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Comparison of the electric moments obtained from finite basis set and finite-difference Hartree-Fock calculations for diatomic molecules

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A comparison is made of the accuracy with which the electric moments μ, Θ, Ω, and Φ can be calculated by using the finite basis set approach (the algebraic approximation) and finite-difference method in calculations employing the Hartree-Fock model for the ground states of 16 diatomic molecules at their experimental equilibrium geometries. Specifically, the 2^n-pole moments $n=1,2,3,4$, for the N_2, CO, BF, CN^-, NO^+, BeF, BO, CN, ${N_2}^+$, AlF, GaF, InF, TlF, MgF, CaF, and SrF molecules are determined using basis sets and grids that have been employed in previous studies of the Hartree-Fock energy.

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I. INTRODUCTION

The algebraic approximation or finite basis set expansion approach is ubiquitous in molecular electronic structure calculations. Although this approximation can often introduce errors that are orders of magnitude greater than the molecular properties under investigation, such calculations are invariably performed under the tacit assumption that the approximate expectation values will approach their exact values as the basis set dimension is increased. Klahn and Morgan [1] demonstrated that this assumption is not always justified. They showed that expectation values of high powers of the position and momentum operators obtained from variational wave functions can diverge or even converge to the wrong limit. In general, ‘‘it is not ... true ... that a sequence of approximate wave functions $\{\psi_N\}_{N=1}^{\infty}$ which yield the correct energy in the limit $N\rightarrow\infty$ will also give the correct expectation value of A as $N\rightarrow\infty$.’’ [1] For Gaussian-type basis functions Klahn and Morgan [1] conclude that ‘‘no problem should occur when approximating $\langle r^k\rangle$ $(k=1,2,3,\ldots)$ with Ritz expansions for the case of one-electron atoms and ions. But not even in this simple case has an analytic proof [of convergence] yet been obtained.’’

Finite-difference methods provide high-precision solutions of the Hartree-Fock equations for diatomic molecules with which the results of matrix Hartree-Fock (MHF) calculations can be compared. In 1993, it was demonstrated [2,3] that molecular basis sets can be systematically constructed so as to support total Hartree-Fock energies of an accuracy approaching that achieved in finite-difference calculations [4]; namely, ~ 1 μhartree. Over the past six years, improvements in finite-difference algorithms have supported higher accuracy and facilitated applications to closed-shell diatomic systems containing a heavy atom [5,6], to open-shell species [7] and, very recently, to open-shell systems containing a heavy atom [8]. During the same period, there have been corresponding improvements in the effective implementation of the algebraic approximation [5–8].

The Hartree-Fock model is of particular interest not only because it represents the first stage in the vast majority of contemporary theoretical treatments of the molecular electronic structure problem but also because exact expectations are available from finite-difference techniques within this model that enable a precise measurement of the accuracy of our matrix Hartree-Fock results. It should also be remembered that a knowledge of the exact Hartree-Fock expectation values is an essential ingredient of any study of the correlation effects.

An important application of finite-difference Hartree-Fock studies for diatomic molecules [9,10] is in providing a measure of the basis set truncation error in calculations carried out within the algebraic approximation [5–8,11–14]. Most frequently, this comparison has involved total energies and orbital energies, but visualization techniques have also been used [11] to examine orbital amplitude difference functions. A comparison of the multipole moments obtained from finite basis set calculations in which the algebraic approximation is systematically implemented with the corresponding finite-difference Hartree-Fock moments for diatomic molecules can be expected to afford a more detailed measure of the quality of the finite basis set results than comparisons of total energy value alone. In 1985, Bounds and Wilson [15] made such a comparison for the HF, CO, and N_2 ground states, however, not only were the basis sets employed of lower quality than those used in the present study, but also they compared with partial-wave numerical Hartree-Fock calculations [16,17] that did not match the accuracy achieved in the finite-difference studies reported here. Very recently, we have reported a comparison of dipole moments for three neutral, open-shell systems BeF, BO, and CN [7].

In this paper, we compare Hartree-Fock calculations of the electric moments μ, Θ, Ω, and Φ using finite basis set expansions and finite-difference techniques for sixteen diatomic species for which total Hartree-Fock energies have been reported previously [5–8,11–14]. We aim to provide numerical evidence that, with a suitable choice of Gaussian basis set, it is possible to achieve convergence of molecular multipole moments to their Hartree-Fock values. We compare the pattern of convergence of the multipole-moment expectation values as the size of the basis set is increased with that of the total energy. We report dipole, quadrupole, octupole, and hexadecapole moments for five closed-shell diatomic molecules containing only first-row atoms; for four open-shell, first-row diatomic species; for five closed-shell, group IIIb fluorides containing increasingly heavy atoms, and for four open-shell, group IIa fluorides. Specifically, we report the multipole moments for the following molecules in their ground electronic states at their respective experimental equilibrium geometries: N_2, CO, BF, CN^-, NO^+, BeF, BO, CN, $N_2{}^+$, AlF, GaF, InF, TlF, MgF, CaF, and SrF. The electronic configurations and geometries of the systems studied have been defined in our previous work [5–8,11–14].

In Sec. II, the theoretical aspects of the present study are given. This serves to establish notation and the definitions of the quantities calculated. The computational methods employed are described in Sec. III, while in Sec. IV the results are presented and discussed. Section V contains our conclusions.

