</sub> molecule using the raw data from Table V. Again, the relative error of the total energy is of the order  $10^{-13}$  but the relative errors of the  $\mu_z^e$  and  $\Theta_{zz}^e$  values are even smaller than for the Li<sup>+</sup> ion

TABLE VII. Electric properties of the BH molecule ( $R = 2.3289$ ) calculated by means of the finite field on  $[349 \times 643/200]$  grid using the data from the upper part of the table.  $\mu_z, \alpha_{zz}$ , etc., denote the  $z$  components of the total dipole moment, polarizability, etc., with respect to the center of mass while  $E_T, \mu_z^e$ , and  $\Theta_{zz}^e$  denote the total energy and electric dipole and quadrupole moments for a give field strength. Entries with  $\Delta$  show the properties modified by their respective relative errors  $2 \times 10^{-13}$ ,  $1 \times 10^{-13}$ , and  $5 \times 10^{-13}$ . The bottom part of the table shows the dependence of the properties on the field strength. For each field strength the upper line corresponds to the properties calculated via the differentiation of  $\mu^e(F_z)$  and  $\Theta^e(F_z)$  values while the lower line contains values obtained by the nonlinear least-squares Marquardt-Levenberg algorithm (for  $F_z = 10^{-6}$  the data are missing since in this case the fitting process fails). The last line contains the proposed final values of the properties as derived from the available raw data ( $\mu_z^e, \Theta^e, \Delta\mu_z^e, \Delta\Theta_{zz}^e$ ) and the assessment of the numerical round-off errors.

$F_z$	$E_T$	$\mu_z^e$	$\Theta_{zz}^e$
$-8 \times 10^{-4}$	$-2.513\,202\,401\,817\,104 \times 10^1$	$6.669\,096\,141\,679\,287 \times 10^{-1}$	$-2.675\,820\,974\,028\,706 \times 10^0$
$-4 \times 10^{-4}$	$-2.513\,182\,978\,333\,189 \times 10^1$	$6.759\,377\,210\,087\,856 \times 10^{-1}$	$-2.674\,900\,524\,220\,057 \times 10^0$
$-0 \times 10^0$	$-2.513\,163\,915\,913\,118 \times 10^1$	$6.849\,630\,049\,868\,818 \times 10^{-1}$	$-2.674\,202\,595\,425\,942 \times 10^0$
$+4 \times 10^{-4}$	$-2.513\,145\,214\,466\,877 \times 10^1$	$6.939\,866\,149\,037\,828 \times 10^{-1}$	$-2.673\,726\,944\,061\,716 \times 10^0$
$+8 \times 10^{-4}$	$-2.513\,126\,873\,951\,179 \times 10^1$	$7.030\,096\,933\,983\,243 \times 10^{-1}$	$-2.673\,473\,521\,181\,316 \times 10^0$
$\mu_z$	$6.849\,630\,0 \times 10^{-1}$	$6.849\,630\,049\,869 \times 10^{-1}$	
$\mu_z + \Delta$	$6.849\,629\,9 \times 10^{-1}$	$6.849\,630\,049\,870 \times 10^{-1}$	
$\alpha_{zz}$	$2.256\,062 \times 10^1$	$2.256\,063\,998\,53 \times 10^1$	
$\alpha_{zz} + \Delta$	$2.256\,067 \times 10^1$	$2.256\,063\,998\,52 \times 10^1$	
$\beta_{zzz}$	$-1.04 \times 10^1$	$-1.045\,967\,3 \times 10^1$	
$\beta_{zzz} + \Delta$	$-1.03 \times 10^1$	$-1.045\,967\,2 \times 10^1$	
$\gamma_{zzzz}$		$1.790\,187\,9 \times 10^4$	
$\gamma_{zzzz} + \Delta$		$1.790\,187\,6 \times 10^4$	
$A_{z,zz}$			$-1.466\,914\,254 \times 10^0$
$A_{z,zz} + \Delta$			$-1.466\,914\,256 \times 10^0$
$B_{zz,zz}$			$-1.389\,132\,56 \times 10^3$
$B_{zz,zz} + \Delta$			$-1.389\,132\,57 \times 10^3$

