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Andreas Köhn

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A modified ansatz for explicitly correlated coupled-cluster wave functions that is suitable for response theory

Andreas Köhn^{a)}

Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany

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A modified ansatz for explicitly correlated coupled-cluster wave functions with a single correlation factor is set forward. It is based on the fixed amplitude ansatz of Ten-no [Chem. Phys. Lett. **398**, 56 (2004)] to which an extra term is added that allows for the explicitly correlated description of singly excited configurations. The new approach has been implemented for coupled-cluster singles and doubles with the aid of automated techniques. Numerical results are presented for vertical excitation energies, and ground and excited state equilibrium distances and harmonic frequencies of diatomics. The new approach is shown to provide a nearly unbiased description of ground and predominantly singly excited states, and the improvements seen for explicitly correlated treatments of ground states, as compared to conventional orbital expansions, carry over to excited states. In addition, a correction for contributions from one-electron terms—which are not improved by the correlation factor—is suggested, again with focus on applicability to a response formalism. © 2009 American Institute of Physics. [DOI: 10.1063/1.3079543]

I. INTRODUCTION

The introduction of geminal functions that explicitly depend on the interelectronic distance is known to significantly improve the basis set convergence of the ground state correlation energy, which was already recognized in the early days of quantum mechanics.¹ In particular the so-called R12 ansatz of Kutzelnigg and Klopper² has enabled the application of such correlation factors in molecular calculations,³ and the introduction of Slater-type geminals^{4,5} has led to significant progress in that area (usually called F12 ansatz). Coupled-cluster calculations with Slater-type correlation factors give a fully nonempirical access to highly accurate solutions of the electronic Schrödinger equation and may in the near future play an important role in the development of efficient *ab initio* protocols for the prediction of thermochemical quantities.^{6,7}

In this contribution, we will make a new attempt to transfer the improvements seen for the ground state energy to response properties, in particular, to excitation energies which—in the coupled-cluster linear response framework^{8–10}—are obtained as the poles of response functions. Earlier attempts in this direction have been conducted using linear R12 correlation factors^{11,12} and the approximate coupled-cluster singles and doubles model CC2.¹³

The initial results for excitation energies, however, were disappointing. It turned out that the R12 ansatz is strongly biased toward the ground state, as the correlation factor acts by construction on the reference determinant only.¹¹ The analysis given in Ref. 11 showed that only the ground state contribution is improved, leading to much too large excitation energies which with increasing basis set size more slowly converge to the limit than the conventional results do. An improvement was somewhat later suggested by Neiss *et*

al.,¹² who extended the ansatz such that the correlation factor acts on selected virtual orbitals as well (R12+ ansatz). A much better convergence of the excitation energy was observed now, but for some cases numerical problems occurred (lack of positive definiteness of the *B*-matrix). The same authors also used the approach for the calculation of higher order optical response properties for the CCSD(R12) model.¹⁴

In this work, we will introduce an alternative explicitly correlated coupled-cluster singles and doubles (CCSD) model which is suited for response theory. In order to reduce numerical problems associated with the unitary invariant formulation for optimized pair coefficients,¹⁵ we will make use of Ten-no's SP approach,^{4,16} which is unitary invariant as well, but circumvents the troublesome pair rotation amplitudes; instead it chooses the geminal function such that the first order *s*- and *p*-wave conditions for electron coalescence are fulfilled. We will avoid the selection of orbitals, and include all singly excited configurations by an extension of the geminal operator.

The ansatz will be presented in Sec. II A and motivated by considering a generalized geminal operator. Thereafter, we will discuss the application to the coupled-cluster singles and doubles model and the equations for the ground state correlation energy and for excitation energies, Secs. II B and II C. An extension to correct for the one-electron basis set error is presented in Sec. II D. The equations have been implemented using an automated approach, as outlined in Sec. III. Numerical examples are finally presented in Sec. IV.

II. THEORY

A. Ansatz

Throughout this work, we will consider a Slater-type correlation factor with the interelectronic distance r_{12} and a length scale parameter γ ,

^{a)}Author to whom correspondence should be addressed. Electronic mail: andreas.koehn@uni-mainz.de.

