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Recent Advances in Explicitly Correlated Coupled-Cluster Response Theory for Excited States and Optical Properties

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The derivation of coupled-cluster response theory for explicitly correlated wavefunctions with terms linear in the interelectronic distance r_{12} (CC-R12) or a function f_{12} thereof (CC-F12) is reviewed and an implementation at the CCSD(R12) and CCSD(F12) for excitation energies and the linear, quadratic and cubic reponse functions is reported for ansätze 1 and 2. We discuss the results of first applications for vertical excitation energies, excited state equilibrium structures and vibrational frequencies, polarizabilities and first and second hyperpolarizabilities with focus on present limitations and future prospects of the approach. We show in particular that the standard choice of the geminal functions and wavefunction expansion can in certain cases lead to a bias towards the unperturbed ground state and how this can be avoided by extending the geminal space. If taken care of this, in particular CCSD(F12)/ansatz 2 shows for the potential energy curves of excited states and for optical properties a similar enhanced basis set convergence of the correlation contribution due to connected double excitations as for ground state energies. For diffuse excited states and hyperpolarizbilities the correlation contribution converges with CCSD(F12)/ansatz 2 often faster than orbital relaxation contributions. The convergence of the latter can be improved by allowing single excitations into a space spanned by a complementary auxiliary basis set.

1. Introduction

Explicity correlated coupled-cluster methods have experienced during the last decade a tremendous increase in efficiency and accuracy and are becoming now a standard tool of computational chemistry for the calculation of accurate ground state energies [1]. The slow convergence of the correlation contribution to the

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electronic wavefunction is also a severe bottleneck in the calculation of linear and nonlinear optical properties. The extension of explicitly correlated techniques to coupled-cluster response theory thus proffers the possibility to extend considerably the applicability of coupled-cluster response theory towards larger systems by lowering the arduous basis demands of such calculations.

The application of the techniques and approximations developed within R12 (or F12) theory for ground state calculations in the framework of coupled-cluster response theory to allow for the calculation of excited states or optical properties is, however, not as straight forward as one might at first expect. As is known, for example from local correlation methods [2,3], the requirements for the excitation vectors, which describe in response theory the excited states, or for responses of the cluster amplitudes to e.g. external electric fields are quite different from those for the ground state cluster amplitudes or wavefunction. While the cluster amplitudes for the unperturbed ground state only account for correlation effects, the excitation vectors describe the excitation process beside differential correlation and orbital relaxation effects. In coupled-cluster response theory usually the unperturbed Hartree-Fock wavefunction is used as reference state to avoid in the frequency-dependent case spurious unphysical poles and orbital relaxation effects are described through the cluster operator. Thus the response of the cluster amplitudes to external fields describes the polarization not only of the correlation contribution to the wavefunction but also of the orbitals. As will be shown below, the balanced desription of these contributions is a challenge for R12 theory which requires at least in some situations an extension of the wavefunction ansatz which is usually used in CC-R12 or CC-F12 calculations.

2. Theory

CC-R12 and CC-F12 methods include in the coupled-cluster wavefunction ansatz

$$|\mathrm{CC}\rangle = \exp(\hat{T})|\mathrm{HF}\rangle \tag{1}$$

in addition to connected single ($\hat{T}_1$), double ($\hat{T}_2$), triple ($\hat{T}_3$), etc. excitations into the virtual space of the molecular orbital basis also double excitations into explicitly correlated pair functions (geminals):

$$\chi_{xy}(1,2) = \hat{Q}_{12} f_{12}(r_{12}) |\varphi_x(1)\varphi_y(2)\rangle \,, \tag{2}$$

where φ_x and φ_y are taken from a suitable chosen subset of the molecular orbitals (for ground state energies usually the active occupied MOs) and $\hat{Q}_{12}$ is a projection operator ensuring strong orthogonality which for ansatz 1 and 2 is defined as, respectively,

$$\hat{Q}_{12}^{(1)} = (1-\hat{P}_1)(1-\hat{P}_2) \quad \text{and} \quad \hat{Q}_{12}^{(2)} = (1-\hat{O}_1)(1-\hat{O}_2) - \hat{V}_1\hat{V}_2 \,. \tag{3}$$

