

First-order relativistic corrections to response properties: the hyperpolarizability of the Ne atom

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Abstract

The computation of first-order relativistic corrections to electrical response properties has been implemented into the Dalton program at the level of closed-shell coupled-cluster theory, within the framework of the direct perturbation theory (DPT) of relativistic effects. Calculations of the first-order relativistic DPT corrections to the static and frequency-dependent dipole polarizability (α) and second dipole hyperpolarizability (γ) of the Ne atom illustrate possible applications of the new code.

1. Introduction

The coupled-cluster response approach to the calculation of frequency-dependent (hyper)polarizabilities of atoms and small molecules has in recent years developed into a computational tool capable of providing highly accurate results [1–4]. When the effect of the connected triple excitations is considered, the accuracy of the nonrelativistic coupled-cluster response calculations is sufficiently high for the largest deficiencies to arise from the neglect of vibrational and relativistic corrections, even for first-row atoms or small molecules containing such atoms. In this paper, we report our implementation—into the Dalton program—of the calculation of relativistic corrections to static and frequency-dependent polarizabilities and hyperpolarizabilities, within the framework of the relativistic direct perturbation theory (DPT) [5]. For light atoms, a first-order treatment suffices.

In a previous work, one of the present authors has shown that the calculation of (spin-free) first-order relativistic DPT corrections can be implemented very easily using computer codes

for analytical molecular gradients [6]. This approach has since then been realized at the levels of the second-order Møller–Plesset perturbation theory (MP2) [7] and the coupled-cluster theory with single and double connected excitations (CCSD) [8]. In this work, we have extended the latter implementation to the level of the CCSD(T) theory—that is, the CCSD theory with perturbative treatment of connected triple excitations—using the computer code recently developed in [9].

In addition to the implementation of the analytical calculation of first-order DPT corrections to the CCSD(T) energy of a field-free molecular Hamiltonian, we have considered the calculation of the first-order DPT correction for a molecule in a finite electric field. We have furthermore implemented, in the spirit of [6], the numerical perturbation of the one- and two-electron Hamiltonian integrals, so as to compute the first-order DPT correction to a molecular (response) property by numerical differentiation.

We have applied our new codes to the calculation of relativistic corrections to (frequency-dependent) response properties of the Ne atom. Our interest in this atom was motivated by a discrepancy that we found in the literature between reported values of the relativistic correction to its static second dipole hyperpolarizability. Franke *et al* report a correction of 3.1 au, obtained from first-order DPT corrections at the MP2 level [10]. By contrast, Nakajima and Hirao report a correction of only 0.6 au, obtained using a spin-free modification of the third-order Douglas–Kroll method (DK3) at the CCSD(T) level [11]. Furthermore, we were not only puzzled by this discrepancy but also by the estimate of the basis-set limit of the static second dipole hyperpolarizability of Ne at the CCSD(T) level reported by Franke *et al* [10]. These authors obtained a value of 104.8 au, which is significantly below the value of 107.2 au obtained by Hättig and co-workers in a very large, triply-augmented correlation-consistent core–valence quintuple-zeta (t-aug-cc-pCV5Z) basis [3, 4]. Accidentally, Franke *et al*'s relativistic DPT and nonrelativistic CCSD(T) values add up to a value of 107.9 au, which almost coincides with the value of 107.8 au obtained by adding the relativistic correction of Nakajima and Hirao to the nonrelativistic CCSD(T) value of Hättig and co-workers. Since a comparison with experiment cannot resolve the discrepancy, we decided to reinvestigate both the relativistic correction and the basis-set limit CCSD(T) value.

In the following, we present the technical details of our calculations in section 2, the numerical results for Ne in section 3, and finally our conclusions in section 4.

