

The convergence of energy expansions for molecules in electrostatic fields: A linear-response coupled-cluster study

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The radii of convergence of power series expansions describing energy of a molecule in external electrostatic field are investigated using D'Alembert ratio test, standard and generalized Cauchy–Hadamard criteria, and Padé approximants. The corresponding coefficients at various field and field-gradient components, representing multipole moments and (hyper)polarizabilities and including terms of tenth or even twentieth order, are determined using an *ab initio* linear response coupled-cluster theory. Most calculations are performed for the HF molecule described by the basis set of double zeta quality, while the role of basis set is discussed by comparing the results with estimates of the radii of convergence obtained with the basis set of [5s3p2d/3s2p] quality. Emphasis is placed on the dependence of the interval of convergence of power series expansion describing energy of a molecule in applied electrostatic field on the nuclear geometry. The results might have important implications for various numerical methods used to calculate electrostatic molecular properties as functions of the internuclear geometry, including the finite-field and fixed-point-charge approaches.

1. Introduction

The energy of a molecule in an external electrostatic field is usually represented by a multiple power series in the components of the field and its gradients. Various forms of this expansion exist in the literature, using either Cartesian [2,8,20,37] or spherical tensor [19] formulations. In the following, we use Buckingham's classical expression, i.e., [8],

$$E = E^{(0)} - \mu_i F^i - \frac{1}{2} \alpha_{ij} F^i F^j - \frac{1}{6} \beta_{ijk} F^i F^j F^k - \frac{1}{24} \gamma_{ijkl} F^i F^j F^k F^l - \dots \\ - \frac{1}{3} \Theta_{ij} F^{ij} - \frac{1}{3} A_{i,jk} F^i F^j F^k - \frac{1}{6} B_{ij,kl} F^i F^j F^{kl} - \frac{1}{6} C_{ij,kl} F^{ij} F^{kl} - \dots, \quad (1)$$

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where $E^{(0)}$ designates the energy of a molecule in the absence of the field, $\mathbf{F} = (F^1, F^2, F^3) \equiv (F^x, F^y, F^z)$ the Cartesian components of the field, and F^{ij} the Cartesian components of the field gradient $\nabla\mathbf{F} = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z})\mathbf{F}$, i.e.,

$$F^{ij} = \frac{\partial F^i}{\partial x_j} = \frac{\partial F^j}{\partial x_i} \quad (x_1 = x, x_2 = y, x_3 = z),$$

calculated at the origin of the molecular coordinate system. Note that the Einstein summation convention over repeated upper and lower indices is implied in equation (1). In general, the expansion (1) contains higher gradients of the field, i.e., $\nabla^n\mathbf{F} = (\dots, F^{i_1 i_2 \dots i_n}, \dots)$, where

$$F^{i_1 i_2 \dots i_n} = \frac{\partial^{n-1}}{\partial x_{i_1} \partial x_{i_2} \dots \partial x_{i_{n-1}}} F^{i_n} = \dots = \frac{\partial^{n-1}}{\partial x_{i_2} \partial x_{i_3} \dots \partial x_{i_n}} F^{i_1},$$

which are important to describe nonuniform electric fields. For spatially uniform fields, characterized by the condition $\nabla\mathbf{F} = 0$, the only terms which do not vanish are those involving field components F^i , $i = 1, 2, 3$.

The coefficients in equation (1) designate permanent multipole moments (dipole moment $\boldsymbol{\mu}$, traceless quadrupole moment $\boldsymbol{\Theta}$, etc.), polarizabilities (dipole polarizability $\boldsymbol{\alpha}$, dipole-quadrupole polarizability \mathbf{A} , quadrupole polarizability \mathbf{C} , etc.), and various hyperpolarizabilities (first dipole hyperpolarizability $\boldsymbol{\beta}$, second dipole hyperpolarizability $\boldsymbol{\gamma}$, first dipole-dipole-quadrupole hyperpolarizability \mathbf{B} , etc.), which describe the response of a molecular charge cloud to an applied electric field. They can be defined as derivatives of the energy E with respect to field components F^i or their gradients $F^{ij\dots}$ at the zero field (cf. equation (1)) or, alternatively, via the corresponding quantum-mechanical expressions of the expectation value (for $\boldsymbol{\mu}$, $\boldsymbol{\Theta}$, etc.) or sum-over-states (for $\boldsymbol{\alpha}$, \mathbf{A} , \mathbf{C} , $\boldsymbol{\beta}$, $\boldsymbol{\gamma}$, \mathbf{B} , etc.) type (cf., e.g., [8,19,29]).

The fundamental role of these properties in the interpretation of molecular spectra and description of intermolecular interactions is well known. Thus, various experimental techniques have been designed to determine these quantities. An alternative and quite often more reliable approach is to calculate multipole moments and (hyper)polarizabilities using standard *ab initio* methods of quantum chemistry [6,16]. In this case, large and flexible basis sets must be used and electron correlation effects need to be accounted for to obtain accurate results, particularly for higher-order properties, such as $\boldsymbol{\beta}$ or $\boldsymbol{\gamma}$. In addition, *ab initio* determination of molecular properties may require the inclusion of rovibrational corrections [7,16,18] and, in some cases, of even relativistic effects (cf., e.g., [35]).

In both experimental determination of multipole moments and polarizabilities and in various *ab initio* calculations based on equation (1), we silently assume that the series (1) converges for the range of values of the electric field employed. Thus, we trust that the truncated expansion (1) at a conveniently chosen term reasonably approximates the actual energy of a molecule in the presence of external field. This is, in fact, the fundamental principle of the widely used finite-field [13] and fixed-point-charge [24] calculations of electrostatic molecular properties (cf., also, [16]).

In the finite-field approach, properties are determined by calculating energies of a molecule for a few suitably chosen values of the field or one or more of its gradients followed by the subsequent numerical differentiation of the field-dependent energies using one of the available interpolation techniques. In the fixed-point-charge method, charges of variable magnitude are placed at various distances from a molecule in order to generate external electrostatic field and properties are extracted from the relevant energy expansions describing the interaction of a molecule with point charges.

Several problems may arise when one uses numerical differentiation of the type employed in the finite-field approach. Clearly, the accuracy of the numerical differentiation can be affected by the number of the employed field or field-gradient values and by the magnitude of those fields. In addition, the results depend on the interpolation technique employed and on the precision of the preceding energy calculations, particularly when high-order properties need to be evaluated. For example, in the case of the first and second hyperpolarizabilities β and γ , energy must be differentiated three and four times, respectively, which means that we must use relatively large field values to achieve reasonable accuracy (too small values of the field may result in a total loss of accuracy when three- or four-fold differentiation is carried out; cf. [22]). It may thus happen that the required field or field-gradient values fall outside the radius of convergence of expansion (1), which puts the entire finite-field procedure in serious doubt.

Even near yet within the radius of convergence, results from numerical differentiation can be questionable. We observed this in our recent study on molecular properties of HF, where we were unable to determine hyperpolarizabilities β and γ for significant stretches of the H–F bond due to instabilities of numerical differentiation procedure [22]. In this case, the components β_{zzz} and γ_{zzzz} were shown to change by a few orders of magnitude when the H–F bond was stretched, indicating a possibility of a poor convergence of expansion (1) in this region and resulting in a total loss of accuracy in the finite-field calculations. We can expect that quadrupolar analogs of β and γ (for example, \mathbf{B} ; cf. equation (1)) are even more difficult to determine using the finite-field method when chemical bonds are stretched or broken. This may pose a serious problem for the reliability of finite-field calculations of property functions describing the dependence of various molecular properties on nuclear geometry. The same remark applies to calculations of property functions using the fixed-point-charge method, since point charges may generate fields outside the range of convergence of equation (1), making the truncated energy expansions used in the fixed-point-charge method totally useless for any calculation. From this point of view, it is much better to use the so-called “analytical” *ab initio* methods, such as the linear-response (LR) coupled-cluster (CC) theory [21,22,25] employed in this paper, which eliminate the need for numerical differentiation and which do not use the truncated equation (1). In analytical approaches, the first and higher-order molecular properties are calculated by solving the corresponding systems of equations for the relevant components of the molecular electronic wave function (only those components which are needed to find a given property; cf. [21,22] and references therein), thus putting aside the problem

of convergence of equation (1) (the only assumption of analytical *ab initio* approaches is that of the nonzero value of the radius of convergence of the series (1)).