In the last equation $\hat{O} = \Sigma_I |\varphi_I\rangle\langle\varphi_I|$ is a projector onto the space spanned by all occupied MOs, $\hat{V} = \Sigma_a |\varphi_a\rangle\langle\varphi_a|$ projects onto the space spanned by the virtual MOs, and $\hat{P} = \hat{O}+\hat{V}$ onto the space of all MOs. The function $f_{12}(r_{12})$ is in R12

methods just r_{12}, in F12 methods usually a slater function $\exp(-\gamma r_{12})$ with a preoptimized exponent γ. If we introduce a formally complete one-electron basis $\{\varphi_\alpha\}$, the explicitly correlated connected double excitations can (assuming that $|\mathrm{HF}\rangle$ is closed-shell) be written as

$$\hat{T}_{2'} = \sum_{ix \geq yj} c_{ij}^{xy} \sum_{\alpha\beta} F_{xy}^{\alpha\beta} E_{\alpha i} E_{\beta j} = \sum_{ix \geq jy} c_{ij}^{xy} \tau_{xiyj} \,, \tag{4}$$

with $F_{xy}^{\alpha\beta} = \langle \alpha\beta | \hat{Q}_{12} f_{12} | xy \rangle$. In the following we refer for brevity to the amplitudes t_{ai}, t_{aibj}, … and c_{ij}^{xy} collectively as t_μ and to the single (E_{ai}), double ($E_{ai}E_{bj}$), etc. excitation operators and τ_{xiyj} as τ_μ, so that we can write the cluster operator as $\hat{T} = \Sigma_\mu \, t_\mu \, \tau_\mu$.

We can now combine this wavefunction ansatz with coupled-cluster response theory to derive expressions for linear and nonlinear response functions and excitation energies. For this we introduce the time-dependent Lagrange function:

$$L_{\mathrm{CC}} = \langle \mathrm{HF} | (H - i\tfrac{d}{dt}) e^{\hat{T}} | \mathrm{HF} \rangle + \sum_\mu \bar{t}_\mu \langle \mu | e^{-\hat{T}} (H - i\tfrac{d}{dt}) e^{\hat{T}} | \mathrm{HF} \rangle \tag{5}$$

Response functions are obtained as derivatives of the real part of L_{CC} with respect to strengths ε_i of external (e.g. electromagnetic) fields:

$$\langle\langle X_1, X_2, \ldots, X_n \rangle\rangle_{\omega_2,\ldots,\omega_n} = \left(\frac{d^n \mathrm{Re}(L_{\mathrm{CC}})}{d\epsilon_1(\omega_1) \ldots \epsilon_n(\omega_n)} \right)_{\epsilon_i = 0} \,, \tag{6}$$

and excitation energies are obtained as solutions of the eigenvalue problem

$$\sum_\mu A_{\nu\mu} E_\mu = \omega \sum_\mu S_{\nu\mu} E_\mu \,, \tag{7}$$

where $A_{\mu\nu}$ and $S_{\nu\mu}$ are, respectively, the Jacoby and metric matrices:

$$A_{\nu\mu} = \frac{\partial^2 L_{\mathrm{CC}}}{\partial \bar{t}_\nu \partial t_\mu} \qquad \text{and} \qquad S_{\nu\mu} = \langle \nu | \tau_\mu | \mathrm{HF} \rangle \,. \tag{8}$$

By restricting now the cluster operator to at most double excitations one obtains the CCSD-R12 or CCSD-F12 models. If one accounts in addition for connected triple excitations, e.g. as in the CC3 model, one arrives at CC3-R12 or CC3-F12. However, it turned out that contributions which are higher-order in the explicitly correlated double excitations are negligible. Thus the computational costs of the explicitly correlated CCSD variants can without significant loss in accuracy be reduced by approximating the doubles equations as,

$$0 = \langle \mu_2 | e^{-\hat{T}_1} (H + [H, \hat{T}_2 + \hat{T}_2'] + \tfrac{1}{2}[[H, \hat{T}], \hat{T}_2 + 2\hat{T}_2']) e^{\hat{T}_1} | \mathrm{HF} \rangle \,, \tag{9}$$

$$0 = \langle \mu_{2'} | [F, \hat{T}_{2'}] + e^{-\hat{T}_1} (H + [H, \hat{T}_2]) e^{\hat{T}_1} | \mathrm{HF} \rangle \,, \tag{10}$$

which leads to the CCSD(F12) model [4,5], where – similar as for CC2 and CC3 – all similarity transformations with $\hat{T}_1$ are kept since the single excitations play an important role in response theory. For the CCSD(F12) model the computational costs are approximately those of an MP2-F12 calculation plus 5–7 times those of a conventional CCSD calculation. Since they give typical results of