2. Computational details

We compute the first-order relativistic DPT corrections to the static electrical response properties in two different ways. In both cases, we use double perturbation theory, adding the electric fields and the relativistic DPT operators as perturbations. The two approaches differ mainly with respect to the terms in the perturbation series that are evaluated analytically. In the first approach, we apply the electric field as a finite perturbation, while the relativistic corrections to the molecular properties are determined by numerical differentiation of first-order DPT energies calculated analytically in the presence of the electric fields (cf section 2.1). In the second approach, the relativistic DPT operators are added as a finite field, while the relativistic corrections to the molecular properties are determined by numerical differentiation of response properties that are calculated analytically in the presence of the DPT fields (cf section 2.2). These two approaches give identical results except for differences related to different physical descriptions in the two approaches—for example, different treatments of orbital relaxation. In the practical implementations of the two approaches—using, for example, the CCSD method—the Hartree–Fock orbitals are in the first method allowed to relax both to the electric field and to the DPT perturbation, whereas, in the second method

(where analytical CCSD response properties are evaluated), the Hartree–Fock orbitals are not allowed to relax to the electric field. The main advantage of the first approach is that it gives us an easy access to the relativistic correction to a static response property at all levels of the coupled-cluster theory for which the energy can be computed (e.g., explicitly-correlated coupled-cluster methods). The advantage of the second approach, on the other hand, is that we obtain an easy access to the relativistic correction to frequency-dependent response properties for the selection of coupled-cluster models where analytic response functions have been implemented. In the following two subsections, we describe the implementations of the two approaches in more detail.

2.1. Analytical calculation of the scalar first-order DPT energy

As pointed out in [6], the scalar first-order relativistic DPT correction to the ground-state energy of a closed-shell system can be implemented into an existing nonrelativistic *ab initio* electronic-structure code by regarding this correction as a perturbation that modifies the overlap integrals as well as the one- and two-electron integrals of the nonrelativistic Hamiltonian. In particular, the scalar first-order relativistic perturbation is introduced through the following differentiated integrals:

$$S'_{pq} = (4c^2)^{-1} \langle \chi_p | \mathbf{p} \cdot \mathbf{p} | \chi_q \rangle = (2c^2)^{-1} T_{pq}, \quad (1)$$

$$H'_{pq} = (4c^2)^{-1} \langle \chi_p | \mathbf{p} V \cdot \mathbf{p} | \chi_q \rangle, \quad (2)$$

$$(pq|rs)' = (4c^2)^{-1} (\chi_p \chi_q | \mathbf{p} \chi_r \cdot \mathbf{p} \chi_s) + (4c^2)^{-1} (\mathbf{p} \chi_p \cdot \mathbf{p} \chi_q | \chi_r \chi_s). \quad (3)$$

Here T_{pq} is an element of the kinetic-energy matrix, the χ_p are basis functions (e.g., contracted Gaussians), and V is the one-electron nuclear-attraction potential given by

$$V = - \sum_K Z_K r_K^{-1} = - \sum_K Z_K |\mathbf{r} - \mathbf{K}|^{-1}. \quad (4)$$

The position of the nucleus K with the charge Z_K is here denoted by \mathbf{K} , the conjugate momentum by $\mathbf{p} = -i\nabla$ and the velocity of light by $c \approx 137.036$ au.

Let us now consider a second external perturbation that can be represented by a modification of the one-electron nuclear-attraction potential, for instance,

$$\tilde{V} = V + \eta z_C, \quad (5)$$

where $z_C = z - C_z$ is the z component of the dipole-length operator with respect to the origin \mathbf{C} . In all of our calculations for which we present results, we have chosen $\mathbf{C} = \mathbf{0}$.

Although in this subsection we calculate the first-order correction of the first perturbation analytically (i.e., the first-order DPT correction), we introduce the second perturbation by adding it with a given finite field strength η to the one-electron Hamiltonian. Then, obviously, the modified potential must be inserted into the differentiated integrals of equation (2):

$$\tilde{H}'_{pq} = (4c^2)^{-1} \langle \chi_p | \mathbf{p} \tilde{V} \cdot \mathbf{p} | \chi_q \rangle = H'_{pq} + \eta (4c^2)^{-1} \langle \chi_p | \mathbf{p} z_C \cdot \mathbf{p} | \chi_q \rangle. \quad (6)$$

The last term is related to the change of picture [12, 13] and its contributions are therefore referred to as picture-change effects.