It is the purpose of the present paper to examine the convergence of expansion (1) by calculating its radii of convergence for the HF molecule. Two types of fields will be considered, namely, the dipolar field along the internuclear axis and its quadrupolar (field-gradient) analog. We are particularly interested in examining the radius of convergence of equation (1) as a function of geometry of the HF molecule, which may allow us to better understand the problems encountered by the finite-field approach when higher-order property functions are to be determined.

Our work parallels to a certain extent the study by Larter and Malik [23], who investigated the effects of nonuniform electric fields on the convergence of expansion (1) for LiH. Although their main conclusion that the application of a field gradient decreases the radius of convergence of expansion (1) regarded as a series in field components F^i , particularly for shorter internuclear distances, is likely to be a valid one, the quantitative results could be of a concern. As the authors themselves acknowledge, their estimates of the radii of convergence of equation (1) may not be very accurate due to the low order of the multivariable rational approximants [12] employed in their study. In fact, the [1/1] two-variable approximant used by Larter and Malik reduces to the well-known [1/1] Padé approximant [3–5,39] when one of the two variables (field or field-gradient component) is set to zero. It is often the case that the radius of convergence of the resulting single variable series is not well approximated by the pole of the [1/1] Padé approximant. It is usually conjectured that poles of the $[L/L]$ Padé approximants converge to singularities of the power series, which they approximate, as $L \rightarrow \infty$ [3–5,39] (cf. section 2.1 for more details).

Already the qualitative results of the kind just mentioned may help one to understand the behavior of the fixed-point-charge method, in which the field and field-gradient components cannot be separated in the calculation. However, in order to better understand the behavior of the finite-field approach as well as of the fixed-point-charge method, it is important to know a reasonably accurate value of the radius of convergence of expansion (1). Moreover, in order to understand why the finite-field approach usually breaks down for large internuclear separations, it is important to know the radius of convergence for nonequilibrium geometries as well. We thus examine in this paper the HF molecule for the equilibrium and very highly stretched geometries (up to the five times the equilibrium H–F bond length). This would not have been very meaningful in the above mentioned study of the LiH molecule [23], since the authors relied on the multipole moment and (hyper)polarizability values obtained using the derivative Hartree–Fock method of Dykstra and Jasien [17]. For large stretches of chemical bonds, it becomes absolutely essential to use the correlated approach, such as the size extensive coupled-cluster theory used in this study, as amply documented in our recent papers on property functions of HF and N₂ [22,33,38].

Similarly as for the general power series, the convergence of expansion (1) must strongly depend on higher-order terms, which contain fifth and higher powers of the field or field-gradient components. Truncation of the series (1) on quartic terms de-

scribing hyperpolarizabilities γ may not always be sufficient to determine its radius of convergence. In this study, we calculate terms containing sixth, seventh, and, in some cases, even twentieth power of the field component employed, which allows us to calculate radii of convergence of expansion (1) using different mathematical techniques, including D'Alembert ratio test, Cauchy–Hadamard formula and its extensions, and Padé approximants (see section 2.2). Calculation of the higher-order terms in expansion (1) is made possible thanks to our recursive formulation of the LRCC theory described in [22]. We thus hope that our estimates of the radii of convergence of expansion (1) are sufficiently accurate to enable a meaningful assessment of the behavior of expansion (1) for real molecular systems, such as the HF molecule.

2. Formal considerations

2.1. Determination of the energy expansion for a molecule in external electrostatic field

As mentioned in the introduction, the purpose of the present paper is to estimate the radii of convergence of expansion (1) for the HF molecule. We assume that either a uniform electrostatic field along the internuclear axis (designated here by z) or the zz field gradient are applied. The first case is characterized by the condition $F^1 = F^2 = F^{i_1 i_2 \dots i_n} = 0$, where $i_1, i_2, \dots, i_n = 1, 2, 3$ and $n \geq 2$, whereas in the second case $F^i = F^{11} = F^{22} = F^{ij} = F^{i_1 i_2 \dots i_n} = 0$, where $i \neq j$ and $n \geq 3$. In either case, equation (1) reduces to a power series in a single variable (designated by λ),

$$E(\lambda) = \sum_{n=0}^{\infty} \lambda^n E^{(n)}, \quad (2)$$

where for the uniform field case $\lambda = F^3 \equiv F^z$ and for the pure field-gradient zz component $\lambda = (1/3)F^{33} \equiv (1/3)F^{zz}$. The coefficients $E^{(n)}$ can be identified as follows. When $\lambda = F^z$, we obtain

$$E^{(1)} = -\mu_z, \quad (3)$$

$$E^{(2)} = -\frac{1}{2}\alpha_{zz}, \quad (4)$$

$$E^{(3)} = -\frac{1}{6}\beta_{zzz}, \quad (5)$$

$$E^{(4)} = -\frac{1}{24}\gamma_{zzzz}, \quad \text{etc.}, \quad (6)$$

whereas for $\lambda = (1/3)F^{zz}$, we have

$$E^{(1)} = -\Theta_{zz}, \quad (7)$$

$$E^{(2)} = -\frac{3}{2}C_{zz,zz}, \quad \text{etc.} \quad (8)$$

Although the energy expansion (1) or its special case, equation (2), permit a purely classical interpretation (they describe a response of a polarizable charge cloud defined by a set of multipole moments and (hyper)polarizabilities to an applied electrostatic

field), we use in this paper a quantum-mechanical description. Thus, the energy $E(\lambda)$ is interpreted as the lowest eigenvalue of the perturbed Hamiltonian

$$\hat{H}(\lambda) = \hat{H} + \lambda\hat{W}, \quad (9)$$

describing a given N -electron system (in our case, the HF molecule) in the presence of an external electrostatic field characterized by the parameter λ . Here, $\hat{H} \equiv \hat{H}(0)$ is the unperturbed Hamiltonian for a molecule in the absence of the field and \hat{W} is the pertinent multipole moment operator corresponding to the applied field. In our case, $\hat{W} = -\hat{\mu}_z$ when $\lambda = F^z$ and $\hat{W} = -\hat{\Theta}_{zz}$ when $\lambda = (1/3)F^{zz}$. We assume that the electronic wave function $|\Psi(\lambda)\rangle$ for a molecule in the field, being a solution of the Schrödinger equation,

$$\hat{H}(\lambda)|\Psi(\lambda)\rangle = E(\lambda)|\Psi(\lambda)\rangle, \quad (10)$$

can be represented by the CC exponential ansatz,

$$|\Psi(\lambda)\rangle = e^{\hat{T}(\lambda)}|\Phi_0\rangle, \quad (11)$$

where $|\Psi(0)\rangle \equiv |\Psi\rangle = e^{\hat{T}}|\Phi_0\rangle$ is the CC solution of the unperturbed (field-free) problem,

$$\hat{H}_N|\Psi\rangle = \Delta E|\Psi\rangle, \quad \Delta E = E(0) - \langle\Phi_0|\hat{H}|\Phi_0\rangle. \quad (12)$$