quintuple-ζ quality already in triple-ζ basis sets, this reduces tremendously the computational costs, since for a (conventional) CCSD calculation in a quintuple-ζ basis they are typically by more than a factor of 50 higher than in a triple-ζ basis. For example with the present implementation in the Dalton program used for the present study we find for the BF molecule in the t-aug-cc-pVTZ basis set that one iteration for a conventional CCSD calculation takes 211 seconds. For CCSD(F12) an iteration takes 1314 seconds, i.e. roughly 6 times longer. But to reach the same accuracy as CCSD(F12)/t-aug-cc-pVTZ with conventional CCSD the basis set must be improved to t-aug-cc-pV5Z which increases the required CPU time per iteration to 14784 seconds, roughly an order magnitude more than for CCSD(F12)/t-aug-cc-pVTZ.

For the calculation of ground state energies further approximations can be made which reduce the computational costs of the explicitly correlated CCSD approaches essentially to the costs of a conventional CCSD and an MP2-F12 calculation [6,7]. For computational convenience CC3(F12) and CCSD(F12)(T) neglect in addition all coupling terms between connected triple excitations and double excitations into the explicitly correlated pair functions. In the following we will in addition present some results for the CC2-R12 or CC2-F12 models, which are obtained by approximating the equations for $\hat{T}_2$ and $\hat{T}_{2'}$ to first order in the fluctuation potential in exactly the same manner as it is done in the conventional CC2 model.

3. Excited states

Excitation energies play a decisive role in response theory as they are not only important for the description of excited states but determine also the dispersion of frequency-dependent optical properties. As indicated in the introduction, a balanced description of ground and excited states can be a challenge for R12 methods since the usual construction of the geminal space with φ_x and φ_y in Eq. (1) restricted to occupied orbitals is tuned for ground state energies. For small highly symmetric molecules this choice can bias the results for excitation energies and response properties.

Two illustrative examples which highlight this problem are the vertical excitation energies of Be and BH for which some results are reported in Table 1. For the ^{1}P state of Be and the $^1\Pi$ state of BH CC2-R12 overestimates in the smaller basis sets considerably the excitation energies and converges in fact slower to the basis set limit than the corresponding conventional CC2 results. The convergence of CC2-R12 is evidently slower than that of the conventional CC2 model. CC2-R12 improves the basis set convergence only for the $^1\Sigma^+$ state of BH.

Table 1. Vertical excitation energies (eV) for Be and BH with CC2 (R12 results obtained with ansatz 1). *X* denotes the cardinal number of orbital basis sets. For details about basis and bond lengths see Ref. [8].

	Be ^{1}P			BH $^1\Pi$			BH $^1\Sigma^+$		
X	conv	R12	R12+	conv	R12	R12+	conv	R12	R12+
2	5.54	5.70	5.30	2.87	2.99	2.92	6.40	6.49	6.49
3	5.21	5.27	5.13	2.83	2.89	2.86	6.44	6.49	6.49
4	5.15	5.17	5.12	2.82	2.85	2.83	6.47	6.49	6.49
5	5.13	5.14	5.11	2.82	2.84	2.82	6.47	6.49	6.48
∞	5.11±0.005			2.81±0.005			6.48±0.005		

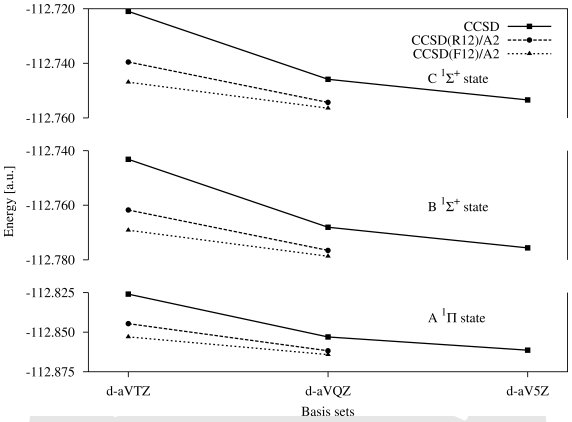


Fig. 1. Basis set dependence of total energies for excited states of CO with ansatz 2.