For the calculations with the Dalton program (*vide infra*), we have applied finite electric fields with field strengths η obeying $\eta^2 = k \times 250 \times 10^{-6}$ au for $k = 0, 1, \dots, 4$. The energies were then fitted to a fourth-order polynomial in η^2 . To obtain numerically stable results from the explicitly-correlated coupled-cluster calculations with the DIRCCR12-OS program

(*vide infra*), we needed more than four external fields. For the calculations with this program, we fitted a second-order polynomial in η^2 to the linear combination of energies

$$\bar{E}(\eta^2) = E(\eta^2) - E(2\eta^2)/4 + E(3\eta^2)/27 \quad (7)$$

with $\eta^2 = k \times 25 \times 10^{-6}$ au for $k = 0, 1, \dots, 5$. The field strengths involved in this procedure are similar to those used by Franke *et al*, who applied 21 fields with $\eta = k \times 0.001$ au for $k = 0, 1, \dots, 20$ [10].

It takes almost no effort to implement the analytical calculation of the scalar first-order DPT correction at a given level of theory, provided analytical nuclear gradients are available for that level. Since analytical nuclear gradients have recently become available in the Dalton program for the CCSD(T) level [9], we could simply take that code and consider equations (1)–(3) and (6) as differentiated integrals.

2.2. First-order DPT corrections from numerical differentiation

With the Dalton program, linear, quadratic, and cubic response properties can be computed analytically at various levels of coupled-cluster theory, providing both static and frequency-dependent results. It is then straightforward to calculate the first-order relativistic DPT correction to these analytically computed results simply by modifying the integrals that enter the calculation of the response property. It is only necessary to modify the one- and two-electron Hamiltonian integrals, the overlap integrals and the one-electron integrals of the dipole length operator, for example, its z -component z_C ,

$$\tilde{S}_{pq} = S_{pq} + \xi S'_{pq}, \quad (8)$$

$$\tilde{H}_{pq} = H_{pq} + \xi H'_{pq}, \quad (9)$$

$$\tilde{Z}_{pq} = Z_{pq} + \xi Z'_{pq} = \langle \chi_p | z_C | \chi_q \rangle + \xi (4c^2)^{-1} \langle \chi_p | \mathbf{p} z_C \cdot \mathbf{p} | \chi_q \rangle, \quad (10)$$

$$(pq|\tilde{r}s) = (pq|rs) + \xi (pq|rs)'. \quad (11)$$

Having carried out calculations with two applied DPT fields with $|\xi| = 0.1$ au, the DPT correction Q' to the property Q is obtained from the central-difference formula

$$Q' = \{Q(\xi) - Q(-\xi)\}/(2\xi). \quad (12)$$

This approach, which consists of computing the response properties analytically in the presence of finite DPT fields, is computationally faster and numerically more stable than that of section 2.1. Obviously, the preferable approach is to compute the first derivative with respect to one perturbation numerically and the higher derivatives with respect to the other perturbation analytically.

However, care must be taken when applying finite DPT fields. If the magnitude of the negative field strength $-\xi$ is chosen larger than some critical value ξ_{crit} , the perturbed overlap matrix of equation (8) is no longer positive definite. The magnitude of the field strength must be chosen smaller than this critical value, which depends on the basis set used (see section 3).

2.3. Coupled-cluster models

We have investigated various coupled-cluster models as well as the Hartree–Fock and MP2 levels. The relevant models are the coupled-cluster model with connected single and double excitations (CCSD [14]) and the CCSD model with a perturbative correction for connected triple excitations, both in the CCSD[T] [15] and CCSD(T) [16] forms. Coupled-cluster

Table 1. 5s5p4d3f3g3h3i3k Gaussian basis set of diffuse functions.

Type	Exponents (au)				
s	0.025 000 0	0.012 500 0	0.006 250 0	0.003 125 0	0.001 562 5
p	0.025 000 0	0.012 500 0	0.006 250 0	0.003 125 0	0.001 562 5
d	0.074 720 0	0.034 470 0	0.015 900 0	0.007 334 0	
f	0.096 070 0	0.044 320 0	0.020 440 0		
g	0.117 400 0	0.054 160 0	0.024 980 0		
h	0.313 000 0	0.150 400 0	0.072 210 0		
i	0.766 800 0	0.375 200 0	0.183 600 0		
k	1.815 000 0	0.907 500 0	0.453 700 0		

linear response [17] and coupled-cluster cubic response [1] calculations were performed at the (unrelaxed) CCSD level. The calculations were performed in an integral-direct manner [18]. In addition, explicitly-correlated [19, 20] MP2 and coupled-cluster calculations were carried out. The corresponding models are denoted by MP2-R12/A, MP2-R12/B, CCSD-R12/B, CCSD[T]-R12/B and CCSD(T)-R12/B, where the extension -R12 indicates the inclusion of terms linear in the interelectronic distances r_{ij} , and where the extension /A or /B refers to the standard approximation (either A or B) of the explicitly-correlated coupled-cluster theory [21–23]. All electrons were correlated in all post-Hartree–Fock calculations.