II. THEORY

Our purpose here is both to establish notation and to give definitions of the multipole moments in the case of diatomic molecules.

The Hamiltonian operator for a molecule in weak interaction with a fixed external field may be written as a Taylor expansion about some chosen point [18–24]

$$H=H_0-\sum_{\alpha}\mu_\alpha F_\alpha-\frac{1}{3}\sum_{\alpha,\beta}\Theta_{\alpha\beta}F_{\alpha\beta}-\frac{1}{15}\sum_{\alpha,\beta,\gamma}\Omega_{\alpha\beta\gamma}F_{\alpha\beta\gamma}-\frac{1}{105}\sum_{\alpha,\beta,\gamma,\delta}\Phi_{\alpha\beta\gamma\delta}F_{\alpha\beta\gamma\delta}-\cdots\quad(\alpha,\beta=x,y,z),\qquad(1)$$

where H_0 is the Hamiltonian of the free molecule. F_α is the field at the origin, $F_{\alpha\beta}$ is the field gradient at the chosen expansion center, etc. μ_α is the dipole moment, $\Theta_{\alpha\beta}$ is the quadrupole moment, $\Omega_{\alpha\beta\gamma}$ is the octupole moment, and $\Phi_{\alpha\beta\gamma\delta}$ is the hexadecapole moment. The energy of the molecule is

$$\begin{aligned}E&=\langle\Psi|H|\Psi\rangle\\&=E_0-\sum_{\alpha}\mu_\alpha^{(0)}F_\alpha-\frac{1}{2!}\sum_{\alpha,\beta}\alpha_{\alpha\beta}F_\alpha F_\beta\\&\quad-\frac{1}{3!}\sum_{\alpha,\beta,\gamma}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma\\&\quad-\frac{1}{4!}\sum_{\alpha,\beta,\gamma,\delta}\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta-\cdots-\frac{1}{3}\sum_{\alpha,\beta}\Theta_{\alpha\beta}^{(0)}F_{\alpha\beta}\\&\quad-\frac{1}{3}\sum_{\alpha,\beta,\gamma}A_{\gamma,\alpha\beta}F_\gamma F_{\alpha\beta}-\frac{1}{6}\sum_{\alpha,\beta,\gamma,\delta}B_{\alpha\beta,\gamma\delta}F_\alpha F_\beta F_{\gamma\delta}-\cdots\\&\quad-\frac{1}{15}\sum_{\alpha,\beta,\gamma}\Omega_{\alpha\beta\gamma}^{(0)}F_{\alpha\beta\gamma}-\frac{1}{6}\sum_{\alpha,\beta,\gamma,\delta}C_{\alpha\beta,\gamma\delta}F_{\alpha\beta}F_{\gamma\delta}-\cdots\\&\quad-\frac{1}{105}\sum_{\alpha,\beta,\gamma,\delta}\Phi_{\alpha\beta\gamma\delta}^{(0)}F_{\alpha\beta\gamma\delta}-\frac{1}{15}\sum_{\alpha,\beta,\gamma,\delta}E_{\alpha,\beta\gamma\delta}F_\alpha F_{\beta\gamma\delta}\\&\quad-\cdots,\end{aligned}\qquad(2)$$

where $\mu_\alpha^{(0)}$ is the permanent dipole moment, $\Theta_{\alpha\beta}^{(0)}$ is the permanent quadrupole moment, $\Omega_{\alpha\beta\gamma}^{(0)}$ is the permanent octupole moment, and $\Phi_{\alpha\beta\gamma\delta}^{(0)}$ is the permanent hexadecapole moment. $\alpha_{\alpha\beta}$ is the dipole polarizability and $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ are the hyperpolarizabilities. $A_{\gamma,\alpha\beta}$ is the dipole-quadrupole polarizability, $E_{\alpha,\beta\gamma\delta}$ is the dipole-octupole polarizability, $C_{\alpha\beta,\gamma\delta}$ is the quadrupole polarizability and $B_{\alpha\beta,\gamma\delta}$ is the dipole-dipole-quadrupole hyperpolarizability.

The dipole moment may be written as the expansion

$$\begin{aligned}\mu_\alpha&=\mu_\alpha^{(0)}+\sum_{\beta}\alpha_{\alpha\beta}F_\beta+\frac{1}{2}\sum_{\beta,\gamma}\beta_{\alpha\beta\gamma}F_\beta F_\gamma\\&\quad+\frac{1}{3}\sum_{\beta,\gamma,\delta}\gamma_{\alpha\beta\gamma\delta}F_\beta F_\gamma F_\delta+\cdots+\frac{1}{3}\sum_{\beta,\gamma}A_{\alpha,\beta\gamma}F_{\beta\gamma}\\&\quad+\frac{1}{6}\sum_{\beta,\gamma,\delta}B_{\alpha\beta,\gamma\delta}F_\beta F_{\gamma\delta}+\cdots,\end{aligned}\qquad(3)$$

the quadrupole moment as the expansion

$$\begin{aligned}\Theta_{\alpha\beta}&=\Theta_{\alpha\beta}^{(0)}+\sum_{\gamma}A_{\gamma,\alpha\beta}F_\gamma+\frac{1}{2}\sum_{\gamma,\delta}B_{\gamma\delta,\alpha\beta}F_\gamma F_\delta+\cdots\\&\quad+\sum_{\gamma,\delta}C_{\alpha\beta,\gamma\delta}F_{\gamma\delta}+\cdots,\end{aligned}\qquad(4)$$

and the octupole moment may be expressed in the form

$$\Omega_{\alpha\beta\gamma}=\Omega_{\alpha\beta\gamma}^{(0)}+\sum_{\delta}E_{\delta,\alpha\beta\gamma}F_\delta+\cdots.\qquad(5)$$