The reason for the unbalanced description of the Be ^{1}P and BH $^1\Pi$ states is that the geminal space constructed by multiplying f_{12} with products of only occupied orbitals does not contain any pair functions with, respectively, P or Π symmetry which can correlated the excited state. A remedy for this problem is to extend the set of orbitals used in the construction of the geminal functions with a few additional virtual orbitals [9], which is indicated in the following with R12+. Typically, the inclusion of a few additional valence orbitals is sufficient to correlate the excited states with a similar accuracy as the ground state and to obtain a fast basis set convergence. This is demonstrated by the CC2-R12+ results in Table 1. It should, however, pointed out that such an extreme loss of balance as for the Be ^{1}P and BH $^1\Pi$ states is a pecularity of small highly symmetric molecules. For example, without including virtual orbitals in the construction of the pair functions, the total energies of several singlet excited states for CO (c.f. Fig. 1) show with CCSD(R12) and CCSD(F12) a remarkably improved convergence which is similar to what is observed for ground state energies.

Accurate total energies for excited states are important for their equilibrium structures and vibrational frequencies. Some results for equilibrium bond lengths

Table 2. Bond lengths (R_e in pm) with CCSD(R12) and CCSD(F12) using ansatz 2 and d-aug-cc-pVXZ basis sets (indicated as XZ). Results parentheses include a d-aV5Z correction for the Hartree-Fock value. For further technical details see Ref. [13].

		CCSD			CCSD(R12)		CCSD(F12)	
		TZ	QZ	∞	TZ	QZ	TZ	QZ
N_2	$a'^1\Sigma_u^-$	125.4	125.1	124.9	125.2	124.9	125.1	124.9
		(125.3)			(125.0)		(125.0)	
	$a^1\Pi_g$	120.7	120.3	120.1	120.4	120.2	120.4	120.2
		(120.6)			(120.3)		(120.2)	
	$w^1\Delta_u$	124.9	124.5	124.4	124.6	124.4	124.6	124.4
		(124.7)			(124.5)		(124.4)	
CO	$A^1\Pi$	123.1	122.5	122.3	122.7	122.3	122.6	122.3
		(122.8)			(122.4)		(122.4)	
	$B^1\Sigma^+$	111.6	111.2	111.0	111.3	111.0	111.2	111.0
		(111.4)			(111.1)		(111.0)	
	$C^1\Sigma^+$	111.5	111.0	110.8	111.2	110.9	111.1	110.9
		(111.2)			(111.0)		(110.9)	
BF	$A^1\Pi$	131.1	130.5	130.2	130.7	130.3	130.6	130.3
		(130.7)			(130.3)		(130.2)	
	$B^1\Sigma^+$	121.2	120.7	120.5	121.0	120.6	120.9	120.6
		(120.9)			(120.6)		(120.5)	
	$C^1\Sigma^+$	122.5	122.0	121.8	122.3	121.9	122.2	121.9
		(122.1)			(121.9)		(121.8)	

obtained in Ref. [12] with CCSD(R12) and CCSD(F12) using ansatz 2 (cmp. Eq. 3) are shown in Table 2. With conventional CCSD the bond lengths of most states deviate even with the 5Z basis by 0.1 pm from the basis set limit. The CCSD(R12) and CCSD(F12) results in the QZ basis are for all investigated states close to the basis set limits, which have been extrapolated from the conventional QZ and 5Z results, and surpass the conventional 5Z values. With the triple-ζ basis set the improvements are less satisfactory. The reason for this is, however, not the correlation treatment, but the uncorrelated wavefunction which limits now the overall basis set convergence. This becomes obvious when the TZ potential energy curves are approximately corrected for this error by adding the differences between HF response results in the d-aug-cc-pV5Z and d-aug-cc-pVTZ basis sets. With this correction (c.f. results given in Table 2 in parentheses) the CCSD(R12) and CCSD(F12) results in the triple-ζ basis agree for all states with the extrapolated basis set limits within the accuracy of the latter.

Results for harmonic frequencies are presented in Table 3. The conventional CCSD results deviate for most states even with the 5Z basis still by several wavenumbers from the extrapolated basis set limit. With CCSD(R12) and CCSD(F12) the convergence is significantly improved and all frequencies are already in the QZ basis very close to the basis set limit. With the triple-ζ basis

Table 3. Harmonic vibrational frequencies (ω_e in cm^{-1}) with CCSD(R12) and CCSD(F12) using ansatz 2 and d-aug-cc-pVXZ basis sets (indicated as XZ). Results parentheses include a d-aV5Z correction for the Hartree-Fock value. For further technical details see Ref. [13].