Here, $|\Phi_0\rangle$ is the independent particle model (in our case, restricted Hartree–Fock or RHF for short) reference configuration, $\hat{T}(\lambda)$ and \hat{T} are the cluster operators for the perturbed (equation (10)) and unperturbed (equation (12)) problems, and $\hat{H}_N \equiv \hat{H}_N(0) = \hat{H} - \langle\Phi_0|\hat{H}|\Phi_0\rangle$ is the unperturbed (zero-order) Hamiltonian in the normal product form relative to the Fermi vacuum $|\Phi_0\rangle$. In order to solve equation (10), or its normal product analog,

$$\hat{H}_N(\lambda)|\Psi(\lambda)\rangle = \Delta E(\lambda)|\Psi(\lambda)\rangle, \quad \Delta E(\lambda) = E(\lambda) - \langle\Phi_0|\hat{H}(\lambda)|\Phi_0\rangle, \quad (13)$$

we use the LRCC formalism of Monkhorst [25], in which both the cluster operator $\hat{T}(\lambda)$ and the energy $\Delta E(\lambda)$ are expanded in a power series in terms of the parameter λ ,

$$\hat{T}(\lambda) = \sum_{n=0}^{\infty} \lambda^n \hat{T}^{(n)}, \quad (14)$$

$$\Delta E(\lambda) = \sum_{n=0}^{\infty} \lambda^n \Delta E^{(n)}, \quad \Delta E^{(n)} = \frac{1}{n!} \left(\frac{\partial^n \Delta E(\lambda)}{\partial \lambda^n} \right)_{\lambda=0}, \quad (15)$$

where $\hat{T}^{(0)} \equiv \hat{T}$ is the cluster operator describing the unperturbed wave function $|\Psi\rangle = |\Psi(0)\rangle$ and $\Delta E^{(0)} = \Delta E$ is the unperturbed energy relative to the reference energy $\langle\Phi_0|\hat{H}|\Phi_0\rangle$, equation (12) (in our case, correlation energy since we use the RHF reference $|\Phi_0\rangle$). Clearly, there is a simple relationship between quantum-mechanical corrections $\Delta E^{(n)}$ and their classical counterparts $E^{(n)}$ defining expansion (2),

$$E^{(0)} = \Delta E^{(0)} + \langle\Phi_0|\hat{H}|\Phi_0\rangle, \quad (16)$$

$$E^{(1)} = \Delta E^{(1)} + \langle \Phi_0 | \hat{W} | \Phi_0 \rangle, \quad (17)$$

$$E^{(n)} = \Delta E^{(n)} \quad (n \geq 2). \quad (18)$$

Thus, we can easily relate the LRCC corrections $\Delta E^{(n)}$ with various molecular properties (cf. equations (3)–(8)). At this point, the magnitude of the radius of convergence of expansions (14) and (15) is irrelevant, as long as it does not vanish. This is, in fact, one of the reasons for using the LRCC theory. In this theory, the corrections $\Delta E^{(n)}$ are determined by solving a recursive system of equations, which we describe below, rather than by numerically differentiating $\Delta E(\lambda)$ at $\lambda = 0$ (cf. equation (15)). Note also that when the exact full CC wave function is used, i.e., when no further approximations are made for the cluster components $\hat{T}^{(n)}$, the radius of convergence of the LRCC formalism and that of the expansion (2) are the same.

To solve equations (12)–(15) for the unknown corrections $\hat{T}^{(n)}$ and $E^{(n)}$, some approximation must be introduced. We thus restrict each $T^{(n)}$ to its one- and two-body cluster components (CCSD approximation), i.e.,

$$\hat{T}^{(n)} \approx \hat{T}_{\text{CCSD}}^{(n)} = \hat{T}_1^{(n)} + \hat{T}_2^{(n)}. \quad (19)$$

Numerous results in the literature indicate that CCSD is a very good approximation. Indeed, it yields a remarkably good description of the potential energy curve and property functions for the HF molecule studied in this paper [22,33,38]. The resulting system of equations for $\hat{T}_i^{(n)}$ ($i = 1, 2$) and $\Delta E^{(n)}$ then takes the form

$$(\hat{H}_N e^{\hat{T}^{(0)}})_C |\Phi_0\rangle = \Delta E^{(0)} |\Phi_0\rangle, \quad n = 0, \quad (20)$$

$$(\hat{H}_N e^{\hat{T}^{(0)}} \hat{T}^{(1)} + \hat{W}_N e^{\hat{T}^{(0)}})_C |\Phi_0\rangle = \Delta E^{(1)} |\Phi_0\rangle, \quad n = 1, \quad (21)$$

$$(\hat{H}_N e^{\hat{T}^{(0)}} \hat{\Omega}^{(n)} + \hat{W}_N e^{\hat{T}^{(0)}} \hat{\Omega}^{(n-1)})_C |\Phi_0\rangle = \Delta E^{(n)} |\Phi_0\rangle, \quad n \geq 2, \quad (22)$$

with

$$\hat{\Omega}^{(n)} = \hat{T}^{(n)} + \sum_{k_1, \dots, k_{n-1} \geq 0} \prod_{i=1}^{n-1} (k_i!)^{-1} (\hat{T}^{(i)})^{k_i} \quad (n \geq 1),$$

$$\sum_{j=1}^{n-1} j k_j = n$$

$$\hat{\Omega}^{(0)} \equiv 1, \quad (23)$$

where $\hat{T}^{(n)}$ is given by equation (19), \hat{W}_N is the normal product form of \hat{W} , and C designates the connected part of a given expression.

Equations (20)–(23), along with equation (19), define the LRCCSD formalism of [21,22]. As described in [22], we solve equations (20)–(23) recursively (first, the original unperturbed problem, equation (20), then, the subsequent first and higher-order problems, equations (21) and (22); using in each case a suitably designed iterative algorithm). Note that except for the unperturbed problem (20), each equation of order n ($n \geq 1$) is linear in the unknown cluster components $\hat{T}_i^{(n)}$ ($i = 1, 2$), reflecting the linear response nature of the approach. Although the recursive formulation of the

LRCCSD theory, given by equations (20)–(23), does not always represent an optimal choice (one could, for example, exploit Wigner’s $(2n + 1)$ rule instead of solving for $\hat{T}^{(n)}$ to calculate $\Delta E^{(n)}$ of the same order; cf. [21,22]), it certainly provides a very transparent formulation, enabling an easy encoding and actual computation of $\Delta E^{(n)}$ for very high orders ($n \sim 10$ – 20). This is particularly important when we wish to estimate radii of convergence of series (2) by examining its high-order terms.

Detailed LRCCSD equations were given in [21,22]. Their solution gives the CCSD approximation for the exact corrections $\Delta E^{(n)}$, equation (15), and through relationships (3)–(8) and (16)–(18), also for the corresponding static properties. In particular, the LRCCSD value of the dipole or quadrupole moment (or, for that matter, of any first-order property) represents an approximation to the corresponding quantum-mechanical expectation value $\langle \Psi | \hat{W} | \Psi \rangle / \langle \Psi | \Psi \rangle$. Only in the exact (full CC) case, in which the Hellmann–Feynman theorem is satisfied, we can write

$$\frac{\langle \Psi | \hat{W} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \Delta E^{(1)} + \langle \Phi_0 | \hat{W} | \Phi_0 \rangle \quad (24)$$

(cf. [21,22,25]). We believe, however, that the CCSD approach provides us with very good estimates of the corrections $\Delta E^{(n)}$, so that our estimates of the radii of convergence based on these values are also reasonable. Since CCSD is often used to evaluate molecular properties via finite-field approach, our estimates of the radii of convergence of series (2) should tell us a good deal about the appropriateness of this or other approximate quantum-chemical methods for property function determination. Thanks to the size consistency of CC theory, we can examine the dependence of the radii of convergence of expansions (2) or (15) on the nuclear geometry, including the difficult bond breaking region. This may not always be possible using other methods (e.g., finite-order many-body perturbation theory or limited configuration interaction).

As in most quantum-chemical approaches, there is one more approximation to be invoked, namely that of the finite basis set. To define the reference (RHF) configuration $|\Phi_0\rangle$ and the cluster operators $\hat{T}_i^{(n)}$ ($i = 1, 2$), we employ the finite atomic orbital (AO) basis set. Consequently, we are not solving the original infinite-dimensional eigenvalue problem (13) (not even its infinite-dimensional CCSD counterpart), but rather its finite-dimensional algebraic analog defined by the basis set. It is well known that large and flexible basis sets must be used in realistic property calculations. On the other hand, it may not be possible to calculate the corrections $\Delta E^{(n)}$ for large values of n (say, $n \geq 5$) with the available computer codes, when employing large basis sets. At the same time (see the Introduction), the radii of convergence estimated from the first few terms of equations (2) or (15) may be incorrect. We will thus consider a relatively small, albeit reasonable, basis set when calculating high-order corrections $\Delta E^{(n)}$. Our experience indicates that the qualitative behavior of quantum-mechanical systems does not substantially change with the basis set. In fact, this is what we observed in our recent study of property functions of HF [22] (relevant for this paper), where we showed that there is no qualitative difference in the form of the μ_z , α_{zz} , β_{zzz} , γ_{zzzz} , Θ_{zz} , and $C_{zz,zz}$ property functions obtained with small and large basis sets. We

thus believe that our estimates of the radii of convergence of energy expansion (2), obtained with a relatively small basis set, indicate the qualitatively correct dependence on the nuclear geometry and are in fact very reasonable, even in a quantitative sense. Mathematical techniques used to calculate these radii are described below.