In the matrix Hartree-Fock calculations carried out in the present study, the total multipole moments for a given molecule were determined as tensor quantities, the 2^n-pole being an n-rank tensor that has the following explicit form for the first five values of n:

$$q=\sum_A Z_A-\int\rho dv,\quad n=0,\qquad(6)$$

$$\mu_\alpha=\sum_A Z_A R_{A\alpha}-\int r_\alpha\rho dv,\quad n=1,\qquad(7)$$

$$Q_{\alpha\beta}=\sum_A Z_A R_{A\alpha}R_{A\beta}-\int r_\alpha r_\beta\rho dv,\quad n=2,\qquad(8)$$

$$R_{\alpha\beta\gamma}=\sum_A Z_A R_{A\alpha}R_{A\beta}R_{A\gamma}-\int r_\alpha r_\beta r_\gamma\rho dv,\quad n=3,\qquad(9)$$

$$S_{\alpha\beta\gamma\delta}=\sum_A Z_A R_{A\alpha}R_{A\beta}R_{A\gamma}R_{A\delta}-\int r_\alpha r_\beta r_\gamma r_\delta\rho dv,\quad n=4.\qquad(10)$$

In these expressions, Z_A is the charge of nucleus A and (R_{Ax},R_{Ay},R_{Az}) are its Cartesian coordinates. ρ is the total electronic charge distribution and r_α is the α coordinate of the electronic charge. The multipole moments are symmetric in all indices. Only the lowest nonzero moment is independent of the choice of origin. In the present matrix Hartree-Fock calculations, the moments were calculated with respect to the center of nuclear charge in cases where only atom-centered basis functions were used and with respect to an arbitrarily chosen center when bond-centered functions were employed. However, for quadrupole moments and higher moments it is often convenient to use alternative definitions.

For a system with an axis of symmetry, it is convenient to define the multipole moments as irreducible tensors [21]. In such a case, there is only one independent component for each electric multipole moment and this can be defined as follows:

$$M^{(k)}=\sum_{A} Z_A R_{Az}^{k}-\int r^k P_k(z/r)\rho dv, \tag{11}$$

where P_k are Legendre polynomials of degree k. Values of $M^{(k)}$, $k=1,2,3,4$ were evaluated from the orbitals determined by the finite-difference Hartree-Fock program. Specifically, the first four moments defined in this way are

$$M^{(1)}\equiv\mu=\mu_z, \tag{12}$$

$$M^{(2)}\equiv\Theta=\Theta_{zz}, \tag{13}$$

$$M^{(3)}\equiv\Omega=\Omega_{zzz}, \tag{14}$$

$$M^{(4)}\equiv\Phi=\Phi_{zzzz}. \tag{15}$$

These moments were determined with respect to the geometrical center, i.e., the bond midpoint, in the finite-difference Hartree-Fock (FD-HF) calculations.

The multipole moments determined from the matrix Hartree-Fock calculations can be related to irreducible tensor form evaluated by the finite-difference Hartree-Fock program as follows:

$$\Theta_{zz}=Q_{zz}-\frac{1}{2}(Q_{xx}+Q_{yy}),$$

$$\Omega_{zzz}=R_{zzz}-\frac{3}{2}(R_{xxz}+R_{yyz}), \tag{16}$$

$$\Phi_{zzzz}=S_{zzzz}-3(S_{xxzz}+S_{yyzz})+\frac{3}{8}(S_{xxxx}+2S_{xxyy}+S_{yyyy}),$$

in which all quantities are transformed so as to refer to the same origin, the bond midpoint.

III. COMPUTATIONAL METHODS

The finite basis sets of even-tempered, spherical harmonic Gaussian functions [25] employed in the present study are those defined in our previous work [5–8,11–14] on the titled species. Basis subsets were centered on each atomic center. Functions of *s*, *p*, *d*, and *f* symmetry were located on the nuclei of first-row atoms, while on heavier atoms the highest symmetry type included was $l+2$, where l is the highest symmetry type arising in the Hartree-Fock description of the closed-shell atom. For example, for *Sr* the highest symmetry type included is $l+2=4$, i.e., *g* functions. A basis subset of functions centered on the bond midpoint, designated *bc*, was also included. The functions in this subset were of *s*, *p*, *d*, and *f* symmetry. The finite basis set calculations were performed with the commercially available GAUSSIAN94 programs of Frisch *et al.* [26].

Most of the multipole moments derived from finite-difference Hartree-Fock calculations were determined using the grids defined in our previous studies of the titled systems [5–8,11–14]. Improved grids were employed for BF and for N_2. All finite-difference Hartree-Fock calculations reported in this paper were carried out with the program[1] of Kobus *et al.* [27–29]. The formulation of the restricted open-shell Hartree-Fock problem for diatomic molecules employed in the present study follows the standard treatment given by, for example, Hurley [30] (p. 242 ff), with the N particle wave function taken to be a single Slater determinant.