		CCSD			CCSD(R12)		CCSD(F12)	
		TZ	QZ	∞	TZ	QZ	TZ	QZ
N_2	$a'^1\Sigma_u^-$	1714	1725	1730	1725	1729	1724	1729
		(1711)			(1722)		(1721)	
	$a^1\Pi_g$	1830	1848	1854	1846	1854	1847	1854
		(1836)			(1851)		(1852)	
	$w^1\Delta_u$	1733	1744	1749	1744	1748	1744	1748
		(1734)			(1745)		(1745)	
CO	$A^1\Pi$	1561	1581	1592	1579	1589	1580	1589
		(1566)			(1583)		(1584)	
	$B^1\Sigma^+$	2221	2244	2253	2241	2252	2246	2253
		(2230)			(2248)		(2254)	
	$C^1\Sigma^+$	2259	2281	2289	2277	2289	2282	2289
		(2267)			(2284)		(2289)	
BF	$A^1\Pi$	1258	1271	1279	1271	1278	1275	1278
		(1260)			(1273)		(1277)	
	$B^1\Sigma^+$	1704	1715	1720	1714	1720	1717	1720
		(1708)			(1717)		(1720)	
	$C^1\Sigma^+$	1620	1632	1637	1630	1637	1633	1637
		(1625)			(1635)		(1638)	

the CCSD(R12) and CCSD(F12) results have very much the same accuracy as the conventional results in the QZ basis. Again, the accuracy is at this level limited by the basis set error in the uncorrelated part and can be improved by applying the above described correction scheme. With this correction the CCSD(F12) results for all Σ^+ states agree with the extrapolated basis set limit within its accuracy and also the frequencies for the $a^1\Pi_g$ and $w^1\Delta_u$ states of N_2 are close to quintuple-ζ quality. Slightly larger deviations are found for the $^1\Pi$ states of BH, CO and BF.

4. Linear and nonlinear optical properties

In this section, we turn to the assessment of recents results [13] obtained with the CCSD(R12) and CCSD(F12) approaches with ansatz 2 for static and frequency-dependent higher-order properties.

Before discussing polarizabilities and hyperpolarizabilities we briefly comment on results for dipole moments as an example of first-order properties to show that the RI approximation used in the CCSD(R12) and CCSD(F12) methods represents accurately the important matrix elements with the perturbation

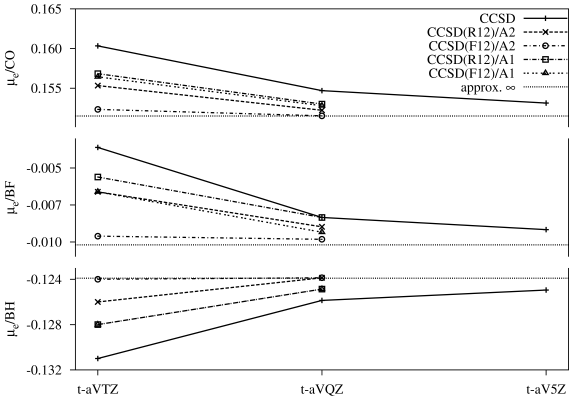


Fig. 2. Basis set convergence of the correlation contributions to total eletrcic dipole moments μ_e for BH (bottom), BF (middle) and CO (top) diatomic molecules (in a.u.) in the t-aug-cc-pVXZ basis sets. A1 and A2 denote, respectively ansatz 1 and 2.

operators. Figure 2 shows some results for dipole moments of BH, BF and CO. This comparison reveals that the CCSD(F12) model with ansatz 2 gives in the t-aug-cc-pVTZ basis dipole moments which are better converged than the t-aug-cc-pV5Z results with conventional CCSD. With the quadruple-ζ basis the CCSD(F12)/ansatz 2 calculations agree with the extrapolated basis set limits and may even surpass them in accuracy. CCSD(R12) and also CCSD(F12) with ansatz 1 are less accurate and improve the basis set convergence compared to conventional CCSD only by one cardinal number.