TABLE I. Index conventions used in this work.

p, q, r, \dots	Orbitals in finite basis
i, j, k, \dots	Occupied (hole) orbitals
a, b, c, \dots	Virtual (particle) orbitals in finite basis
$\alpha, \beta, \gamma, \dots$	Virtual orbitals in complete basis
p'', q'', r'', \dots	Virtual orbitals in complementary space spanned by auxiliary basis functions
μ_1	Single excitations into virtual orbitals in finite basis
μ_1'	Single excitations into virtual orbitals in the complementary space
μ	Generic n -fold excitations into virtual orbitals in finite basis

$$f(r_{12}) = \frac{1}{\gamma} e^{-\gamma r_{12}}. \quad (1)$$

The integrals over this factor will be scaled and antisymmetrized in order to fulfill the coalescence conditions for both singlet and triplet pairs.¹⁶ In a spin-orbital formalism, we have

$$\mathcal{R}_{\alpha\beta}^{pq} = \mathcal{S}_{pq} \langle \alpha\beta | \mathcal{Q}_{12} f(r_{12}) | pq \rangle, \quad (2)$$

where the symmetrization operator is defined as

$$\mathcal{S}_{pq} = \frac{1 - \mathcal{P}_{pq}}{4} \quad \text{if } \sigma_p = \sigma_q, \quad (3)$$

$$\mathcal{S}_{pq} = \frac{3 + \mathcal{P}_{pq}}{8} \quad \text{if } \sigma_p \neq \sigma_q, \quad (4)$$

and where \mathcal{P}_{pq} is an operator that permutes spin-orbital indices p and q , and σ_p is the m_s value of the spin orbital with index p . The index conventions are given in Table I. \mathcal{Q}_{12} is the strong-orthogonality projector.

Using these integrals, we can introduce the geminal operator

$$\begin{aligned} \mathcal{R} &= \frac{1}{4} \mathcal{R}_{\alpha\beta}^{ij} a_{ij}^{\alpha\beta} + \frac{1}{2} \mathcal{R}_{\alpha\beta}^{ia} a_{ia}^{\alpha\beta} + \frac{1}{4} \mathcal{R}_{\alpha\beta}^{ab} a_{ab}^{\alpha\beta} \\ &= \mathcal{R}^{(hh)} + \mathcal{R}^{(ph)} + \mathcal{R}^{(pp)}, \end{aligned} \quad (5)$$

which falls into three blocks, depending on the type of orbital pair on which it acts. The symbols $a_{qs}^{pr} = a^p a^r a_s a_q$ denote strings of creation operators a^p , and annihilation operators a_p .

The usual parameterization of the wave operator in explicitly correlated coupled-cluster calculations is e^S with $S = T + T'$, where T is the conventional cluster operator, which in the case of CCSD reads

$$T = T_1 + T_2 = t_a^i a_i^a + \frac{1}{4} t_{ab}^{ij} a_{ij}^{ab}, \quad (6)$$

and T' incorporates explicitly correlated electron pairs,

$$T' = \frac{1}{8} \mathcal{R}_{\alpha\beta}^{kl} c_{kl}^{ij} a_{ij}^{\alpha\beta}. \quad (7)$$

The coefficients c_{kl}^{ij} are either optimized or—in the SP ansatz—chosen equal to unity (note that we have appropriately normalized and symmetrized the integrals in order to satisfy the singlet and triplet coalescence conditions).