In this work, 2^n-pole moments are given in D Å^{n-1}. The relevant conversion factors [31] to SI units are 1D $\approx 3.33\,564\times10^{-30}$ Cm and 1 Å$=10^{-10}$ m.

IV. RESULTS AND DISCUSSION

A. Convergence of μ, Θ, Ω, and Φ for BeF in the algebraic approximation

In 1960, Löwdin [32] presented a simple example of a sequence of approximate wave functions that converged correctly in the *mean* but for which the corresponding dipole moments do not converge. In 1984, Klahn and Morgan [1] made the distinction between operators A that are *relatively form-bounded* by the kinetic energy operator T, i.e.,

$$|\langle f|A|f\rangle|\leqslant a\langle f|f\rangle+b\langle f|T|f\rangle,\quad |f\rangle\in D(T), \tag{17}$$

where a and b are positive constants and $D(T)$ is the domain of T, and those operators that are not. For operators satisfying Eq. (17) completeness of the basis set in the Sobolev space $\mathbf{W}_2^{(1)}$, which is required for convergence of the energy, also guarantees convergence of the expectation value of A. For operators that do not satisfy Eq. (17), Klahn and Morgan [1] showed that $\mathbf{W}_2^{(1)}$ completeness of the basis set and thus convergence of the energy is not sufficient to support convergence of the expectation value. They showed that convergence of an expectation value of A is closely related to the *rate* of convergence of the energy which, in turn, is known to depend on the ability of the basis functions to describe singularities in the exact solutions [33].

In this work, we compare

$$\langle A\rangle_N-\langle A\rangle=\langle\psi_N|A|\psi_N\rangle-\langle\psi|A|\psi\rangle \tag{18}$$

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[1] The finite-difference Hartree-Fock program of Kobus, Laaksonen and Sundholm is available at http://www.csc.fi/~laaksone/Num2d.html

TABLE I. Multipole moments and total Hartree-Fock energies for the BeF ground state for a sequence of even-tempered basis sets and for two grids.

Key[a]	μ[b]	Θ[c]	Ω[d]	Φ[e]	E_{MHF}[f]
A	1.7471	−4.7600	5.2936	−7.3890	49 797.3
B	1.7338	−4.7080	5.0393	−6.7973	50 167.8
C	1.3024	−4.0364	5.5505	−6.2023	71 281.7
D	1.2744	−4.1313	5.9385	−7.4481	71 508.2
E	1.2889	−4.1133	5.7757	−7.5722	72 525.5
F	1.2728	−4.1623	5.8712	−7.5922	72 615.5
G	1.3180	−4.2176	5.7366	7.5686	71 274.2
H	1.3180	−4.2176	5.7366	−7.5686	71 274.2
I	1.3180	−4.2176	5.7366	−7.5686	71 274.2
J	1.3180	−4.2176	5.7366	−7.5686	71 274.2
K	1.3180	−4.2176	5.7366	−7.5686	71 274.2
L	1.3180	−4.2176	5.7366	−7.5686	71 274.0
M	1.2727	−4.1616	5.8769	−7.5818	72 667.7
N	1.2726	−4.1624	5.8727	−7.5843	72 683.8
[169×193;40]	1.2726	−4.1622	5.8728	−7.5857	72 685.0
[319×415;40]	1.2726	−4.1622	5.8728	−7.5857	72 685.0

[a] The basis sets and grids employed are defined as follows: A, [Be, F: $30s15p$]; B, [Be: $32s17p$; F: $30s15p$]; C, [Be, F: $30s15p15d$]; D, [Be: $32s17p17d$; F: $30s15p15d$]; E, [Be, F: $30s15p15d15f$]; F, [Be: $32s17p17d17f$; F: $30s15p15d15f$]; G, [Be: $32s17p$; F: $30s15p$; bc: $30s15p$]; H, [Be: $32s17p$; F: $30s15p$; bc:$20s15p$]; I, [Be: $32s17p$; F: $30s15p$; bc:$18s14p$]; J, [Be: $32s17p$; F: $30s15p$; bc: $16s13p$]; K, [Be: $32s17p$; F: $30s15p$; bc: $14s12p$]; L, [Be: $32s17p$; F: $30s15p$; bc: $12s11p$]; M, [Be: $32s17p17d$; F: $30s15p15d$; bc: $9s9p10d$]; N, [Be: $32s17p17d17f$; F: $30s15p15d15f$; bc: $9s8p9d8f$].

[b] μ in D.

[c] Θ in D Å.

[d] Ω in D Å^2.

[e] Φ in D A^3.

[f] $(E_{MHF}+114.1E_H)$ in $10^6 E_h$.

with

$$E_N - E = \langle \psi_N | H | \psi_N \rangle - \langle \psi | H | \psi \rangle, \quad (19)$$

where we have assumed that both the exact wave function ψ, and the approximation ψ_N, are normalized, within the Hartree-Fock model. $\langle A \rangle$ and E are given by finite-difference Hartree-Fock calculations using grids capable of supporting sub-μhartree levels of accuracy and $\langle A \rangle_N$ and E_N are given by finite basis set Hartree-Fock calculations using basis sets that have been shown previously to support an accuracy approaching the sub-μhartree level.

In Table I, the multipole moments and total Hartree-Fock energies for the ground state of the BeF molecule are displayed for a sequence of even-tempered basis sets and for two grids.