  

$F_z$	$\Delta\mu_z^e/\Delta\Theta_{zz}^e$	$\alpha_{zz}$	$\beta_{zzz}$	$\gamma_{zzzz}$	$A_{z,zz}$	$B_{zz,zz}$
$1 \times 10^{-6}$	$2 \times 10^{-13}/5 \times 10^{-13}$	$2.256\,064\,0 \times 10^1$	$-1.0 \times 10^1$	$5 \times 10^5$	$1.466\,91 \times 10^0$	$-1.39 \times 10^3$
$1 \times 10^{-5}$	$1 \times 10^{-13}/5 \times 10^{-13}$	$2.256\,064\,01 \times 10^1$	$-1.046 \times 10^1$	$1.79 \times 10^4$	$1.466\,914 \times 10^0$	$-1.389\,1 \times 10^3$
		$2.256\,064\,01 \times 10^1$	$-1.046 \times 10^1$	$1.79 \times 10^4$	$1.466\,914 \times 10^0$	$-1.389\,1 \times 10^3$
$1 \times 10^{-4}$	$1 \times 10^{-13}/5 \times 10^{-13}$	$2.256\,064\,013 \times 10^1$	$-1.045\,98 \times 10^1$	$1.789\,56 \times 10^4$	$1.466\,914\,4 \times 10^0$	$-1.389\,133 \times 10^3$
		$2.256\,064\,013 \times 10^1$	$-1.046\,04 \times 10^1$	$1.789\,56 \times 10^4$	$1.466\,927\,3 \times 10^0$	$-1.389\,157 \times 10^3$
$2 \times 10^{-4}$	$2 \times 10^{-13}/4 \times 10^{-13}$	$2.256\,064\,012\,7 \times 10^1$	$-1.045\,97 \times 10^1$	$1.789\,66 \times 10^4$	$1.466\,914\,4 \times 10^0$	$-1.389\,132\,6 \times 10^3$
		$2.256\,064\,012\,7 \times 10^1$	$-1.046\,27 \times 10^1$	$1.789\,66 \times 10^4$	$1.466\,966\,1 \times 10^0$	$-1.389\,229\,5 \times 10^3$
$4 \times 10^{-4}$	$1 \times 10^{-13}/5 \times 10^{-13}$	$2.256\,063\,998\,5 \times 10^1$	$-1.045\,967\,3 \times 10^1$	$1.790\,188 \times 10^4$	$1.466\,914\,25 \times 10^0$	$-1.389\,132\,6 \times 10^3$
		$2.256\,063\,998\,5 \times 10^1$	$-1.047\,194\,6 \times 10^1$	$1.790\,188 \times 10^4$	$1.467\,121\,46 \times 10^0$	$-1.389\,520\,2 \times 10^3$
$6 \times 10^{-4}$	$2 \times 10^{-13}/5 \times 10^{-13}$	$2.256\,063\,936\,7 \times 10^1$	$-1.045\,967\,0 \times 10^1$	$1.791\,079\,3 \times 10^4$	$1.466\,913\,85 \times 10^0$	$-1.389\,132\,34 \times 10^3$
		$2.256\,063\,936\,7 \times 10^1$	$-1.048\,730\,3 \times 10^1$	$1.791\,079\,3 \times 10^4$	$1.467\,381\,26 \times 10^0$	$-1.390\,005\,18 \times 10^3$
$4 \times 10^{-4}$	$1 \times 10^{-13}/5 \times 10^{-13}$	$2.256\,064\,0 \times 10^1$	$-1.045\,97 \times 10^1$	$1.790 \times 10^4$	$1.466\,914 \times 10^0$	$-1.389\,133 \times 10^3$