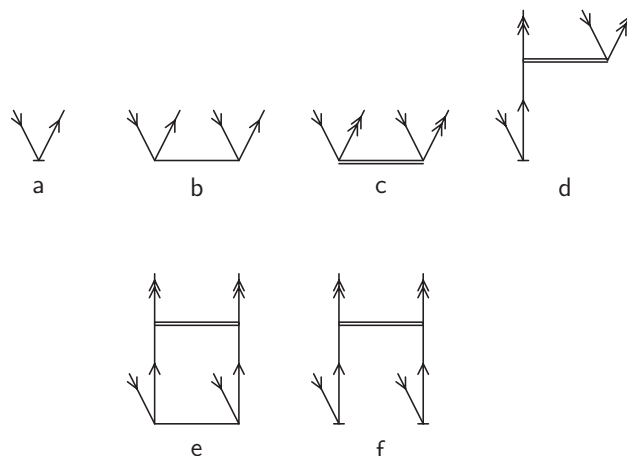


FIG. 1. Diagrammatic representation of the terms in Eq. (9) for the case of CCSD. Terms a and b represent the usual excitation operators, term c is the SP excitation operator, where double arrows denote excitations into the formally complete virtual space (we implicitly assume the presence of the strong-orthogonality projector \mathcal{Q}_{12}). Diagram d is the new term included for the XSP approach, diagrams e and f are not considered in the present work.

In order to motivate possible extensions of this ansatz, we consider the action of the exponential of the general geminal operator (5) on the wave operator e^T ,

$$e^{\mathcal{R}} e^T = e^T e^{-T} e^{\mathcal{R}} e^T = e^T \exp(\mathcal{R} + [\mathcal{R}, T] + \frac{1}{2} [[\mathcal{R}, T], T]). \quad (8)$$

Analysis of the right-hand side of this equations suggests the following: First of all, one might prefer those terms which are pure excitation operators with respect to the reference function, e.g., $\mathcal{R}^{(hh)}$, as only these give a contribution in linear order, and discard the remainder (thereby avoiding other unfortunate properties of noncommuting operators in the exponential). As these pure excitation operators commute with T , we can again join the arguments of the two exponentials and arrive at the following cluster operator

$$T + \mathcal{R}^{(hh)} + [\mathcal{R}^{(ph)}, T] + ([\mathcal{R}^{(pp)}, T])_{\text{c.b.}} + \frac{1}{2} [[\mathcal{R}^{(pp)}, T], T], \quad (9)$$

where $(\)_{\text{c.b.}}$ indicates “closed from below,” i.e., only those terms of $[\mathcal{R}^{(pp)}, T]$ should be considered which are pure excitation operators with respect to the reference determinant. The terms that contribute to the CCSD cluster operator are given in diagrammatic form in Fig. 1.

Obviously, we arrive at the usual parameterization if we truncate after $T + \mathcal{R}^{(hh)}$, and the expansion in Eq. (9) suggests $[\mathcal{R}^{(ph)}, T]$ as the natural next term to be considered. For CCSD, only the term $[\mathcal{R}^{(ph)}, T_1]$ remains, as $[\mathcal{R}^{(ph)}, T_2]$ would be a triple excitation. In fact, $[\mathcal{R}^{(ph)}, T_1]$ is the term of which we can expect significant improvement for explicitly correlated response calculations, as it includes the action of an r_{12} -dependent correlation factor on occupied-virtual orbital pairs. As the response of T_1 will generate the principal configurations of single-excitation dominated states, this term will include the action of $f(r_{12})$ on singly excited determinants. Of course, for double-excitation dominated states, we will by construction miss important explicit correlation contributions, but we note that CCSD does not properly re-

cover these states anyway. Therefore, it seems justified to restrict the present study to the $[\mathcal{R}^{(ph)}, T_1]$ term.

For consistency, $\mathcal{R}^{(hh)}$ and $\mathcal{R}^{(ph)}$ should employ the same correlation factor, in this work a Slater function determined by the γ parameter (*vide supra*). Additional flexibility can be gained by replacing the T_1 operator entering into the additional term by a new single-excitation operator \tilde{T}_1 which can be optimized separately.

We will in the following denote approaches which use the cluster operator:

$$S_{\text{SP}} = T_1 + T_2 + \mathcal{R}^{(hh)} \quad (10)$$

as SP ansatz, those using

$$S_{\text{XSP}} = T_1 + T_2 + \mathcal{R}^{(hh)} + [\mathcal{R}^{(ph)}, T_1] \quad (11)$$

as extended SP (XSP) ansatz and if the latter term is chosen to contain new amplitudes \tilde{T}_1

$$S_{\text{XSP}_{\text{opt}}} = T_1 + T_2 + \mathcal{R}^{(hh)} + [\mathcal{R}^{(ph)}, \tilde{T}_1], \quad (12)$$

we will call that approach the optimized extended SP (XSP_{opt}) ansatz.