2.2. Numerical determination of the radii of convergence

Once the corrections $\Delta E^{(n)}$ or $E^{(n)}$ are known, particularly those for sufficiently large n , one should be able to determine the radii of convergence of power series (2) or (15) by using the available convergence criteria. Perhaps the most commonly used criterion is that of D'Alembert (the well-known ratio test) which, when applied to equation (15), yields the following expression for the radius of convergence R :

$$R = R^A \equiv \lim_{n \rightarrow \infty} r_n^A, \quad (25)$$

where

$$r_n^A = \left| \frac{\Delta E^{(n)}}{\Delta E^{(n+1)}} \right|. \quad (26)$$

When the above limit does not exist or when the sequence r_n^A , equation (26), displays a highly irregular behavior for the available corrections $\Delta E^{(n)}$, so that it is difficult to estimate the limit (25) numerically, one can use the well-known Cauchy–Hadamard formula,

$$R = R^{\text{CH}} \equiv \liminf_{n \rightarrow \infty} r_n^{\text{CH}}, \quad (27)$$

with

$$r_n^{\text{CH}} = |\Delta E^{(n)}|^{-1/n}. \quad (28)$$

When we do not have enough coefficients $\Delta E^{(n)}$, which may be the case for highly stretched nuclear geometries and for some types of the perturbation \hat{W} (see below), we can use the fact that the differentiation of a power series produces a new series, whose radius of convergence is unaltered (see [27,28]). Application of the Cauchy–Hadamard formula to a k -times differentiated power series (15) gives us one more useful formula for the radius of convergence of expansion (15), namely,

$$R = R^{\text{GCH}}(k) \equiv \liminf_{n \rightarrow \infty} r_n^{\text{GCH}}(k), \quad (29)$$

where

$$r_n^{\text{GCH}}(k) = \left(\frac{n! |\Delta E^{(n)}|}{(n-k)!} \right)^{-1/(n-k)}, \quad (30)$$

which can be regarded as a generalization of equation (27) to nonzero values of k (for $k = 0$, equation (29) reduces to equation (27), i.e., $r_n^{\text{GCH}}(0) = r_n^{\text{CH}}$).

The usefulness of formula (29) stems from the fact that a differentiated power series may approach the desired limit faster or in a different, perhaps more regular,

way, allowing us to determine the required inferior limit of equation (29) from fewer corrections $\Delta E^{(n)}$. In fact, formula (29) can be generalized to noninteger nonnegative k values by using the Euler gamma function, in which case we can always find the “optimum” value of k that guarantees the fastest convergence. Alternatively, we can find two consecutive values of k , which yield decreasing and increasing subsequences of the sequences $r_n^{\text{GCH}}(k)$, enabling us to determine the upper and lower bounds for the radius of convergence R . This has been amply documented in [27,28], where formula (29) was used to determine the radii of convergence of the Rayleigh–Schrödinger perturbation expansions for the Pariser–Parr–Pople and Hubbard models of benzene by varying k and by estimating the corresponding inferior limits.

The generalized Cauchy–Hadamard expression (29), albeit very useful, may not always give us the desired estimate of R . It is thus worthwhile to try an approach based on Padé approximants. In this case, we first construct the Padé approximants $\varepsilon_{[L_1, L_2]}(\lambda)$ to the truncated power series (15), i.e., to

$$\Delta E_M(\lambda) = \sum_{n=0}^M \lambda^n \Delta E^{(n)}, \quad (31)$$

where $L_1 + L_2 = M$, under the condition

$$\Delta E(\lambda) - \varepsilon_{[L_1, L_2]}(\lambda) = \mathcal{O}(\lambda^{M+1}). \quad (32)$$

We recall that [3–5,39]

$$\varepsilon_{[L_1, L_2]}(\lambda) = \frac{P_{L_1}(\lambda)}{Q_{L_2}(\lambda)}, \quad (33)$$

where $P_{L_1}(\lambda)$ and $Q_{L_2}(\lambda)$ are the polynomials of orders L_1 and L_2 , respectively,

$$P_{L_1}(\lambda) = \sum_{m=0}^{L_1} p_m \lambda^m, \quad (34)$$

$$Q_{L_2}(\lambda) = 1 + \sum_{m=1}^{L_2} q_m \lambda^m, \quad (35)$$

whose coefficients can be found by solving the corresponding systems of linear equations involving $\Delta E^{(n)}$, $n = 0, 1, 2, \dots, M$. Padé approximants $\varepsilon_{[L_1, L_2]}(\lambda)$ are expected to provide a good approximation to $\Delta E(\lambda)$, even in the region of λ where series (15) diverges and in the vicinity of its singular points.

The poles of the diagonal Padé approximants $\varepsilon_{[L, L]}(\lambda)$, where $L = M/2$, converge to singularities of $\Delta E(\lambda)$ as L (or M) increases [3–5,39]. It is thus sufficient to determine zeros of the denominators $Q_L(\lambda)$ in order to find an estimate of R . The distance of the nearest zero of $Q_L(\lambda)$ from the origin (in the complex λ plane) gives then an estimate of R , which we designate as $R^{\text{Padé}}$ (the larger the value of L , the better the estimate of R). Obviously, we exclude those zeros of $Q_L(\lambda)$ which turn out to be zeros of $P_L(\lambda)$, since we look for the poles of $\varepsilon_{[L, L]}(\lambda)$. In principle, the same

applies to the off-diagonal approximants $\varepsilon_{[L_1, L_2]}(\lambda)$, whose closest poles to the origin in the complex λ plane (zeros of $Q_{L_2}(\lambda)$ which are not the roots of $P_{L_1}(\lambda)$) should give us a reasonable estimate of R as long as L_1 and L_2 are reasonably large.

The effectiveness of the above procedure is well known [3–5,39] and there are good reasons to believe that a moderate number of corrections $\Delta E^{(n)}$ is sufficient to provide a good estimate of the radius of convergence R . We should thus be able to determine $R^{\text{Padé}}$ from the first few entries $\varepsilon_{[L, L]}(\lambda)$ or $\varepsilon_{[L_1, L_2]}(\lambda)$ of the Padé table, even though we are not going to base our considerations on the lowest available entries $\varepsilon_{[1, 1]}(\lambda)$ or $\varepsilon_{[2, 2]}(\lambda)$ alone, whenever possible. In view of the above remarks we must, at least in principle, look at the poles of $\varepsilon_{[L, L]}(\lambda)$ for a few values of L (or L_1 and L_2) in order to get an idea whether those poles reasonably converge.

All four methods (D'Alembert ratio test, equations (25) and (26), Cauchy–Hadamard formulas, equations (27)–(30), and the Padé approximant method, equations (33)–(35)) are exploited in this paper to estimate the radii of convergence of expansion (15). Comparing the results obtained by these various methods should give us a good idea about their mutual consistency and thus about the reliability of obtained radii.

3. Results and discussion

3.1. Computational details

As mentioned in the introduction, our calculations of the radii of convergence were performed for the HF molecule with two different types of the field: the dipolar field along the internuclear z axis, $\lambda = F^z$, corresponding to $\hat{W} = -\hat{\mu}_z$, and the quadrupolar field, $\lambda = (1/3)F^{zz}$, corresponding to $\hat{W} = -\hat{\Theta}_{zz}$. The origin of the coordinate system was placed at the molecular center of mass, with the F and H atoms located on the negative and positive sides of the z axis, respectively.