The two finite-difference Hartree-Fock calculations employed the grids: [169×193;40], i.e., 32 617 points, and [319×415;40], i.e., 132 385 points. The total Hartree-Fock energies supported by these grids are −114.172 684 996 hartree and −114.172 685 040 hartree, respectively; a difference of 0.044 μhartree. There is no difference between the dipole, quadrupole, octupole, and hexadecapole moments supported by these grids to the accuracy quoted in Table I.

Molecular problems handled by employing finite basis set expansions must explore the convergence with respect to (i) the subset of even-tempered functions associated with a given symmetry on a given expansion center, (ii) the number of symmetries included on a given expansion center, (iii) the number of expansion centers. In our previously reported study of the Hartree-Fock ground-state energy of the BeF molecule, it was found that the addition of even-tempered functions centered on the Be nucleus to the $30s15p\ldots$ sets, which had been employed in studies of closed-shell systems containing first-row atoms, led to an improved description. In Table I, the results of calculations for basis sets containing only atom-centered functions are recorded for both the $30s15p\ldots$ sets and the $32s17p\ldots$ sets. For basis sets containing both atom-centered and bond-centered functions only the $32s17p\ldots$ sets are considered on the Be nucleus. For the isotropic basis set, set B, the dipole moment is in error by 36.2%; an error that is reduced markedly by the introduction of atom-centered polarization functions, first to 0.1% on the addition of *d* functions and still further on adding *f* functions. On the other hand, adding functions of *s* and *p* symmetry centered at the midpoint of the bond to the isotropic basis set reduces the error to ∼3.6% of the exact value. Supplementing this *sp* basis set by functions of *d* symmetry centered both on the atomic nuclei and on the bond midpoint yields a dipole moment expectation value that is in error by less than 0.01%.

TABLE II. Differences for multipole moments and total Hartree-Fock energies for the BeF ground state for sequences of even-tempered basis sets.

Key[a]	$\delta\mu$[b]	$\delta\Theta$[c]	$\delta\Omega$[d]	$\delta\Phi$[e]	δE_{MHF}[f]
A	0.4744	0.5978	0.5792	−0.1967	22 887.7
C	0.0297	−0.1259	0.3222	−1.3834	1 403.3
E	0.0162	−0.0489	0.0971	−0.0136	159.5
B	0.4611	0.5458	0.8334	−0.7884	22 517.2
D	0.0017	−0.0309	−0.0658	−0.1376	1 176.8
F	0.0001	0.0000	0.0016	0.0065	69.5
L	0.0453	0.0554	0.1362	−0.0171	1 411.0
M	0.0000	−0.0007	−0.0041	−0.0039	17.3
N	−0.0001	0.0002	0.0001	0.0015	1.2

[a] See footnote a in Table I.
[b] See footnote b in Table I.
[c] See footnote c in Table I.
[d] See footnote d in Table I.
[e] See footnote e in Table I.
[f] $\delta E_{MHF}=E_{MHF}-E_{FD\text{-}HF}$.

In Table II, δ is used to denote the differences between the finite basis set and finite-difference expectation values $\langle A\rangle_N-\langle A\rangle$, and between the corresponding energy values E_N-E. In Table II, the basis sets defined in Table I are arranged into three sequences: A, C, E, which are atom-centered sets containing a $30s15p\ldots$ subset on the Be atom; B, D, F, which are atom-centered sets containing a $32s17p$ set on the Be atom, and L, M, N, which are sets containing both atom-centered and bond-centered subsets with a $32s17p$ subset centered on the Be atom and $30s15p$ subsets centered on the F atom and the bond midpoint. The convergence of the expectation values of the dipole moment, quadrupole moment, octupole moment, and hexadecapole moment is markedly improved for the sequence of basis sets (L, M, N) that include both atom-centered and bond-centered basis subsets. This improved convergence reflects that observed for the total matrix Hartree-Fock energies.

B. Comparison of finite-difference and finite basis set moments for diatomic molecules in the Hartree-Fock approximation

A comparison of finite-difference and finite basis set moments in the Hartree-Fock approximation was made for four groups of diatomic molecules that have been the subject of previously reported studies [5–14] of the total energy and orbital energies. We consider each group in turn.

The calculated dipole, quadrupole, octupole, and hexadecapole moments for the five closed-shell diatomic molecules containing only first-row atoms are collected in Table III. All moments are given relative to the geometrical center of the molecule. For the anion CN^-, results corresponding to two different basis sets are presented. The first set is similar to

TABLE III. Multipole moments for some closed-shell diatomic molecules containing first-row atoms calculated relative to the geometrical center. See Table I for definitions of symbols and units.