2.4. Basis sets and programs

The standard MP2 and standard CCSD and CCSD(T) calculations were carried out in the doubly-augmented correlation-consistent polarized core–valence quadruple-zeta (d-aug-cc-pCVQZ), triply-augmented correlation-consistent polarized core–valence quintuple-zeta (t-aug-cc-pCV5Z) and quadruply-augmented correlation-consistent polarized core–valence sextuple-zeta (q-aug-cc-pCV6Z) basis sets [24–27]⁶. The explicitly-correlated CCSD-R12/B, CCSD[T]-R12 and CCSD(T)-R12 calculations were carried out in a large uncontracted Gaussian basis of the composition 25s19p15d12f10g8h6i4k, derived from the 20s14p11d9f7g5h3i basis of [28] and [29] by adding first a set of k functions with exponent 3.629 959 au and then a set of diffuse functions of the composition 5s5p4d3f3g3h3i3k (cf table 1).

All calculations were done with the Dalton program [30] except those in table 8, which were obtained from calculations with the DIRCCR12-OS program [31].

3. Results

The results of our Hartree–Fock, MP2, CCSD and CCSD(T) calculations of the static dipole polarizability α of Ne are collected in table 2 and compared with the results of Franke *et al* [10] and Nakajima and Hirao [11]. The basis-set dependence of the DPT correction is almost negligible for the basis sets considered. At the MP2 level, Franke *et al*'s DPT correction is slightly smaller than our values but still similar. The DK3 corrections of Nakajima and Hirao are in agreement with our DPT corrections except at the Hartree–Fock level, where their DK3

⁶ Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 10/21/03, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, PO Box 999, Richland, Washington 99352, USA, and funded by the US Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the US Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.

Table 2. Static dipole polarizability α (in au) of Ne. The relativistic DPT correction is computed analytically in the presence of finite electric fields. The DPT and DK3 corrections from [10] and [11], respectively, are given for comparison.

	Hartree–Fock	MP2	CCSD	CCSD(T)
		d-aug-cc-pCVQZ		
Nonrelativistic	2.379 90	2.702 02	2.623 23	2.672 11
DPT correction	0.003 03	0.004 55	0.004 06	0.004 32
Relativistic	2.382 94	2.706 57	2.627 29	2.676 43
		t-aug-cc-pCV5Z		
Nonrelativistic	2.377 18	2.696 01	2.614 56	2.663 54
DPT correction	0.003 02	0.004 52	0.004 02	0.004 28
Relativistic	2.380 20	2.700 54	2.618 58	2.667 83
		q-aug-cc-pCV6Z		
Nonrelativistic	2.375 36	2.691 93	2.609 70	2.658 69
DPT correction	0.003 14	0.004 67	0.004 16	0.004 43
Relativistic	2.378 50	2.696 60	2.613 86	2.663 12
		Reference [10]		
DPT correction		0.004		
		Reference [11]		
DK3 correction	0.002	0.005	0.004	0.004

Table 3. Static second dipole hyperpolarizability γ (in au) of Ne. The relativistic DPT correction is computed analytically in the presence of finite electric fields. The DPT and DK3 corrections from [10] and [11], respectively, are given for comparison.

	Hartree–Fock	MP2	CCSD	CCSD(T)
		d-aug-cc-pCVQZ		
Nonrelativistic	67.78	107.81	97.86	106.62
DPT correction	0.32	0.58	0.51	0.57
Relativistic	68.10	108.40	98.37	107.19
		t-aug-cc-pCV5Z		
Nonrelativistic	68.64	108.83	98.31	107.18
DPT correction	0.32	0.58	0.51	0.57
Relativistic	68.96	109.41	98.82	107.75
		q-aug-cc-pCV6Z		
Nonrelativistic	68.79	108.77	98.17	107.02
DPT correction	0.33	0.60	0.52	0.59
Relativistic	69.12	109.37	98.69	107.61
		Reference [10]		
DPT correction		3.1		
		Reference [11]		
DK3 correction	0.33	0.6	0.5	0.6

correction of 0.002 au seems a little too small. A correction of 0.003 au, as found in this work, was also found in previous work [33] for all of the theories: Dirac–Fock–Coulomb, first-order DPT, IORA (infinite-order regular approximation) and scaled-ZORA (scaled zeroth-order regular approximation).