We probed three internuclear distances r : the experimental equilibrium distance $r = r_e = 1.7328$ a.u., three times the equilibrium distance, $r = 3r_e = 5.1984$ a.u., and five times the equilibrium distance, $r = 5r_e = 8.6640$ a.u. The equilibrium bond length is the distance at which most finite-field or “analytical” property calculations are performed. The internuclear separation $r = 3r_e$ is the distance where the potential energy curve for HF begins to approach its dissociation limit, resulting in dramatic changes in the values of hyperpolarizabilities β_{zzz} and γ_{zzzz} , and substantial changes in the values of α_{zz} . This is also a region where the first signs of the unstable behavior of the finite-field procedure using numerical differentiation of energy $\Delta E(\lambda)$ begin to manifest themselves [22]. Finally, the largest internuclear separation, $r = 5r_e$, is well inside the bond breaking region, where the finite-field procedure can hardly be used to determine β_{zzz} or γ_{zzzz} , even when the exact, full configuration interaction (or full CC) energies $\Delta E(\lambda)$ are used for numerical differentiation [22]. In fact, for $3r_e \leq r < 5r_e$ we observe an almost complete loss of accuracy, even when the energy

is differentiated only twice, making the resulting α_{zz} values rather inaccurate (only one significant digit can be guaranteed; see [22]).

The CCSD and LRCCSD calculations, required to generate the zero- and higher-order energy corrections, $\Delta E^{(0)}$ and $\Delta E^{(n)}$ ($n \geq 1$), respectively, were carried out using our own codes [21,22,32] employing the orthogonally spin-adapted formulation of CC theory [1,26,30,31]. The zero-order CCSD equations were converged to fourteen decimal places for the energy (fifteen decimal figures for the CC amplitudes), whereas the LRCCSD equations for each order n ($n \geq 1$) were converged to twelve decimal places for the energy corrections $\Delta E^{(n)}$, unless the energy values were so large (as it happens for larger values of n) that we had to reduce the above thresholds to fewer decimals while maintaining the accuracy of fourteen or fifteen significant figures. These tight convergence criteria were imposed to maximize the accuracy of the resulting energy corrections $\Delta E^{(n)}$.

The initial RHF calculations were performed with GAMESS [15,36]. GAMESS was also used to obtain the standard one- and two-electron atomic and molecular integrals. The property one-electron integrals, defining the operator \hat{W} , were obtained using our own routines [21,22]. In the post Hartree–Fock CC calculations all ten electrons were correlated.

The *ab initio* results for the energy corrections $\Delta E^{(n)}$ were transferred to a MAPLE [9–11] session in order to evaluate the desired expressions for r_n^A , r_n^{CH} , and $r_n^{\text{GCH}}(k)$, as well as to compute Padé approximants $\varepsilon_{[L_1, L_2]}(\lambda)$. Poles of $\varepsilon_{[L_1, L_2]}(\lambda)$ (zeros of $Q_{L_2}(\lambda)$) were evaluated using MAPLE commands `solve` and `fsolve`. In each case, we verified whether a given root of the denominator $Q_{L_2}(\lambda)$ is or is not a zero of the numerator $P_{L_1}(\lambda)$ (within the available numerical accuracy). We also analyzed the effectiveness of Padé approximants in representing $\Delta E_M(\lambda)$, equation (31), in the vicinity of the computed singular points.

To obtain high-order corrections $\Delta E^{(n)}$, with n as large as 20, we used the relatively small [4s2p/2s] double zeta (DZ) basis set of Dunning [14]. As pointed out in section 2, the qualitative behavior of various property functions barely changes when different (small and large) basis sets are used [21,22]. The comparison of our results obtained here with a DZ basis set and of the estimates of the radii of convergence based on realistic values for the first through fourth-order properties from our recent study of the HF molecule [22], where we employed a medium-size [5s3p2d/3s2p] basis set of Sadlej that was specifically designed for the calculation of static molecular properties [34], is made at the end of section 3.2.

3.2. Results

Results of our calculations for the DZ HF model are shown in tables 1–6. We present as many energy corrections $\Delta E^{(n)}$ as we could generate in reasonable time with our computer facilities and programs. The behavior of the D’Alembert, Cauchy–Hadamard, and generalized Cauchy–Hadamard sequences r_n^A , r_n^{CH} , and $r_n^{\text{GCH}}(k)$ (with $k = 1$ and 2) for $r = r_e$, $r = 3r_e$, and $r = 5r_e$ is shown in tables 1–3, respectively.

Table 1

The calculated LRCCSD energy corrections $\Delta E^{(n)}$ and the corresponding D'Alembert, Cauchy–Hadamard, and generalized Cauchy–Hadamard sequences r_n^A , r_n^{CH} , and $r_n^{GCH}(k)$ (with $k = 1, 2$), respectively, for the DZ HF molecule with the equilibrium internuclear separation $r = r_e = 1.7328$ a.u. Two types of the perturbation \hat{W} ($\hat{W} = -\hat{\mu}_z$ and $\hat{W} = -\hat{\Theta}_{zz}$) are considered. If the behavior of a given sequence is sufficiently regular, the resulting estimate of the radius of convergence R (or of its lower or upper bound) is also given. The question mark indicates that no estimate of R can be given due to highly irregular behavior of the corresponding sequence r_n^X ($X = A, CH, GCH$).

n	$\hat{W} = -\hat{\mu}_z$					$\hat{W} = -\hat{\Theta}_{zz}$				
	$\Delta E^{(n)}$	r_n^A	r_n^{CH}	$r_n^{GCH}(1)$	$r_n^{GCH}(2)$	$\Delta E^{(n)}$	r_n^A	r_n^{CH}	$r_n^{GCH}(1)$	$r_n^{GCH}(2)$
0	-0.136696	3.416464				-0.136696	5.096151			
1	0.040011	0.019147	24.993207			0.026823	0.005554	37.280982		
2	-2.089640	0.715904	0.691774	0.239276		-4.829456	0.392000	0.455041	0.103531	
3	2.918883	0.619650	0.699726	0.337933	0.057099	12.320029	0.249669	0.432975	0.164488	0.013528
4	-4.710538	1.236521	0.678785	0.375800	0.133007	-49.345383	0.256322	0.377301	0.171750	0.041095
5	3.809508	0.334579	0.765290	0.478674	0.235885	192.513562	0.327901	0.349227	0.179532	0.063802
6	11.385963	0.170882	0.666712	0.429631	0.232609	-587.109448	0.750516	0.345579	0.195266	0.086804
7	-66.630683	0.383289	0.548877	0.359091	0.204463	782.273900	0.125304	0.386067	0.238190	0.124933
8	173.839378	1.020674	0.524785	0.355603	0.216410	6242.988819	0.091276	0.335410	0.213200	0.119143
9	-170.318216	0.229904	0.565044	0.399772	0.260564	-68397.108925	0.165112	0.290251	0.188947	0.110649
10	-740.824629	0.162931	0.516450	0.371562	0.249462	414246.443535	0.238131	0.274331	0.183971	0.113126
11	4546.873188	0.359400	0.465030	0.338914	0.232684	1739577.214340	0.460870	0.270824	0.186989	0.120170
12	-12651.272206	0.983768	0.455151	0.338043	0.238632	3774548.167896	0.231451	0.283092	0.201370	0.134976
13	12860.019161	0.209427	0.482953	0.367058	0.267336	16308161.804953	0.062484	0.278740	0.202366	0.139621
14	61405.625851	0.158501	0.454972	0.349553	0.258609	-260996162.626416	0.135614	0.250502	0.183824	0.128906
15	-387413.815338	0.349618	0.424087	0.328729	0.246325	1924555818.726228	0.192019	0.240461	0.178989	0.127994
16	1108106.562071	0.979859	0.419000	0.328665	0.250166	-10022752773.61886		0.237104	0.179058	0.130505
17	-1130883.711380	0.194093	0.440470	0.350557	0.271728					
18	-5826494.568038	0.157338	0.420866	0.337439	0.264122					
19	37031738.613476	0.345815	0.399626	0.322464	0.254524					
20	-107085270.666431		0.396747	0.322781	0.257385					
R		?	< 0.40	0.32	> 0.25		?	< 0.24	0.18	> 0.13