Molecule	Method	μ	Θ	Ω	Φ	E_{HF}
BF	*FD-HF*[a]	0.8713	−3.9523	4.5293	−3.6677	−124.1687800
	MHF[b]	0.8713	−3.9522	4.5290	−3.6732	−124.1687770
	δ	0.0000	−0.0001	0.0003	0.0055	3.0
N_2	*FD-HF*[c]	0.0000	−1.2642	0.0000	−2.7838	−108.9938256
	MHF[d]	0.0000	−1.2642	0.0000	−2.7849	−108.9938247
	δ	0.0000	0.0000	0.0000	0.0011	0.9
NO^+	*FD-HF*[c]	−0.4753	0.6587	0.8938	−1.3233	−128.9777407
	MHF[e]	−0.4754	0.6587	0.8938	−1.3234	−128.9777375
	δ	0.0001	0.0000	0.0000	0.0001	3.2
CO	*FD-HF*[c]	−0.2650	−2.1006	2.6456	−3.0928	−112.7909072
	MHF[f]	−0.2650	−2.1003	2.6455	−3.0957	−112.7909046
	δ	0.0000	−0.0003	0.0001	0.0029	2.6
CN^-	*FD-HF*[c]	0.1904	−4.4464	2.4804	−5.8944	−92.3489505
	MHF[g]	0.1627	−4.3862	2.3679	−5.7704	−92.348837
	δ	0.0277	−0.0602	0.1125	−0.1240	114
	MHF[h]	0.1903	−4.4461	2.4790	−5.8983	−92.348928
	δ	0.0001	−0.0003	0.0014	0.0039	22.5

[a] [169×193;40] (present work).
[b] [B: $26s18p18d18f$; F: $26s18p18d18f$; bc: $23s13p13d14f$].
[c] [169×193;40] (present work).
[d] [N: $30s15p15d15f$; bc: $27s12p10d10f$] [14].
[e] [N, O: $30s15p15d15f$; bc: $27s12p10d$] [14].
[f] [C, O: $30s15p15d15f$; bc: $27s12p10d$] [14].
[g] [C, N: $20s10p10d10f10g9h$; bc: $17s7p8d7f8g7h$] [17].
[h] [C, N: $20s10p10d10f10g+(spdf\ diffuse)$; bc: $17s7p8d8f9g$] [33].

TABLE IV. Multipole moments for some open-shell diatomic molecules containing first-row atoms calculated relative to the geometrical center. See Table I for definitions of symbols and units.

Molecule	Method	μ	Θ	Ω	Φ	E_{HF}
BO	*FD-HF*[a]	−3.0130	−0.7307	1.9407	−3.8796	−99.562 712 5
	MHF[b]	−3.0130	−0.7306	1.9408	−3.8802	−99.562 711 6
	δ	0.0000	−0.0001	−0.0001	0.0006	0.9
N_2^+	*FD-HF*[a]	0.0000	2.6035	0.0000	0.0628	−108.405 142 5
	MHF[c]	0.0000	2.6035	0.0001	0.0608	−108.405 141 0
	δ	0.0000	0.0000	−0.0001	0.0020	1.5
CN	*FD-HF*[a]	−2.3031	0.8489	−1.4991	−1.8980	−92.225 134 1
	MHF[d]	−2.3032	0.8486	−1.4989	−1.8938	−92.225 132 7
	δ	0.0001	0.0003	−0.0002	−0.0042	1.4
BeF	*FD-HF*[a]	−1.2727	−4.1622	5.8728	−7.5857	−114.172 685 0
	MHF[e]	−1.2726	−4.1624	5.8727	−7.5843	−114.172 683 8
	δ	−0.0001	0.0002	0.0001	−0.0014	1.2

[a] [319×415;40] [7].
[b] [B: $31s16p16d16f$; O: $30s15p15d15f$; bc: $9s8p9d8f$] [7].
[c] [N: $30s15p15d15f$; bc: $8s7p9d8f$] [7].
[d] [C, N: $30s15p15d15f$; bc: $8s8p9d8f$] [7].
[e] [Be: $32s17p17d17f$; F: $30s15p15d15f$; bc: $9s8p9d8f$] [7].

the basis sets employed to describe neutral species and positive ions [14] while the second set includes additional diffuse functions which, it has been shown previously [33], are required to describe the extended charge distribution of negatively charged species.

The absolute difference between the 2^n-pole moments obtained from the finite-difference and finite basis set increase with *n* for each of the systems considered in Table III. However, the size of the 2^n-pole moments increases with *n*. It is useful to define the average absolute difference

TABLE V. Multipole moments for some closed-shell diatomic fluorides containing an increasingly heavy atom calculated relative to the geometrical center. See Table I for definitions of symbols and units.

Molecule	Method	μ	Θ	Ω	Φ	E_{HF}
BF	*FD-HF*[a]	0.8713	−3.9523	4.5293	−3.6677	−124.168 779 2
	MHF[b]	0.8713	−3.9522	4.5290	−3.6732	−124.168 777 0
	δ	0.0000	−0.0001	0.0003	0.0055	2.2
AlF	*FD-HF*[c]	−1.3227	−5.8863	5.9769	−7.2501	−341.488 382 8
	MHF[d]	−1.3228	−5.8859	5.9754	−7.2482	−341.488 369 5
	δ	0.0001	−0.0004	0.0015	−0.0019	13.3
GaF	*FD-HF*[e]	−2.2235	−5.9097	6.1715	−9.7471	−2022.836 882 2
	MHF[f]	−2.2255	−5.9048	6.1630	−9.7719	−2022.836 862 3
	δ	0.0020	−0.0049	0.0085	0.0248	19.9
InF	*FD-HF*[e]	−2.8551	−7.8301	8.2079	−16.3040	−5839.729 193 5
	MHF[g]	−2.8574	−7.8218	8.1887	−16.2744	−5839.729 178 0
	δ	0.0023	−0.0083	0.0192	−0.0296	15.5
TlF	*FD-HF*[h]	−3.2138	−8.6314	9.0890	−20.3563	−19061.376 349
	MHF[i]	−3.2168	−8.6202	9.0615	−20.3067	−19061.376 288
	δ	0.0030	−0.0112	0.0275	−0.0496	61