B. Explicitly correlated coupled cluster

In this work, we will use the truncated CCSD-F12 model CCSD(F12),^{17–19} which recently was confirmed to be a very good approximation to the full model.^{20,21} Applying the SP approach, we obtain the following Lagrange function:

$$\begin{aligned} \mathcal{L}_{\text{SP}} = & E_0 + \langle 0 | H(T_2 + \frac{1}{2}T_1^2) | 0 \rangle + \langle 0 | H\mathcal{R} | 0 \rangle \\ & + \langle 0 | \mathcal{R}^\dagger e^{-T} H e^T | 0 \rangle + \langle 0 | \mathcal{R}^\dagger F \mathcal{R} | 0 \rangle + \sum_{\mu} \Lambda_{\mu} \Omega_{\mu}, \end{aligned} \quad (13)$$

where $|0\rangle$ is the reference state, E_0 is the reference energy, and F is the Fock operator. For the index conventions cf. Table I. The Lagrange multipliers Λ_{μ} are associated with the residuals

$$\Omega_{\mu} = \langle 0 | \tau_{\mu}^{\dagger} e^{-T} H e^T | 0 \rangle + \langle 0 | \tau_{\mu}^{\dagger} [e^{-T} H e^T, \mathcal{R}] | 0 \rangle \quad (14)$$

that result from projection onto the excited determinants $\tau_{\mu}|0\rangle$, and from which the optimal amplitudes in the T operator are obtained. Here and in the following we have dropped the (hh) and (hp) superscripts of \mathcal{R} , and it is understood that in the present context $\mathcal{R}^{(hh)}$ is meant; $\mathcal{R}^{(ph)}$ will always appear in the context of a commutator with a single-excitation operator (*vide infra*).

Next, we turn to the XSP_{opt} approach, noting that the XSP approach is just a special case of the former. We augment the cluster operator with $[\mathcal{R}^{(ph)}, \tilde{T}_1]$ and arrive at the following Lagrange functional:

$$\begin{aligned} \mathcal{L}_{\text{XSP}_{\text{opt}}} = & \mathcal{L}_{\text{SP}} + \langle 0 | H[\mathcal{R}, \tilde{T}_1] | 0 \rangle + \langle 0 | \mathcal{R}^\dagger F[\mathcal{R}, \tilde{T}_1] | 0 \rangle \\ & + \sum_{\mu} \Lambda_{\mu} \Omega'_{\mu} + \sum_{\mu_1} \tilde{\Lambda}_{\mu_1} \tilde{\Omega}_{\mu_1}. \end{aligned} \quad (15)$$

The residual function for the T operators is extended with the coupling term

TABLE II. Definition of the integrals and intermediates used in this work.

$E_0 = \langle 0 H 0 \rangle$	$G_{rs}^{pq} = \langle pq r_{12}^{-1} rs \rangle$
$F_q^p = \langle p F(1) q \rangle$	$\mathcal{R}_{rs}^{pq} = \mathcal{S}_{rs} \langle pq \mathcal{Q}_{12} f(r_{12}) rs \rangle$
	$B_{rs}^{pq} = \mathcal{S}_{pq} \mathcal{S}_{rs} \langle pq f(r_{12}) \mathcal{Q}_{12} [F(1) + F(2)] \mathcal{Q}_{12} f(r_{12}) rs \rangle$
	$X_{rs}^{pq} = \mathcal{S}_{pq} \mathcal{S}_{rs} \langle pq f(r_{12}) \mathcal{Q}_{12} f(r_{12}) rs \rangle$
	$V_{rs}^{pq} = \mathcal{S}_{rs} \langle pq r_{12}^{-1} \mathcal{Q}_{12} f(r_{12}) rs \rangle$
	$C_{rs}^{pq} = \mathcal{S}_{rs} \langle pq [F(1) + F(2)] \mathcal{Q}_{12} f(r_{12}) rs \rangle$
$B_0 = \sum_{ij} B_{ij}^{ij}$	$B_r^p = \sum_j B_{rj}^{pj}$
$\tilde{B}_0 = \sum_{ikl} X_{ik}^{il} F_k^l$	$\tilde{B}_r^p = \sum_{kl} X_{rl}^{pk} F_k^l$
	$X_r^p = \sum_j X_{rj}^{pj}$
$V_0 = \sum_{ij} V_{ij}^{ij}$	$V_q^p = \sum_j V_{qj}^{pj}$