( $3 \times 10^{-11}$  and  $2 \times 10^{-12}$ , respectively). The accuracy of these moments is only slightly worse than the orbitals themselves because the dipole and quadrupole moments are relatively large quantities for nonzero field strengths. That is why the polarizability can be quoted with 9 significant digits and the second hyperpolarizability with 4. Calculations for atoms and heteronuclear molecules are rather straightforward once the grid is chosen. However, homonuclear systems pose a problem since a weak external electric field breaks the inversion symmetry, and the SCF/SOR iteration process fails to deliver well-converged solutions. It has recently been shown that the problem encountered is due to a near degeneracy of some of the orbitals and consequently the results obtained were not always satisfactory [23,24]. Therefore the electric properties of  $\text{Be}_2$  could be calculated to a desired accuracy and the properties of the  $\text{N}_2, \text{O}_2$ , and  $\text{F}_2$  systems calculated afresh to produce results that are collected in Table VI. Usually the static electric properties are obtained not via

the differentiation of the dipole or quadrupole moments with respect to the field strength but rather by fitting a polynomial to a set of energy values for different field strengths. In order to demonstrate the high quality of the electric properties derived by the numerical differentiation we also calculated them using the nonlinear least-squares Marquardt-Levenberg algorithm (also known as the damped least-squares method) as implemented in the GNU PLOT program [30].  $\alpha_{zz}, \beta_{zzz}$ , and  $\gamma_{zzzz}$  parameters were obtained by fitting a third degree polynomial to five values of the dipole moment while  $A_{z,zz}$  and  $B_{zz,zz}$ —a second-degree polynomial to five values of the quadrupole moment. As one can see both approaches are in perfect agreement except for only small discrepancies in  $B_{zz,zz}$  values.

Now, let's examine the quality of the electric properties one can expect to obtain by applying the finite-field 2D HF method to heteronuclear diatomic systems. Table VII contains the raw data and the derived electric properties for the BH molecule.



TABLE VIII. Polarizabilities and hyperpolarizabilities (in a.u.) of selected diatomic heteronuclear molecules obtained by means of the finite field method. The first column lists the systems studied together with the internuclear distance in parentheses (a.u.), the grid ( $[N_v \times N_\mu/R_\infty]$ ), and the electric field strength  $F_z$  (in a.u.) used. The second set of the values was obtained using the nonlinear least-squares Marquardt-Levenberg algorithm. The  $\alpha_{zz}, \beta_{zzz}$ , and  $\gamma_{zzzz}$  parameters were obtained by fitting a third-degree polynomial to five dipole moment values while  $A_{z,zz}$  and  $B_{zz,zz}$  to a polynomial of the second degree and five quadrupole moments.