[a] [169×193;40].
[b] [B: $26s18p18d18f$ F: $26s18p18d48f$; bc: $23s13p13d14f$].
[c] [169×193;40] [5].
[d] [Al: $28s20p20d20f$; F: $26s18p18d18f$; bc: $22s15p17d17f$] [5].
[e] [295×295;40] [5,6].
[f] [Ga: $48s24p24d24f$; F: $30s15p15d15f$; bc: $27s12p14d15f$] [5,6].
[g] [In: $56s28p28d28f28g$; F: $30s15p15d15f$; bc: $51s23p24d25f25g$] [6].
[h] [595×595;45] [6].
[i] [Tl: $58s29p29d29f29g$; F: $30s15p15d15f$; bc: $53s24p26d25f25g$] [6].

TABLE VI. Multipole moments for some open-shell diatomic fluorides containing an increasingly heavy atom calculated relative to the geometrical center. See Table I for definitions of symbols and units.

Molecule	Method	μ	Θ	Ω	Φ	E_{HF}
BeF	*FD-HF*[a]	−1.2727	−4.1622	5.8728	−7.5857	−114.172 685 0
	MHF[b]	−1.2726	−4.1624	5.8727	−7.5843	−114.172 683 8
	δ	−0.0001	0.0002	0.0001	−0.0014	1.2
MgF	*FD-HF*[a]	−3.1005	−6.7716	9.3090	−17.1685	−299.159 119 3
	MHF[c]	−3.1005	−6.7715	9.3074	−17.1509	−299.159 112 9
	δ	0.0000	−0.0001	0.0016	−0.0176	6.4
CaF	*FD-HF*[d]	−2.6450	−10.6872	14.2460	−26.7662	−776.329 958 3
	MHF[e]	−2.6451	−10.6871	14.2432	−26.7324	−776.329 956 0
	δ	0.0001	−0.0001	0.0028	−0.0338	2.3
SrF	*FD-HF*[f]	−2.5759	−11.8026	14.1228	−26.1455	−3231.119 630 2
	MHF[g]	−2.5760	−1.8024	14.1225	−26.1506	−3231.119 629 2
	δ	0.0001	−0.0002	0.0003	0.0051	1.0

[a] [319×415;40] [8].
[b] [Be: $32s17p17d17f$; F: $30s15p15d15f$; bc: $9s8p9d8f$] [8].
[c] [Mg: $32s17p17d17f$; F: $30s15p15d15f$; bc: $9s9p10d8f$] [8].
[d] [349×499;80] [8].
[e] [Ca: $48s27p27d27f$; F: $30s15p15d15f$; bc: $10s9p9d11f$] [8].
[f] [391×547;80] [8].
[g] [Sr: $56s31p31d31f31g$; F: $30s15p15d15f$; bc: $9s9p9d9g$] [8].

$$\Delta A = S^{-1}\sum_{S} |\langle A\rangle_N - \langle A\rangle|, \tag{20}$$

where S is the number of diatomic systems in a given set that have a nonzero expectation value $\langle A\rangle$. Neglecting the results obtained for the CN^- anion without supplementary diffuse basis functions, the average difference between the nonzero dipole moments values obtained from the finite-difference and finite basis set calculations is only 0.0001 D. The dipole moments obtained from the matrix Hartree-Fock calculations are in excellent agreement with the finite-difference values. For the quadrupole moments this average difference is also 0.0001 D Å while for the octupole moments the average difference increases to 0.0005 D Å^2. The largest absolute difference in the expectation values of the octupole moments is 0.0014 D Å^2 recorded for the negative ion CN^-, which represents an error of ~0.06% of the exact (finite-difference) value. The average difference between the hexadecapole moments obtained from finite-difference and finite basis set Hartree-Fock calculations is 0.0027 D Å^3. The largest absolute difference in the hexadecapole expectation values occurs for BF for which an error of 0.0055 D Å^3 amounts to some ~0.15% of the exact value.

In Table IV, the calculated dipole, quadrupole, octupole, and hexadecapole moments for open-shell diatomic molecules containing first-row atoms are given. Again, all moments are given relative to the geometrical center of the molecule. The average difference between the nonzero dipole moments values obtained from the finite-difference and finite basis set calculations is 0.0001 D. For the quadrupole moments this average difference is 0.0002 D Å and for the octupole moments the average difference is 0.0001 D Å^2. The average absolute difference between the hexadecapole moments obtained from finite-difference and finite basis set Hartree-Fock calculations is 0.0021 D Å^3. The largest absolute difference in the expectation values of the hexadecapole moments displayed in Table IV is 0.0042 D Å^3 for the CN molecule; a difference representing ~0.2% of the finite-difference value.