$$\Omega'_{\mu} = \langle 0 | \tau_{\mu}^{\dagger} [e^{-T} H e^T, [\mathcal{R}, \tilde{T}_1]] | 0 \rangle \quad (16)$$

and amplitudes defining the new \tilde{T}_1 operator are obtained by requiring the following residual expression to vanish:

$$\tilde{\Omega}_{\mu_1} = \langle 0 | [\tau_{\mu_1}^{\dagger}, \mathcal{R}^{\dagger}] ([F, \mathcal{R} + [\mathcal{R}, \tilde{T}_1]] + e^{-T} H e^T) | 0 \rangle. \quad (17)$$

In the XSP approach we do not optimize these new amplitudes but rather require them to be $\tilde{T}_1 = T_1$. In this case the F12 projection (17) is added to the conventional $\langle 0 | \tau_{\mu_1}^{\dagger}$ projection of Eq. (14), thus using Λ_{μ_1} as common Lagrange multiplier.

The computer generated explicit expressions for the resulting Lagrangians are given in the Appendix. As for the usual F12 ansatz, the geminal factors give rise to three and four-electron integrals which can be approximated by the usual techniques.³ The relevant intermediates are listed in Table II. Note that the SP ansatz and the special symmetrization convention used for the geminal, Eqs. (2)–(4), allow the formulation of contracted rank zero and rank one intermediates, as outlined in Table II.

C. Coupled-cluster excitation energies

In the coupled-cluster response framework, we obtain excitation energies as poles of response functions, or—more explicitly—as eigenvalues of the Jacobian,^{8,10}

$$A_{\mu\nu} = \frac{\partial \mathcal{L}}{\partial \Lambda_{\mu} \partial t_{\nu}}. \quad (18)$$

In case of XSP_{opt}, additional blocks arise due to derivatives with respect to \tilde{T}_1 and $\tilde{\Lambda}_1$ (*vide infra*).

Also, one has to consider the derivatives of the overlap

$$\Sigma_{\mu\nu} = \frac{\partial}{\partial \Lambda_{\mu} \partial t_{\nu}} \langle 0 | \Lambda S | 0 \rangle, \quad (19)$$

which arises from the time derivative in the quasienergy Lagrangian.¹⁰ Unlike for conventional coupled cluster, we have to take care of a nonunit metric due to the nonorthogonality of the geminal functions.¹¹

The secular equations arising for the XSP_{opt} ansatz thus assume the form

$$\begin{pmatrix}
\langle 0|\tau_1^\dagger[e^{-S}He^S,\tau_1]|0\rangle & \langle 0|\tau_1^\dagger e^{-S}He^S,[\mathcal{R},\tau_1]|0\rangle & \langle 0|\tau_1^\dagger[e^{-S}He^S,\tau_2]|0\rangle \\
\langle 0|[\tau_1^\dagger,\mathcal{R}^\dagger][e^{-S}He^S,\tau_1]|0\rangle & \langle 0|[\tau_1^\dagger,\mathcal{R}^\dagger][e^{-S}He^S,[\mathcal{R},\tau_1]|0\rangle & \langle 0|[\tau_1^\dagger,\mathcal{R}^\dagger][e^{-S}He^S,\tau_2]|0\rangle \\
\langle 0|\tau_2^\dagger[e^{-S}He^S,\tau_1]|0\rangle & \langle 0|\tau_2^\dagger[e^{-S}He^S,[\mathcal{R},\tau_1]|0\rangle & \langle 0|\tau_2^\dagger[e^{-S}He^S,\tau_2]|0\rangle
\end{pmatrix}
\times \begin{pmatrix} E_1 \\ \tilde{E}_1 \\ E_2 \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 & 0 \\ 0 & \langle 0|[\tau_1^\dagger,\mathcal{R}^\dagger][\mathcal{R},\tau_1]|0\rangle & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} E_1 \\ \tilde{E}_1 \\ E_2 \end{pmatrix}. \quad (20)$$