Table 3 displays the results of our calculations of the static second dipole hyperpolarizability γ , again in comparison with [10] and [11]. The agreement with [11]

Table 4. Static dipole polarizability α (in au) of Ne at the Hartree–Fock level as a function of the basis set. The polarizability is computed analytically in the presence of finite DPT fields.

	d-aug-cc-pCVQZ	t-aug-cc-pCV5Z	q-aug-cc-pCV6Z
Nonrelativistic	2.379 904	2.377 180	2.375 360
DPT w/o picture change	0.002 984	0.002 972	0.003 093
Picture-change effect	0.000 050	0.000 050	0.000 050
Total DPT correction	0.003 035	0.003 022	0.003 143
Relativistic	2.382 939	2.380 202	2.378 503

Table 5. Static second dipole hyperpolarizability γ (in au) of Ne at the Hartree–Fock level as a function of the basis set. The hyperpolarizability is computed analytically in the presence of finite DPT fields.

	d-aug-cc-pCVQZ	t-aug-cc-pCV5Z	q-aug-cc-pCV6Z
Nonrelativistic	67.7778	68.6406	68.7884
DPT w/o picture change	0.3203	0.3221	0.3326
Picture-change effect	−0.0004	−0.0004	−0.0004
Total DPT correction	0.3199	0.3217	0.3322
Relativistic	68.0977	68.9623	69.1206

is perfect, and we strongly believe that the MP2-DPT correction of 3.1 au as reported by Franke *et al* [10] is a factor of 5 too large. As for the static dipole polarizability, the basis-set dependence of the DPT correction to the hyperpolarizability is very small.

At the Hartree–Fock level, we have also computed the static dipole polarizability and second dipole hyperpolarizability of Ne analytically in the presence of finite DPT fields. The results, which are in full agreement with the Hartree–Fock results presented in tables 2 and 3, respectively, are collected in tables 4 and 5.

The analytical computation of the response property allows us to present the results with the number of decimal places that is required to reveal the picture-change effect, which amounts to 0.000 050 au for α and −0.0004 au for γ in all of the three basis sets. These are very small effects indeed, which one might be tempted to neglect. However, in our implementation of the first-order DPT correction to electrical response properties, the inclusion of the $\mathbf{p}_{zC} \cdot \mathbf{p}$ integrals in equations (6) and (10) not only takes care of the picture change but also ensures gauge invariance of the results. We checked this by choosing various origins \mathbf{C} , for which we obtained identical results. Note that the orbital energies are all shifted by a constant value if the origin is not chosen on the nucleus of the Ne atom. The change induced by the shifted orbital energies is exactly compensated for by the same constant shift in the $\mathbf{p}_{zC} \cdot \mathbf{p}$ integrals.

If we manipulate the one- and two-electron integrals as discussed in section 2.2, we can calculate the first-order DPT corrections to frequency-dependent electrical response properties from linear (for α) and cubic (for γ) coupled-cluster response calculations. The corresponding results are presented in tables 6 and 7 for the d-aug-cc-pCVQZ and d-aug-cc-pCV5Z basis sets (in view of the small basis-set effects and the costs of the calculations, we did not carry out the calculations with the q-aug-cc-pCV6Z basis). For both α and γ , we have chosen the frequencies $\omega = 0.042 823$ au (which corresponds to the wavelength of $\lambda = 1064$ nm) and $\omega = 0.093 215$ au ($\lambda = 488.8$ nm), which are experimentally relevant frequencies for γ [4]. In tables 6 and 7, we observe that the first-order DPT correction increases with increasing frequencies, as does the (hyper)polarizability.