The CCSD, CCSD(R12) and CCSD(F12) results for the polarizability (α) and the second hyperpolarizability ($\gamma_\parallel$) for Ne are shown Fig. 3. The explicitly correlated models reach in a basis with cardinal number X for both α and $\gamma_\parallel$ about the same accuracy as standard CCSD calculations with X+1 for ansatz 1 and X+2 for ansatz 2. In variance to total energies and first-order properties we observe for (hyper-)polarizabilities with the present approach no advantage of CCSD(F12)/ansatz 2 compared to CCSD(R12)/ansatz 2. In particular for α the CCSD(R12) results are closer to the basis set limit than the CCSD(F12) values, which underestimate the polarizability. A possible cause of this problem might be that the exponent in the F12 geminal function, which has been optimized for ground state correlation energies, leads in the response calculations to a bias towards the unperturbed state.

The BH molecule has been a critical case for assessing the performance of R12 or F12 response theory as the standard choice for the geminal space contains only pair functions of σ symmetry, which biases the results for excitations into the A $^1\Pi$ state [8,10]. A similar bias is observed for the xx component of the polarizability α unless a few virtual orbitals with π symmetry are included in the construction of the geminal functions. However, this does not necessarily affect

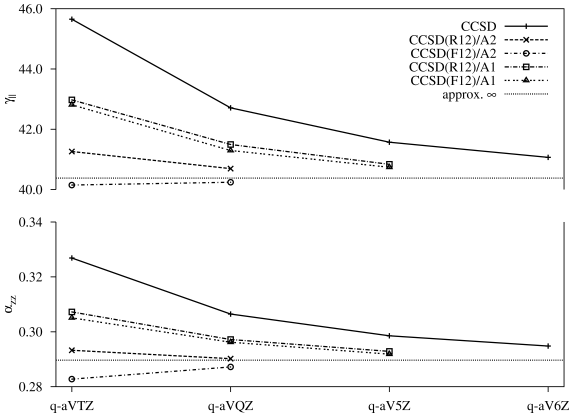


Fig. 3. Convergence of the correlation contributions to the static polarizabilities α_{zz} and second hyperpolarizabilities $\gamma_{\|}$ of Ne (in a.u.) with the q-aug-cc-pVXZ basis sets. A1 and A2 denote ansatz 1 and 2, respectively.

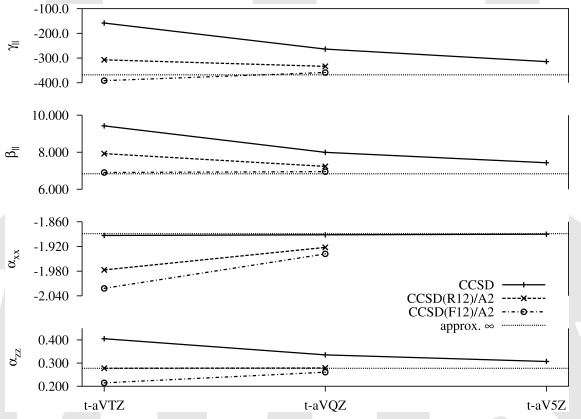


Fig. 4. Basis set convergence of the electronic correlation contributions to static polarizabilities α_{zz} and α_{xx}, first and second hyperpolarizabilities $\beta_{\|}$ and $\gamma_{\|}$ for BH (in a.u.) using the t-aVXZ basis sets with triply augmented diffuse functions. A2 stands for ansatz 2.

the parallel components of the polarizability (α_{zz}) and the first and second hyperpolarizabilities ($\beta_{\|}$ and $\gamma_{\|}$) presented in Table 4 and Fig. 4. With CCSD(R12)/ansatz 2 and the t-aug-cc-pVTZ basis the correlation contribution to α_{zz} deviates by less then 0.001 a.u. from the basis set limit. CCSD(F12) gives again a slightly to small polarizability, while for $\beta_{\|}$ and $\gamma_{\|}$ the CCSD(F12) results are closest to the extrapolated basis set limits.

Table 4. Static polarizabilities α_{zz} and α_{xx} and second hyperpolarizabilities $\gamma_{\|}$ for BH, BF, CO and N_2 (in a.u.) with conventional CCSD and CCSD(R12) and CCSD(F12) with ansatz 2 and t-aug-cc-pVXZ basis sets.