Table 2
Same as table 1 for $r = 3r_e = 5.1984$ a.u.

n	$\hat{W} = -\hat{\mu}_z$					$\hat{W} = -\hat{\Theta}_{zz}$				
	$\Delta E^{(n)}$	r_n^A	r_n^{CH}	$r_n^{\text{GCH}}(1)$	$r_n^{\text{GCH}}(2)$	$\Delta E^{(n)}$	r_n^A	r_n^{CH}	$r_n^{\text{GCH}}(1)$	$r_n^{\text{GCH}}(2)$
0	-0.287792	0.132316				-0.287792	0.028447			
1	2.175044	1.009574	0.459761			10.116845	0.232278	0.098845		
2	-2.154417	0.069023	0.681295	0.232081		-43.554916	0.011492	0.151524	0.011480	
3	-31.212952	0.047489	0.317606	0.103341	0.005340	-3790.081386	0.010839	0.064138	0.009378	0.000044
4	-657.260224	0.049796	0.197499	0.072455	0.011260	-349661.050695	0.011171	0.041123	0.008942	0.000488
5	-13198.954587	0.050174	0.149931	0.062391	0.015589	-31300418.505015	0.011337	0.031688	0.008941	0.001169
6	-263061.623393	0.051377	0.124927	0.057591	0.018867	-2760899436.1687	0.011623	0.026699	0.009040	0.001864
7	-5120232.377917	0.052343	0.110035	0.055073	0.021552	-237545979473.59		0.023708	0.009187	0.002513
8	-97820332.461891	0.053571	0.100276	0.053641	0.023818					
9	-1826010539.69350	0.054949	0.093529	0.052848	0.025799					
10	-33231227422.486		0.088684	0.052460	0.027576					
R		0.05	< 0.09	0.05	> 0.027		0.01	< 0.024	0.009	> 0.002

Table 3
Same as tables 1 and 2 for $r = 5r_e = 8.6640$ a.u. The question mark between parentheses indicates that too few terms are available to give a definite estimate of the radius of convergence R .

n	$\hat{W} = -\hat{\mu}_z$					$\hat{W} = -\hat{\Theta}_{zz}$				
	$\Delta E^{(n)}$	r_n^A	r_n^{CH}	$r_n^{\text{GCH}}(1)$	$r_n^{\text{GCH}}(2)$	$\Delta E^{(n)}$	r_n^A	r_n^{CH}	$r_n^{\text{GCH}}(1)$	$r_n^{\text{GCH}}(2)$
0	-0.363063	0.104363				-0.363063	0.013591			
1	3.478861	9.151822	0.287450			26.713446	3.067891	0.037434		
2	-0.380128	0.085343	1.621942	1.315347		8.707430	0.004553	0.338887	0.057422	
3	4.454134	0.043774	0.607779	0.273563	0.037418	1912.423055	0.005727	0.080564	0.013202	0.000087
4	101.752172	0.043258	0.314858	0.134937	0.028618	333908.548124		0.041600	0.009080	0.000500
5	2352.232803	0.043697	0.211692	0.096026	0.027701					
6	53831.032950		0.162740	0.079098	0.028052					
R		0.04	< 0.16	< 0.08	0.03		< 0.01(?)	< 0.04	< 0.01	> 0.0005(?)

Table 4

Poles of Padé approximants $\varepsilon_{[L_1, L_2]}(\lambda)$ nearest to the origin ($\lambda_c^{[L_1, L_2]}$) and their distance from the origin in the complex plane resulting from the LRCCSD calculations of the corrections $\Delta E^{(m)}$ for the HF DZ molecule and $\hat{W} = -\hat{\mu}_z$. The results are given for three internuclear separations, $r = r_e = 1.7328$ a.u., $r = 3r_e = 5.1984$ a.u., and $r = 5r_e = 8.6640$ a.u. The corresponding estimates of the radii of convergence R are designated by $R^{\text{Padé}}$ and (a, b) is the complex number $a + bi$.

$r = r_e$			$r = 3r_e$			$r = 5r_e$			
$L_1 = L_2 = L$	$\lambda_c^{[L_1, L_2]}$	$ \lambda_c^{[L_1, L_2]} $	$L_1 = L_2 = L$	$\lambda_c^{[L_1, L_2]}$	$ \lambda_c^{[L_1, L_2]} $	L_1	L_2	$\lambda_c^{[L_1, L_2]}$	$ \lambda_c^{[L_1, L_2]} $
1	-0.019147	0.019147	1	-1.009574	1.009574	1	1	-9.151822	9.151822
2	-0.630084	0.630084	2	0.047783	0.047783	2	2	0.042857	0.042857
3	-0.303079	0.303079	3	0.050290	0.050290	3	3	(0.041710, 0.003866)	0.041888
4	(-0.257157, 0.226822)	0.342897	4	(0.049257, 0.006835)	0.049729	2	4	0.043690	0.043690
5	(-0.257699, 0.231967)	0.346724	5	(0.050639, 0.007403)	0.051177	4	2	0.043494	0.043494
6	(-0.256484, 0.227760)	0.343013							
7	(-0.226261, 0.218330)	0.314423							
8	(-0.256484, 0.227760)	0.343013							
9	(-0.226244, 0.218520)	0.314543							
10	(-0.256484, 0.227760)	0.343013							
$R^{\text{Padé}}$		0.32-0.34			0.05				0.04

Table 5

Same as table 4 for $\hat{W} = -\hat{\Theta}_{zz}$. The question mark between parentheses indicates that too few terms are available to determine R .

$r = r_e$			$r = 3r_e$			$r = 5r_e$				
$L_1 = L_2 = L$	$\lambda_c^{[L_1, L_2]}$	$ \lambda_c^{[L_1, L_2]} $	L_1	L_2	$\lambda_c^{[L_1, L_2]}$	$ \lambda_c^{[L_1, L_2]} $	L_1	L_2	$\lambda_c^{[L_1, L_2]}$	$ \lambda_c^{[L_1, L_2]} $
1	-0.005554	0.005554	1	1	-0.232278	0.232278	1	1	3.067891	3.067891
2	-0.279252	0.279252	2	2	0.010841	0.010841	2	2	0.005727	0.005727
3	0.154636	0.154636	3	3	0.011522	0.011522	1	3	0.035991	0.035991
4	(-0.192966, 0.090780)	0.213253	3	4	0.011638	0.011638	3	1	0.005727	0.005727
5	-0.186831	0.186831	4	3	(0.009885, 0.000444)	0.009895				
6	(-0.192966, 0.090780)	0.213253								
7	(-0.164518, 0.092070)	0.188529								
8	(-0.192966, 0.090780)	0.213253								
$R^{\text{Padé}}$		0.19-0.21			0.01				< 0.01(?)	

Table 6

Summary of the results for the DZ HF model: estimates of the radii of convergence of series (15) for various internuclear separations r obtained using the LRCCSD method and the D'Alembert, Cauchy-Hadamard, and generalized Cauchy-Hadamard convergence tests, and Padé approximants. $r_e = 1.7328$ a.u. is the equilibrium bond length and the question mark indicates that the result is uncertain or could not be obtained.

R	$r = r_e$		$r = 3r_e$		$r = 5r_e$	
	$\hat{W} = -\hat{\mu}_z$	$\hat{W} = -\hat{\Theta}_{zz}$	$\hat{W} = -\hat{\mu}_z$	$\hat{W} = -\hat{\Theta}_{zz}$	$\hat{W} = -\hat{\mu}_z$	$\hat{W} = -\hat{\Theta}_{zz}$
R^A	?	?	0.05	0.01	0.04	< 0.01(?)
R^{CH}	< 0.40	< 0.24	< 0.09	< 0.024	< 0.16	< 0.04
$R^{GCH(1)}$	0.32	0.18	0.05	0.009	< 0.08	< 0.01
$R^{GCH(2)}$	> 0.25	> 0.13	> 0.027	> 0.002	0.03	> 0.0005(?)
$R^{Pad\acute{e}}$	0.32–0.34	0.19–0.21	0.05	0.01	0.04	< 0.01(?)