System/grid/ $F_z$	$\alpha_{zz}$	$\beta_{zzz}$	$\gamma_{zzzz}$	$A_{z,zz}$	$B_{zz,zz}$
HeNe (2.750) [349 × 643/200]					
$4 \times 10^{-4}$	$2.256\ 064\ 0 \times 10^1$	$-1.045\ 97 \times 10^1$	$-1.790 \times 10^4$	$-1.466\ 914 \times 10^0$	$-1.389\ 133 \times 10^3$
	$2.256\ 064\ 0 \times 10^1$	$-1.047\ 19 \times 10^1$	$-1.790 \times 10^4$	$-1.467\ 121 \times 10^0$	$-1.389\ 520 \times 10^3$
2.750 0	3.764 768 8	$-5.06 \times 10^{-2}$	106	-7.569 820	-21.033
BH (2.3289) [349 × 643/200]					
$4 \times 10^{-4}$	$2.256\ 064\ 0 \times 10^1$	$-1.045\ 97 \times 10^1$	$-1.790 \times 10^4$	$-1.466\ 914 \times 10^0$	$-1.389\ 133 \times 10^3$
	$2.256\ 064\ 0 \times 10^1$	$-1.047\ 19 \times 10^1$	$-1.790 \times 10^4$	$-1.467\ 121 \times 10^0$	$-1.389\ 520 \times 10^3$
BH (2.308) [349 × 643/200]					
$4 \times 10^{-4}$	$2.223\ 991\ 5 \times 10^1$	$-6.835\ 00 \times 10^0$	$-1.766 \times 10^4$	$-5.323\ 36 \times 10^{-1}$	$-1.370\ 953 \times 10^3$
	$2.223\ 991\ 5 \times 10^1$	$-6.846\ 85 \times 10^0$	$-1.766 \times 10^4$	$-5.324\ 66 \times 10^{-1}$	$-1.371\ 336 \times 10^3$
FH (1.7328) [349 × 643/200]					
$1 \times 10^{-3}$	$5.754\ 254\ 56 \times 10^0$	$-8.448\ 11 \times 10^0$	$-2.726 \times 10^2$	$-3.970\ 450\ 4 \times 10^0$	$-5.331\ 56 \times 10^1$
	$5.754\ 254\ 55 \times 10^0$	$-8.448\ 75 \times 10^0$	$-2.726 \times 10^2$	$-3.970\ 666\ 0 \times 10^0$	$-5.332\ 15 \times 10^1$
CO (2.132) [445 × 841/200]					
$8 \times 10^{-4}$	$1.446\ 684\ 8 \times 10^1$	$-3.141\ 087 \times 10^1$	$-1.191 \times 10^3$	$-1.137\ 927\ 6 \times 10^1$	$-2.363\ 381 \times 10^2$
	$1.446\ 684\ 8 \times 10^1$	$-3.141\ 498 \times 10^1$	$-1.191 \times 10^3$	$-1.138\ 063\ 5 \times 10^1$	$-2.363\ 821 \times 10^2$
CO (2.13221) [445 × 841/200]					
$8 \times 10^{-4}$	$1.446\ 899\ 6 \times 10^1$	$-3.141\ 231 \times 10^1$	$-1.191 \times 10^3$	$-1.137\ 888\ 1 \times 10^1$	$-2.363\ 602 \times 10^2$
	$1.446\ 899\ 6 \times 10^1$	$-3.141\ 873 \times 10^1$	$-1.191 \times 10^3$	$-1.138\ 100\ 4 \times 10^1$	$-2.364\ 289 \times 10^2$
LiCl (3.8185) [445 × 763/200]					
$5 \times 10^{-4}$	$2.453\ 247\ 4 \times 10^1$	$-7.906\ 33 \times 10^1$	$-8.88 \times 10^3$	$-1.597\ 068\ 9 \times 10^1$	$-6.694\ 25 \times 10^2$
	$2.453\ 247\ 4 \times 10^1$	$-7.908\ 36 \times 10^1$	$-8.88 \times 10^3$	$-1.597\ 011\ 6 \times 10^1$	$-6.696\ 03 \times 10^2$
NaCl (4.4613) [445 × 739/200]					
$4 \times 10^{-4}$	$2.870\ 018\ 4 \times 10^1$	$-2.227\ 967 \times 10^2$	$-2.550 \times 10^4$	$-6.955\ 908 \times 10^1$	$-9.384\ 75 \times 10^2$
	$2.870\ 018\ 4 \times 10^1$	$-2.229\ 014 \times 10^2$	$-2.550 \times 10^4$	$-6.955\ 769 \times 10^1$	$-9.389\ 08 \times 10^2$
KF (4.1035) [541 × 907/200]					
$8 \times 10^{-4}$	$1.558\ 821 \times 10^1$	$-5.243 \times 10^1$	$-5.19 \times 10^3$	$-2.404\ 027 \times 10^1$	$-3.221\ 1 \times 10^2$
	$1.558\ 821 \times 10^1$	$-5.250 \times 10^1$	$-5.19 \times 10^3$	$-2.404\ 083 \times 10^1$	$-3.223\ 6 \times 10^2$
LiBr (4.10150) [103 9 × 1747/200]					
$2.5 \times 10^{-4}$	$3.405\ 088\ 5 \times 10^1$	$-1.489\ 766 \times 10^2$	$-1.737 \times 10^4$	$-2.734\ 142 \times 10^0$	$-1.333\ 840 \times 10^3$
	$3.405\ 088\ 5 \times 10^1$	$-1.489\ 904 \times 10^2$	$-1.737 \times 10^4$	$-2.735\ 176 \times 10^0$	$-1.333\ 964 \times 10^3$