BH		α_{zz}	α_{xx}	$\beta_{\|}$	$\gamma_{\|}$
CCSD	TZ	23.01	21.00	64.66	10764
	QZ	22.90	21.01	63.39	10642
	5Z	22.87	21.02	62.91	10593
	∞	22.84	21.02	62.31	10540
CCSD(R12)	TZ	22.88	20.91	63.16	10615
CCSD(F12)	TZ	22.81	20.87	62.14	10531
BF		α_{zz}	α_{xx}	$\beta_{\|}$	$\gamma_{\|}$
CCSD	TZ	18.15	20.05	53.53	6246
	QZ	18.04	20.03	52.41	6172
	5Z	18.00	20.01	52.13	6148
	∞	17.97	20.00	51.83	6111
CCSD(R12)	TZ	17.99	19.96	52.67	6156
CCSD(F12)	TZ	17.93	19.93	51.83	6087
CO		α_{zz}	α_{xx}	$\beta_{\|}$	$\gamma_{\|}$
CCSD	TZ	15.71	11.88	25.25	1410
	QZ	15.64	11.84	25.03	1382
	5Z	15.61	11.82	24.98	1370
	∞	15.58	11.81	24.90	1359
CCSD(R12)	TZ	15.58	11.80	25.07	1376
CCSD(F12)	TZ	15.53	11.76	24.81	1357
N_2		α_{zz}	α_{xx}		$\gamma_{\|}$
CCSD	TZ	14.68	10.19		908
	QZ	14.63	10.15		891
	5Z	14.61	10.15		883
	∞	14.58	10.12		874
CCSD(R13)	TZ	14.57	10.11		883
CCSD(F12)	TZ	14.54	10.08		872

For BF, CO and N_2, which have occupied σ and π orbitals, already the standard construction scheme for the geminal space includes pair functions of σ, π and δ symmetry. For these molecules we do not observe a similar bias in the results for α_{xx} (cmp. Table 4). With ansatz 2 both CCSD(R12) and CCSD(F12) accelerate the convergence with the cardinal number of the basis set considerably. However, as already observed above for Ne, the CCSD(F12) results tend to underestimate the polarizability and hyperpolarizabilities. This might partially be a consequence of the fact that the exponent for the pair functions was optimized for the unperturbed ground state energy. But at this level of accuracy also the limited convergence of the underlying uncorrelated value in the t-aug-cc-pVTZ basis contributes significantly to the remaining basis set incompleteness errors.

Table 5. ESHG second hyperpolarizabilities $\gamma_{\parallel}^{\mathrm{ESHG}}(\omega)$ for N_2 in a.u. at the CCSD as well as CCSD(R12) and CCSD(F12) levels with ansatz 2 and d-aug-cc-pVXZ basis sets.

	CCSD				CCSD(R12)	CCSD(F12)
λ (nm)	TZ	QZ	5Z	est. ∞	TZ	TZ
1055.0	956.5	943.4	937.2	926.7	929.2	918.2
694.3	1038.8	1023.0	1015.8	1004.3	1007.9	995.6
457.9	1272.3	1248.1	1237.8	1223.8	1230.6	1214.0

For CCSD(R12) the polarizabilities are with the t-aug-cc-pVTZ basis similar close to the extrapolated basis set limit as the conventional CCSD/t-aug-cc-pV5Z results, which is partially a result of error cancellation between the correlation contribution and the uncorrelated result. Encouraging is that also the static second hyperpolarizabilities $\gamma_{\parallel}$ confirm the strength of CCSD(R12) and CCSD(F12) with ansatz 2: already the calculations in the triple-ζ basis set give results that are rather close to the estimated basis set limits.

As example for a frequency-dependent higher-order property we investigated the parallel average of the electric field induced second harmonic generation (ESHG) hyperpolarizability for N_2. In Table 5 we listed results for some selected wavelengths. The basis set limits for $\gamma_{\parallel,ESHG}(\omega)$ were estimated using a multiplicative scheme:

$$\gamma_{\parallel,ESHG}^{\infty}(\omega) \approx \gamma_{\parallel,ESHG}^{5Z}(\omega)\left(\frac{\gamma_{\parallel}^{\infty}(0)}{\gamma_{\parallel}^{5Z}(0)}\right), \tag{11}$$

where the $\gamma_{\parallel}^{\infty}(0)$ is obtained by the extroplation scheme described in Refs. [11, 12].

The results demonstrate that both CCSD(R12) and CCSD(F12) with ansatz 2 tremendously improve the basis set convergence of the dispersion, which is for both approaches already in the t-aug-cc-pVTZ basis better than in a conventional CCSD/t-aug-cc-pV5Z calculation. The remaining deviations from the extrapolated basis set limits are less than 10 a.u. (i.e. less than 1%) and the largest deviations occur for the shortest wavelengths and are probably mainly due to errors of the approximation in Eq. (11) which increase with increasing frequency ω, i.e. decreasing wavelengths.