Table 7

The LRCCSD corrections $\Delta E^{(n)}$, $n = 0-4$, the corresponding D'Alembert, Cauchy-Hadamard, and generalized Cauchy-Hadamard sequences r_n^A , r_n^{CH} , and $r_n^{GCH(1)}$, and the distance of the pole $\lambda_c^{[2,2]}$ of the Padé approximant $\varepsilon_{[L_1, L_2]}(\lambda)$ from the origin in the complex plane resulting from the accurate calculations of the μ_z , α_{zz} , β_{zzz} , and γ_{zzzz} functions for HF ($\hat{W} = -\hat{\mu}_z$) using Sadlej's basis set [34] (see [22]). $r_e = 1.7328$ a.u. is the equilibrium bond length. Whenever possible, the rough estimate of the radius of convergence R , or of its lower or upper bound, corresponding to D'Alembert, Cauchy-Hadamard, and generalized Cauchy-Hadamard convergence criteria, is suggested. The question mark indicates that the result is very uncertain or that no estimate of R can be suggested on the basis of the available results.

n	$\Delta E^{(n)}$	$r = r_e$			$r = 3r_e$				$r = 5r_e$			
		r_n^A	r_n^{CH}	$r_n^{GCH(1)}$	$\Delta E^{(n)}$	r_n^A	r_n^{CH}	$r_n^{GCH(1)}$	$\Delta E^{(n)}$	r_n^A	r_n^{CH}	$r_n^{GCH(1)}$
0	-0.215186	3.767790			-0.335996	0.151410			-0.406679	0.113083		
1	0.057112	0.017515	17.509455		2.219121	0.271398	0.450629		3.596281	0.842940	0.278065	
2	-3.260698	1.982305	0.553789	0.153341	-8.176638	0.086825	0.349714	0.061150	-4.266355	0.499124	0.484141	0.117196
3	1.644902	0.105930	0.847136	0.450163	-94.173572	0.042454	0.219798	0.059494	-8.547681	0.024628	0.489084	0.197476
4	-15.52818		0.503756	0.252507	-2218.25635		0.145713	0.048303	-347.074241		0.231683	0.089641
R		?	< 0.5(?)	?		< 0.05	< 0.15	< 0.05		< 0.03	< 0.23	< 0.09
$ \lambda_c^{[2,2]} $	0.424531				0.045138				0.036627			

Poles of Padé approximants $\varepsilon_{[L_1, L_2]}(\lambda)$ that are closest to the origin, designated as $\lambda_c^{[L_1, L_2]}$, are listed for various values of L_1 and L_2 in tables 4 (for $\hat{W} = -\hat{\mu}_z$) and 5 (for $\hat{W} = -\hat{\Theta}_{zz}$). We usually present the diagonal entries $\varepsilon_{[L, L]}(\lambda)$, unless too few energy corrections were available (in view of a very slow convergence of the iterative procedure used to generate $\Delta E^{(n)}$), in which case the off-diagonal entries $\varepsilon_{[L_1, L_2]}(\lambda)$, with $L_1 \neq L_2$, are provided as well. Table 6 then summarizes our calculations of the radii of convergence for the DZ HF molecule.

Let us start with the analysis of the convergence patterns for various convergence tests that we employed. In spite of a large number of corrections $\Delta E^{(n)}$ that are available to us for $r = r_e$, the D'Alembert ratio test, equations (25) and (26), seems to be inconclusive. For both types of the perturbation \hat{W} considered, the behavior of the sequence r_n^A is rather erratic (see table 1). As a result, it is difficult to find the limit R^A , equation (25). A more favorable situation is found when we investigate stretched geometries. Surprisingly enough, in spite of the fact that fewer corrections $\Delta E^{(n)}$, $n \geq 1$, are available to us for $r = 3r_e$ (ten and seven) or $r = 5r_e$ (six and four), the sequences r_n^A seem to stabilize rather fast (see tables 2 and 3). As a result, quite reasonable predictions of the radii of convergence based on equation (25) can be made when $r = 3r_e$ or $5r_e$. The only exception is the case $r = 5r_e$, $\hat{W} = -\hat{\Theta}_{zz}$ when four corrections $\Delta E^{(n)}$ do not suffice for the ratio test.

The Cauchy–Hadamard criterion, equations (27) and (28), is in general more useful, since the sequences r_n^{CH} decrease almost monotonically for all the geometries and perturbations \hat{W} considered (slowly for $r = r_e$, faster for $r = 3r_e$ or $5r_e$). As a result, the Cauchy–Hadamard formula allows us to find the upper bounds of the radii of convergence characterizing the series (15).

The regular behavior of the Cauchy–Hadamard sequences r_n^{CH} can be quite effectively stabilized by considering differentiated series (15) (the generalized Cauchy–Hadamard criterion with $k = 1$, equations (29) and (30)). As a result, we can either identify the required inferior limit (29) (for $r = r_e$ and $r = 3r_e$) or find an upper bound to R (for $r = 5r_e$) thanks to a decreasing behavior of $r_n^{\text{GCH}}(1)$. When the series (15) is differentiated twice ($k = 2$ in equations (29) and (30)), the corresponding sequences $r_n^{\text{GCH}}(2)$ are usually monotonically increasing (almost certainly for $r = r_e$ and $3r_e$, and perhaps for $r = 5r_e$, $\hat{W} = -\hat{\Theta}_{zz}$) allowing us to find the lower bounds to R (see tables 1–3). We must remember, however, that each differentiation reduces the number of the available $\Delta E^{(n)}$ corrections by one. As a result, no definite conclusions can be drawn when only six or four terms $\Delta E^{(n)}$, $n \geq 1$, are available (see the results for $r = 5r_e$ in table 3).

The Cauchy–Hadamard formula, equations (27) and (28), and, particularly, its generalized analog with $k = 1$, equations (29) and (30), give results which agree remarkably well with those obtained with Padé approximants (tables 4 and 5). In fact, no contradiction was ever found between the results obtained using Padé approximants and other methods, including the D'Alembert ratio test. Nonetheless, Padé approximants should be the method of choice, since they yield very stable values of $|\lambda_c^{[L_1, L_2]}|$, even with a relatively few terms $\Delta E^{(n)}$. In fact, except for the $r = r_e$ case, the

$\varepsilon_{[2,2]}(\lambda)$ approximant gives usually the same (numerically) result as its higher-order analogs $\varepsilon_{[L_1, L_2]}(\lambda)$ with $L_1, L_2 \geq 3$. For $r = r_e$, one should consider the approximants $\varepsilon_{[L, L]}(\lambda)$ with $L = 3$ or 4 , indicating that one must be careful with the results obtained using low-order entries with $L = 1$ or 2 (see tables 4 and 5).

Our results show that the radius of convergence of expansions (2) or (15) dramatically decreases with the increasing internuclear separation r . For $r = 3r_e$ or $5r_e$, the radii of convergence become so small that the fields λ that are typically used in the numerical differentiation of the finite-field approach may fall outside the range of convergence. This particularly applies to the third- and fourth-order properties (e.g., β and γ), where three- and four-fold differentiations of the energy $\Delta E(\lambda)$ are required to extract the property values, thus forcing one to use relatively large (of the order of 0.01 a.u.) steps $\Delta\lambda$ in the differentiation. Even when the applied fields λ fall within the interval of convergence $(-R, R)$, they may be too close to the radius of convergence to guarantee the stability of the numerical differentiation. This is what we observed in our recent study of the property functions of HF [22], where – for the sake of comparison – we also exploited the finite-field procedure to calculate μ_z , α_{zz} , β_{zzz} , and γ_{zzzz} using the full configuration interaction energy data. We could not find β_{zzz} and γ_{zzzz} for $r \geq 3r_e$, and obtained rather poor estimates even for α_{zz} in the same region.