Table 6. Static and frequency-dependent dipole polarizability α (in au) of Ne at the (orbital-unrelaxed) CCSD level as a function of the basis set. The polarizability is computed analytically in the presence of finite DPT fields.

	d-aug-cc-pCVQZ	t-aug-cc-pCV5Z
$\omega = 0.0$		
Nonrelativistic	2.674 503	2.664 711
DPT w/o picture change	0.004 252	0.004 209
Picture-change effect	0.000 054	0.000 054
Total DPT correction	0.004 306	0.004 263
Relativistic	2.678 809	2.668 974
$\omega = 0.042\ 823$ au		
Nonrelativistic	2.679 778	2.669 953
DPT w/o picture change	0.004 281	0.004 238
Picture-change effect	0.000 054	0.000 054
Total DPT correction	0.004 335	0.004 292
Relativistic	2.684 113	2.674 245
$\omega = 0.093\ 215$ au		
Nonrelativistic	2.699 751	2.689 802
DPT w/o picture change	0.004 392	0.004 347
Picture-change effect	0.000 053	0.000 053
Total DPT correction	0.004 445	0.004 401
Relativistic	2.704 195	2.694 202

Table 7. Static and frequency-dependent second dipole hyperpolarizability γ (in au) of Ne at the (orbital-unrelaxed) CCSD level as a function of the basis set. The hyperpolarizability is computed analytically in the presence of finite DPT fields.

	d-aug-cc-pCVQZ	t-aug-cc-pCV5Z
$\omega = 0.0$		
Nonrelativistic	108.5484	108.9101
DPT w/o picture change	0.5859	0.5852
Picture-change effect	-0.0003	-0.0003
Total DPT correction	0.5856	0.5849
Relativistic	109.1339	109.4950
$\omega = 0.042\ 823$ au		
Nonrelativistic	111.8272	112.2084
DPT w/o picture change	0.6120	0.6114
Picture-change effect	-0.0003	-0.0004
Total DPT correction	0.6117	0.6110
Relativistic	112.4389	112.8194
$\omega = 0.093\ 215$ au		
Nonrelativistic	125.5181	125.9799
DPT w/o picture change	0.7252	0.7249
Picture-change effect	-0.0004	-0.0005
Total DPT correction	0.7248	0.7245
Relativistic	126.2429	126.7044

Despite the stability of the results shown in tables 2–7 with respect to basis-set size, and despite the agreement between the results obtained from the approaches of sections 2.1 and 2.2, it appears appropriate to analyse in some detail the behaviour of the finite-field procedure

Table 8. Static dipole polarizability α (in au) and second dipole hyperpolarizability γ (in au) of Ne as calculated in the 25s19p15d12f10g8h6i4k basis by numerical differentiation. The ground-state energy E (in au) is also given.

Method	E	α	γ
Hartree–Fock	–128.547 09	2.376 73	68.83
MP2	–128.929 58	2.692 55	108.75
MP2-R12/A	–128.935 28	2.690 32	108.51
MP2-R12/B	–128.935 17	2.689 69	n.a. ^a
CCSD	–128.926 98	2.609 90	97.98
CCSD-R12/B	–128.931 09	2.607 27	97.69
CCSD[T]	–128.933 95	2.668 66	110.20
CCSD[T]-R12/B	–128.938 05	2.665 75	109.83
CCSD(T)	–128.933 75	2.658 97	106.85
CCSD(T)-R12/B	–128.937 85	2.656 21	106.53

^a Not available.

when DPT operators are used as a finite perturbation (cf section 2.2). It is well known that finite-field procedures may give rise to unbound operators, the homogeneous electric field being a prominent example. Although this unboundness has no practical consequences for calculations in finite electric fields in standard Gaussian basis sets (unless extremely diffuse functions are added), one might wonder about the effects of finite DPT fields, in particular when large uncontracted basis sets with tight functions are used. In such basis sets, the finite field consisting of the mass–velocity and Darwin operators of the Breit–Pauli Hamiltonian is known to cause a variational collapse beyond some critical field strength [36].

Thus, we have investigated the performance of the finite-DPT procedure for the calculation of the first-order DPT energy correction at the Hartree–Fock level in the large basis of table 8. This basis comprises tight uncontracted functions, which are likely to cause problems. We explored both a central-difference formula for the DPT energy correction (with field strengths ranging from ± 0.0001 to ± 10 au) and a second-order polynomial fit to only positive values of the field strength, ranging from $k \times 0.0001$ to $k \times 10$ au with $k = 1, 2$.