5. Summary and outlook

The equations for explicitly correlated CC-R12 and CC-F12 response theory with ansatz 1 and 2 have been derived and implemented in the program DALTON [14] for the CC2-R12, CCSD(R12) and CC3(R12) models and the corresponding F12 variants. This has allowed first applications of these approaches to excited states and optical response properties as dipole polarizabilities and hyperpolarizabilities.

The results show that for small and highly symmetric molecules the standard construction scheme for the explicitly correlated pair functions can lead to a bias

towards the electron ground state. Including a few virtual orbitals (e.g. some valence orbitals) rectifies this problem and a considerably improved basis set convergence is observed for energies and structures of excited states and linear and nonlinear response properties.

At the example of equilibrium bond lengths and harmonic vibrational frequencies of singly excited states of N_2, CO, BF and BH we showed that in CCSD(R12) and CCSD(F12) calculations with ansatz 2 it is already in the d-aug-cc-pVTZ basis no longer the correlation contribution but the underlying uncorrelated contribution which limits the overall basis set convergence. If one corrects for these errors (e.g. by using a basis set correction obtained from Hartree-Fock response results) the explicitly correlated results reach in the d-aug-cc-pVTZ basis an accuracy which in conventional CCSD calculations is only obtained with quintuple-ζ basis sets, i.e. much larger computational costs. An alternative way to correct for the incompleteness of the one-electron space in explicitly correlated coupled-cluster response calculations would be to allow single excitations from the occupied space into the space spanned by the complementary auxiliary basis. If we compare CCSD(R12) and CCSD(F12), we see e.g. for equilibrium bond lengths and harmonic vibrational frequencies not such large improvements with the exponential correlation factor of CCSD(F12) as have been observed for ground state energies. A reason for this might be that the exponents optimized for ground state correlation energies are less suitable for excited states.

For ground state properties we find that the CCSD(F12) method with ansatz 2 gives already in a triple-ζ basis correlation contributions to dipole moments and second hyperpolarizabilities with an accuracy which conventional CCSD achieves first in quintuple-ζ or larger basis sets. Here the improvements are comparable to those observed with this approach for ground state correlation energies.

CCSD(R12) with ansatz 2 gives also correlation contributions to polarizabilities in triple-ζ basis sets with quintuple-ζ quality, while CCSD(F12) with ansatz 2 tends to slightly underestimate the polarization. The source of this effect might again be that the exponent for the pair functions is optimized for the unperturbed ground state, but also the remaining basis set incompleteness error in the one-electron space limits at this level the overall basis set convergence. A remedy for the latter problem would again to include in the CC response calculation single excitations into the complementary auxiliary basis. For first hyperpolarizabilities the performance of CCSD(R12) and CCSD(F12) is intermediate between those observed for α and γ.

In conclusion, we find that already with the standard setup CCSD(R12) and in particular CCSD(F12) response theory are very valuable tools to reduce the computational costs for accurate coupled-cluster response calculations. A certain challenge is, however, to obtain a balanced description of the unperturbed ground state and excited states or a polarization of the ground state wavefunction and also a balance between the remaining basis set incompleteness errors in the one-

electron and the pair function space. Concerning the first problem, the influence of the exponents of the Slater-type correlation factor used in CCSD(F12) on the results for excitation energies and (hyper-)polarizabilities needs a more careful examination. For both CCSD(R12) and CCSD(F12) the inclusion of a few unoccupied valence orbitals in the construction of the explicitly correlated pair functions facilitates in difficult cases a balanced description of excited states or the polarizability and hyperpolarizability components. With the accuracy of the correlation treatment reached with this, the errors caused by the incompleteness of the one-electron space limit now in several cases the overall basis set convergence of explicitly correlated coupled-cluster response calculations. This error can, however, be reduced with minor additional costs by including single excitations into the CABS space. This will probably also allow to reduce the large number of diffuse basis functions which is presently needed for accurate calculations of excitation energies and (hyper-)polarizabilities and are a bottleneck in the integral evaluation.

Summing up, with these improvements of both accuracy and computational efficiency the explicitly correlated CCSD(F12) and CC3(F12) response models reduce considerably the computational costs and thereby extent the applicability of accurate coupled-cluster response calculations.

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