For such a system the quality of the raw data must be assessed by looking at the orbital norms since there is no longer  $\pm F_z$  symmetry to be exploited. If a grid is too small or the SCF process is not properly converged orbital norms will deviate from unity substantially. Of course orbitals can always be normalized to unity upon completion of the SCF/SOR process but the problem is to have these norms stable in case some additional SCF/SOR iterations are performed. Therefore we can estimate the relative errors of the dipole and quadrupole moments by looking at their sensitivity to the normalization of orbitals. In the case of the BH molecule the relative errors of the dipole and quadrupole moments are  $10^{-13}$  and  $5 \times 10^{-13}$ , respectively, and therefore even the second hyperpolarizability, which is the most difficult property to calculate, can be quoted with 8 digits. This is the accuracy to be expected for each field strength but what really matters is a relative stability of the  $\gamma_{zzzz}$  (and other properties) to changes of the field strength. The lower part of the table demonstrates vividly that the second hyperpolarizability can be at best given with 4-digits accuracy. When the accuracy of the other properties is also examined we can conclude that the finite field method delivers for the BH

molecule results of the same overall quality as for atoms and homonuclear molecules. The results presented in Table VIII show that this is the case for other heteronuclear diatomics with up to 38 electrons.

Having shown that the FD HF method is capable of generating benchmark quality results one can apply it to study the dependence of the total energy, multipole moments, and the static electric properties of the internuclear separation for any diatomic molecule. However, weakly bound diatomic systems are of special interest since they are difficult to treat using algebraic methods [31,32]. See Supplemental Material [33] for tables that present the results for the following van der Waals systems: He<sub>2</sub>, LiH<sup>+</sup>, Be<sub>2</sub>, and HeNe with two tables per system. The first table of each pair shows the  $R$  dependence of the total and binding energy and dipole and quadrupole moments, the other shows the  $R$  dependence of the (hyper)polarizabilities. It is worth noting that for the homonuclear systems the quadrupole moment values tend to zero when the internuclear distance increases and therefore the  $B_{zz,zz}$  values must be given with fewer significant digits. The  $R$  dependence for the F<sub>2</sub> molecule can be found in [23].

#### IV. CONCLUSIONS

The main purpose of this paper is to show that the finite field approach together with the FD HF method can be used to obtain reliable, most accurate, practically HF limit values (within the double precision arithmetic) of the dipole (hyper)polarizabilities of atoms and diatomic molecules. As such these values can be used to calibrate various basis sets used for HF and post-HF calculations and are indispensable for estimating basis set superposition errors. This is especially important when potential energy curves are studied for weakly bound systems. The comparison between the static electric properties

calculated using the finite difference and algebraic HF methods can be found elsewhere [22,23]. It suffices to say that the best available algebraic calculations match very well the numerical results, e.g., in case of  $N_2$  ( $R = 2.07432$  a.u.). Maroulis gives  $\alpha_{zz} = 15.0289$ ,  $\gamma_{zzzz} = 799$ , and  $B_{zz,zz} = 175$  [34].

#### ACKNOWLEDGMENT

The author would like to thank Jan Wasilewski for valuable comments on the manuscript.