The range of convergence is always smaller for the $\hat{W} = -\hat{\Theta}_{zz}$ case, when compared with the $\hat{W} = -\hat{\mu}_z$ case, which indicates that nonuniform fields decrease the range of convergence, sometimes quite substantially. Our results thus agree with the findings of Larter and Malik [23], who discussed the consequences of this fact for the fixed-point-charge and finite-field methods. Fixed-point-charge calculations can be characterized by relatively large field-gradient values, thus putting in doubt the resulting property values for stretched geometries [23]. In fact, it may be very difficult to apply the finite-field approach (with, e.g., $\lambda = \frac{1}{3}F^{zz}$) to calculate quadrupolar properties, particularly the third- and fourth-order analogs of $C_{zz,zz}$, for stretched geometries. Even $C_{zz,zz}$, regarded as a function of r , may represent a serious problem for the finite-field approach. From this point of view, the analytical approaches, such as our LRCC method, seem to be indispensable.

The finite-field method should be easily applicable at near equilibrium geometries, where the corresponding radii of convergence are quite large, making numerical differentiation very stable and reliable. The same applies to the experimental determination of molecular properties, using, for example, the Stark or electric resonance effect, where the applied fields ($\sim 10^{-7}$ a.u.) are much smaller than the radius of convergence of expansions (2) or (15). We must note, however, that it is difficult to extract the information about property functions from experimental data, which makes any theoretical determination of these functions very desirable (cf. [33,38] and references therein).

Let us finally comment on the role of basis sets in the calculations of radii of convergence. In principle, we can evaluate the LRCCSD energy corrections $\Delta E^{(n)}$ using large AO basis sets. Unfortunately, the calculation of $\Delta E^{(n)}$ with $n \geq 5$ takes

a rather long time on our computers. We thus use the accurate LRCCSD data for the μ_z , α_{zz} , β_{zzzz} , and γ_{zzzz} functions of HF obtained earlier [22] with a good quality basis set of Sadlej [34]. These property functions allow us to calculate $\Delta E^{(n)}$ with $n = 1, \dots, 4$. The corresponding sequences r_n^A , r_n^{CH} , and $r_n^{GCH}(1)$ along with the pole $\lambda_c^{[2,2]}$ are given in table 7.

As we can see, quite good agreement can be found between the radii of convergence estimated in this way (from the high quality but limited number of data) and the results obtained with the DZ basis set using larger number of corrections $\Delta E^{(n)}$. We find this to be encouraging as it basically confirms our expectations that the results obtained with smaller basis sets are at least qualitatively correct.

It would be interesting to examine the radii of convergence of the multiparameter analogs of the series (2) or (15) (using, for example, N -variable approximants; cf. [23]), defining the off-diagonal components of tensors α , β , γ , and \mathbf{C} , and all components of \mathbf{A} or \mathbf{B} , using the results obtained with the DZ (or similar) basis set and higher-order corrections $\Delta E^{(n_1, n_2, \dots)}$. This should be feasible thanks to our recursive formulation of the LRCCSD theory described elsewhere [21,22]. Since the problem of convergence of the energy expansions describing molecules in external fields is seldom mentioned in the context of finite-field or fixed-point-charge calculations, not to mention various experimental studies, we are convinced that some effort should be made in this direction to verify the accuracy of the resulting properties or property functions.

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References

- [1] B.G. Adams and J. Paldus, Phys. Rev. A 20 (1979) 1.
- [2] J. Applequist, Chem. Phys. 85 (1984) 279.
- [3] G.A. Baker, Jr., *Essentials of Padé Approximants* (Academic, New York, 1975) chapter 10.
- [4] G.A. Baker, Jr., and P. Graves-Morris, *Padé Approximants, Part I: Basic Theory* (Addison-Wesley, Reading, MA, 1981) section 2.2.
- [5] G.A. Baker, Jr., and P. Graves-Morris, *Padé Approximants*, 2nd ed. (Cambridge University Press, Cambridge, 1996) section 2.2.
- [6] R.J. Bartlett, in: *Modern Electronic Structure Theory*, ed. D.R. Yarkony (World Scientific, Singapore, 1995) p. 1047.
- [7] D.M. Bishop, Rev. Mod. Phys. 62 (1990) 343.
- [8] A.D. Buckingham, Adv. Chem. Phys. 12 (1967) 107.
- [9] B.W. Char, K.O. Geddes, G.H. Gonnet, M.B. Monagan and S.M. Watt, *Maple Reference Manual*, 5th ed. (Watcom Publications, Waterloo, Ontario, 1988).
- [10] B.W. Char, K.O. Geddes, G.H. Gonnet, M.B. Monagan and S.M. Watt, *MAPLE, First Leaves, A Tutorial Introduction to Maple*, 3rd ed. (Watcom Publications, Waterloo, Ontario, 1990).

- [11] B.W. Char, K.O. Geddes, G.H. Gonnet, B.L. Leong, M.B. Monagan and S.M. Watt, *Maple V, Maple Language Reference Manual*, pre-publication manuscript (Waterloo Maple Publishing, Waterloo, Ontario, 1991).
- [12] J.S.R. Chisholm and J. McEwan, Proc. Roy. Soc. A 336 (1974) 421.
- [13] H.D. Cohen and C.C.J. Roothaan, J. Chem. Phys. 43 (1965) S34.
- [14] T.H. Dunning, J. Chem. Phys. 53 (1970) 2823.
- [15] M. Dupuis, D. Spangler and J.J. Wendoloski, The GAMESS system of programs, National Resource for Computations in Chemistry, Software Catalog, University of California, Berkeley, CA (1980) Program QG01.
- [16] C.E. Dykstra, *Ab Initio Calculation of the Structures and Properties of Molecules* (Elsevier, Amsterdam, 1988).
- [17] C.E. Dykstra and P.G. Jasien, Chem. Phys. Lett. 109 (1984) 388.
- [18] C.E. Dykstra, S.-Y. Liu and D.J. Malik, Adv. Chem. Phys. 75 (1990) 37.
- [19] C.G. Gray and B.W.N. Lo, Chem. Phys. 14 (1976) 73.
- [20] S. Kielich, Acta Phys. Pol. 28 (1965) 459.
- [21] A.E. Kondo, P. Piecuch and J. Paldus, J. Chem. Phys. 102 (1995) 6511.
- [22] A.E. Kondo, P. Piecuch and J. Paldus, J. Chem. Phys. 104 (1996) 8566.
- [23] R. Larter and D.J. Malik, Chem. Phys. 112 (1987) 301.
- [24] A.D. McLean and M. Yoshimine, J. Chem. Phys. 46 (1967) 3682.
- [25] H.J. Monkhorst, Int. J. Quantum Chem. Symp. 11 (1977) 421.
- [26] J. Paldus, J. Chem. Phys. 67 (1977) 303.
- [27] A. Pellégatti, J. Čížek and J. Paldus, J. Chem. Phys. 60 (1974) 4825.
- [28] A. Pellégatti, J. Čížek and J. Paldus, Int. J. Quantum Chem. 21 (1982) 147.
- [29] P. Piecuch, in: *Molecules in Physics, Chemistry and Biology*, Vol. 2, *Physical Aspects of Molecular Systems*, ed. J. Maruani (Kluwer, Dordrecht, 1988) p. 417.
- [30] P. Piecuch and J. Paldus, Int. J. Quantum Chem. 36 (1989) 429.
- [31] P. Piecuch and J. Paldus, Theor. Chim. Acta 78 (1990) 65.
- [32] P. Piecuch and J. Paldus, J. Chem. Phys. 101 (1994) 5875.
- [33] P. Piecuch, A. E. Kondo, V. Špirko and J. Paldus, J. Chem. Phys. 104 (1996) 4699.
- [34] A. Sadlej, Coll. Czech. Chem. Commun. 53 (1988) 1995.
- [35] A.J. Sadlej, J. Chem. Phys. 96 (1992) 2048.
- [36] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis and J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347.
- [37] D.E. Stogryn, Mol. Phys. 22 (1971) 81; 23 (1972) 897.
- [38] V. Špirko, P. Piecuch, A.E. Kondo and J. Paldus, J. Chem. Phys. 104 (1996) 4716.
- [39] M. Takahashi, J. Čížek and J. Paldus, Phys. Rev. B 33 (1986) 1203.