We observed that, when applying the central-difference procedure, the results were stable up to a field strength of 0.001 au in absolute value. In a stronger (negative) field, the metric was corrupted. Furthermore, the results obtained from fitting to positive fields were stable up to a field strength of 0.01 au. Beyond that field strength, a variational collapse occurred. We hence conclude that applying a finite DPT field may not always be a *bona fide* approach, but from a practical point of view, it seems a safe procedure to use the central-difference formula and to find the proper (negative) field strength that does not corrupt the metric. In the above case, -0.001 au was the proper value.

Furthermore, test calculations on the H atom in large basis sets of s-type Gaussians revealed that the critical (negative) DPT field strength at which the overlap matrix is no longer positive definite is roughly equal to the field strength (but positive) at which a variational collapse occurs after adding a finite field of the mass–velocity and Darwin operators of the Breit–Pauli Hamiltonian. In both cases, the magnitude of the critical field strength is inversely proportional to the largest exponent in the basis of uncontracted s-type Gaussians.

Finally, in table 8, we present the results of the explicitly-correlated coupled-cluster calculations in the very large 25s19p15d12f10g8h6i4k basis. The CCSD(T)-R12/B value of $\gamma = 106.53$ au is 0.32 au smaller than the conventional CCSD(T) value in this basis. This difference, which arises from terms linear in the interelectronic distances r_{ij} , may seem

astonishingly large considering the large size of the one-electron basis set in which these calculations were carried out. However, the CCSD(T)-R12/B value can be rationalized by extrapolating the electron-correlation contributions of the standard CCSD(T) calculations in the t-aug-cc-pCV5Z ($X = 5$) and q-aug-cc-pCV6Z ($X = 6$) basis sets. The corresponding electron-correlation contributions amount to 38.54 and 38.23 au, respectively, and a two-point linear extrapolation procedure [34] applied to these values yields a complete-basis-set estimate of 37.80 au. When added to the Hartree–Fock limit of 68.83 au [4], an extrapolated CCSD(T) basis-set limit of $\gamma = 106.63$ au is obtained, significantly (0.22 au) below the conventional CCSD(T) value in the 25s19p15d12f10g8h6i4k basis and only 0.10 au above the CCSD(T)-R12/B value in that basis.

When the same two-point linear extrapolation is attempted for the dipole polarizability, an extrapolated value of 2.6559 au is obtained, in agreement with the directly computed CCSD(T)-R12/B result to within 0.0003 au.

Our CCSD(T)-R12/B value for γ is very different from Franke *et al*'s value of 104.8 au, which appears to be much too low. The reason for the low value of Franke *et al* might be related to the numerical instabilities that sometimes occur in R12 calculations using very large one-electron basis sets [35]. In our present calculations, the MP2-R12/A, CCSD-R12/B, CCSD[T]-R12/B and CCSD(T)-R12/B hyperpolarizabilities scattered about 0.05 au, depending on the field strengths and fitting procedures used. With larger basis sets, it becomes increasingly difficult to extract γ numerically with high accuracy. For the MP2-R12/B level, we were not able to obtain a stable value at all, obtaining instead all sorts of values in the range 105–110 au. By repeating the calculations using the Dalton program, we checked that the scattering of the MP2-R12/B results was not related to a problem of the DIRCCR12-OS program. The Dalton program behaved similarly.

4. Conclusions

We have implemented into the Dalton program the one- and two-electron integrals that are needed to compute the first-order relativistic correction to (frequency-dependent) electrical response properties in the framework of a direct perturbation theory.

The application of our new code is illustrated by calculations of the dipole polarizability and second dipole hyperpolarizability of the Ne atom. For this atom, our results are at variance with the value obtained by Franke and co-workers for the second dipole hyperpolarizability [10] but in agreement with the results obtained by Nakajima and Hirao [11].

It is difficult to obtain numerically stable results from numerical differentiation of energies from explicitly-correlated coupled-cluster calculations, but our CCSD(T)-R12 value for the second dipole hyperpolarizability of the Ne atom agrees with the value obtained by extrapolating the correlation contributions obtained by standard coupled-cluster calculations in multiply augmented correlation-consistent basis sets.

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