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- [1] D. M. Bishop, *Rev. Mod. Phys.* **62**, 343 (1990).  
 [2] D. Burland, *Chem. Rev.* **94**, 1 (1994).  
 [3] H. S. Nalwa and S. Miyata, *Nonlinear Optics of Organic Molecules and Polymers* (CRC Press, Boca Raton, 1997).  
 [4] D. P. Shelton and J. E. Rice, *Chem. Rev.* **94**, 3 (1994).  
 [5] G. H. F. Diercksen and A. J. Sadlej, *J. Chem. Phys.* **90**, 7300 (1987).  
 [6] H. Larsen, C. Hättig, J. Olsen, and P. Jørgensen, *Chem. Phys. Lett.* **291**, 536 (1998).  
 [7] V. E. Ingamells, M. G. Papadopoulos, N. C. Handy, and A. Willetts, *J. Chem. Phys.* **109**, 1845 (1998).  
 [8] G. Maroulis, *J. Chem. Phys.* **108**, 5432 (1998).  
 [9] M. G. Papadopoulos, J. Waite, and A. D. Buckingham, *J. Chem. Phys.* **102**, 371 (1995).  
 [10] G. Maroulis, *J. Mol. Struct. (THEOCHEM)* **633**, 177 (2003).  
 [11] J. Kobus, *Chem. Phys. Lett.* **202**, 7 (1993).  
 [12] J. Kobus, L. Laaksonen, and D. Sundholm, *Comput. Phys. Commun.* **98**, 346 (1996).  
 [13] J. Kobus, D. Moncrieff, and S. Wilson, *Phys. Rev. A* **62**, 062503 (2000).  
 [14] J. Kobus, in *Handbook of Molecular Physics and Quantum Chemistry*, edited by S. Wilson, P. F. Bernath, and R. McWeeny (Wiley, Chichester, 2003), Vol. 2, Chap. 9.  
 [15] J. Kobus, D. Moncrieff, and S. Wilson, *J. Phys. B: At. Mol. Opt. Phys.* **40**, 877 (2007).  
 [16] F. Jensen, *J. Chem. Phys.* **115**, 9113 (2001).  
 [17] F. Jensen, *J. Chem. Phys.* **116**, 7372 (2002).  
 [18] F. Jensen, *J. Chem. Phys.* **117**, 9234 (2002).  
 [19] S. Shahbazian and M. Zahedi, *Theor. Chem. Acc.* **113**, 152 (2005).  
 [20] S. C. A. Halkier, *Chem. Phys. Lett.* **346**, 329 (2001).  
 [21] F. Pawłowski, P. Jørgensen, and C. Hättig, *Chem. Phys. Lett.* **391**, 27 (2004).  
 [22] J. Kobus, *Comp. Lett.* **3**, 71 (2007).  
 [23] J. Kobus, in *Proceedings of International Conference of Computational Methods in Sciences and Engineering (ICCMSE 2009)*, AIP Conf. Proc. No. 1504 (AIP, Melville, NY, 2009), pp. 189–208.  
 [24] J. Kobus, *Comput. Phys. Commun.* **184**, 799 (2013).  
 [25] L. Laaksonen, P. Pyykkö, and D. Sundholm, *Chem. Phys. Lett.* **96**, 1 (1983).  
 [26] L. Laaksonen, P. Pyykkö, and D. Sundholm, *Comput. Phys. Rep.* **4**, 313 (1986).  
 [27] C. F. Fischer, *The Hartree-Fock Method for Atoms. A Numerical Approach* (Wiley, New York, 1977).  
 [28] C. F. Fischer, *Comput. Phys. Commun.* **64**, 431 (1996).  
 [29] V. Koch and D. Andrae, *Int. J. Quantum Chem.* **111**, 891 (2011).  
 [30] T. Williams and C. Kelley, Computer code GNUPLOT 4.6: An Interactive Plotting Program [<http://gnuplot.info>] 2011.  
 [31] R. J. Gdanitz, *Chem. Phys. Lett.* **312**, 578 (1999).  
 [32] I. D. Petsalakis, G. Theodorakopoulos, H.-P. Liebermann, and R. J. Buenker, *J. Chem. Phys.* **115**, 6365 (2001).  
 [33] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevA.91.022501> for Tables IX–XVI containing the  $R$  dependence of the total and binding energy and dipole and quadrupole moments (Tables IX, XI, XIII, XV) and (hyper)polarizabilities (Tables X, XII, XIV, XVI) for  $He_2$ ,  $LiH^+$ ,  $Be_2$ , and  $HeNe$  systems, respectively.  
 [34] G. Maroulis, *J. Chem. Phys.* **118**, 2673 (2003).