Multipole moments for some closed-shell diatomic fluorides containing an increasingly heavy atom and calculated relative to the geometrical center are displayed in Table V. The average absolute difference between the dipole moments values obtained from the finite-difference and finite basis set calculations is 0.0015 D, which is more than an order of magnitude greater then the corresponding difference for the lighter systems described in the preceding two sections. The largest difference in the dipole moment values is for TlF for which a difference of 0.0030 D was observed that represents ~0.1% of the exact value. For the quadrupole moments the average absolute difference is 0.0050 D Å with the largest difference being the 0.0112 D Å measured for TlF, some ~0.13% of the exact value. For the octupole moments the average difference is 0.0114 D Å^2, the largest difference is 0.0275 D Å^2, again for TlF and amounting to ~0.3% of the exact value. The average difference between the hexadecapole moments obtained from finite-difference and finite basis set Hartree-Fock calculations is 0.0223 D Å^3 with the largest being 0.0490 D Å^3, some 0.24% of the exact (finite-difference) value.

In Table VI, multipole moments are presented for some open-shell diatomic fluorides containing an increasingly heavy atom calculated relative to the geometrical center. The average difference between the nonzero dipole moments values obtained from the finite-difference and finite basis set calculations is 0.0001 D, which is comparable with the dif-

TABLE VII. Summary of the comparison of finite difference and finite basis set multipole moments for the four groups of diatomic species studied in this work. See Table I for definitions of symbols and units.

Species		μ	Θ	Ω	Φ	E
first-row,	ΔA	0.0001	0.0001	0.0018	0.0027	
closed-shell	XY	[NO^+, CN^-]	[CO, CN^-]	CN^-	BF	CN^-
	$\max\{\lvert\delta A\rvert\}$	0.0001	0.0003	0.0014	0.0055	22.5
first-row,	ΔA	0.0001	0.0002	0.0001	0.0021	
open-shell	XY	[CN, BeF]	CN	CN	CN	N_2^+
	$\max\{\lvert\delta A\rvert\}$	0.0001	0.0003	0.0002	0.0042	1.5
IIIb fluorides,	ΔA	0.0015	0.0050	0.0114	0.0223	
closed-shell	XY	TlF	TlF	TlF	TlF	TlF
	$\max\{\lvert\delta A\rvert\}$	0.0030	0.0112	0.0275	0.0496	61
IIa fluorides,	ΔA	0.0001	0.0002	0.0012	0.0145	
open-shell	XY	[BeF, CaF, SrF]	[BeF, SrF]	CaF	CaF	MgF
	$\max\{\lvert\delta A\rvert\}$	0.0001	0.0002	0.0028	0.0338	6.4

ferences recorded for the molecules containing first-row atoms. For the quadrupole moments this average difference is 0.0002 D Å, again comparable with the differences recorded for the diatomic species containing only first-row atoms, and for the octupole moments the average difference is 0.0012 D $Å^2$ with the largest being 0.0028 D $Å^2$, some ~0.02% of the exact value, in the case of the CaF ground state. The average difference between the hexadecapole moments obtained from finite-difference and finite basis set Hartree-Fock calculations is 0.0145 D $Å^3$. The largest difference is for the CaF molecules but at 0.0338 D $Å^3$ this corresponds to ~0.13% of the exact, finite-difference value.

A summary of our comparison of finite-difference and finite basis set multipole moments in the Hartree-Fock approximation for the four groups of diatomic molecules studied in this paper is given in Table VII. In this table, ΔA is the average absolute difference of the calculated expectation values defined in Eq. (20). XY denotes the diatomic system for which the measured error in the finite basis set result was largest for a given group and $\max\{|\delta A|\}$ is the corresponding error.

The error for the IIIb fluorides is at least an order of magnitude larger than that for the other systems. This correlates with the accuracy of the corresponding energies and reflects our improved expertise in the construction of basis sets capable of supporting high accuracy.

V. CONCLUSIONS

Dipole, quadrupole, octupole, and hexadecapole moments have been determined for the ground states of sixteen diatomic species within the Hartree-Fock approximation using both finite basis set expansions and the finite-difference technique. For an appropriately chosen grid, the finite-difference method provides exact expectation values of the 2^n-pole moments, $n=1,2,3,4$. The comparison of finite-difference and finite basis set multipole moments has provided a more detailed measure of the quality of the finite basis set approximation than our previously reported comparison of total energy values and orbital energies for these systems [5–8,11–14], and also supplements our study of orbital amplitude difference functions [11]. The basis sets employed in this paper are of the universal even-tempered type [25]. They are not tailored to one particular property or indeed one particular molecular species or environment. They provide a systematic procedure for approaching the complete basis set limit for the chosen theoretical model. We note that the infinite basis set limit is not synonymous with the complete basis set limit. One can trivially generate a sequence of basis set of even-tempered functions of increasing size, N, which is demonstrably incomplete in the limit $N \to \infty$ merely by fixing the parameters α and β defining the exponents. Energy values determined from such sequences can be easily shown to converge to an incorrect limit. For expectation values such as multipole moments, Klahn and Morgan [1] have shown that the situation is more complicated in that a sequence of basis sets that support convergence of the energy may not support convergence of other expectation values. In this paper, we have provided numerical evidence that the 2^n-pole moments $n=1,2,3,4$, for diatomic molecules within the Hartree-Fock approximation can be obtained by systematic implementation of the algebraic approximation. Within the Hartree-Fock approximation, basis subsets located at the bond midpoint have been shown to be particularly effective in calculations of multipole moments. However, the absolute accuracy of the expectation values is seen to degrade somewhat as n increases. The pattern of convergence of the multipole moment expectation values with increasing size of basis set has been shown to be very similar to that observed for the total Hartree-Fock energy.

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