The eigenvalue problem is nonsymmetric which gives rise to an equivalent set of “left-hand” equations, leading to the same eigenvalues but a different set of left-hand eigenvectors, \bar{E}_1 , $\tilde{\bar{E}}_1$, and \bar{E}_2 . These may be normalized to fulfill

$$\bar{E}_1^\dagger E_1 + \tilde{\bar{E}}_1^\dagger \tilde{E}_1 + \bar{E}_2^\dagger E_2 = 1. \quad (21)$$

In the XSP approach, we have only one set of single-excitation amplitudes. The corresponding eigenvalue equations are obtained from Eq. (20) by summing the first two lines and columns.

D. Correction for basis set error in one-electron terms

One problem in basis set extrapolations for excited states is that we cannot properly separate out correlation effects, unlike for the ground state. F12 calculations, however, improve the correlation part only. As the main intent of the F12 approach is the use of comparatively small orbital basis sets in correlated calculations, we are left with the problem that now the one-electron error may dominate the basis set error. One route to go is the development of new basis sets for explicitly correlated calculations, which make use of the fact that part of the basis set flexibility that was formerly necessary for the orbital expansion of the correlation energy can be invested for improving the one-electron error.²² Another, complementary, idea is to employ the additional basis functions of the complementary auxiliary basis set (CABS) for which the relevant matrix elements are available, as these are needed in the evaluation of the special F12 intermediates. This approach was suggested by Adler *et al.*²³ who used an MP2-type expression to get a correction term.

In this work, we will take up the latter idea. As we want to define an energy functional that is suitable for response theory, we propose to include all terms linear in $T_{1'}$, and to approximate the coupling between these single excitations and the coupling to T_2 , by the Fock operator, analogous to the definition of the (F12) truncation.¹⁷ This leads to the following extension of the Lagrange expression:

$$\begin{aligned}
\mathcal{L}_{\text{XSP}_{\text{opt}+T_{1'}}} &= \mathcal{L}_{\text{XSP}_{\text{opt}}} + \langle 0|FT_1|0\rangle + \langle 0|HT_1T_1|0\rangle \\
&+ \langle 0|\mathcal{R}^\dagger[F,T_{1'}]|0\rangle + \sum_{\mu} \Lambda_{\mu} \Omega''_{\mu} \\
&+ \sum_{\mu_1} \tilde{\Lambda}_{\mu_1} \tilde{\Omega}''_{\mu_1} + \sum_{\mu_1'} \Lambda_{\mu_1'} \Omega_{\mu_1'} \quad (22)
\end{aligned}$$

with the additional coupling terms for the T and \tilde{T} residual,

$$\Omega''_{\mu} = \langle 0|\tau_{\mu}^\dagger[e^{-T}He^T,T_1]|0\rangle, \quad (23)$$

$$\tilde{\Omega}''_{\mu_1} = \langle 0|[\tau_1^\dagger,\mathcal{R}^\dagger][F,T_{1'}]|0\rangle, \quad (24)$$

and the $T_{1'}$ residual

$$\Omega_{\mu_1'} = \langle 0|\tau_1^\dagger,e^{-T}He^T|0\rangle + \langle 0|\tau_1^\dagger,[F,\mathcal{R} + [\mathcal{R},\tilde{T}_1] + T_{1'}]|0\rangle. \quad (25)$$

The explicit expression for the Lagrangian can be found in the Appendix. In the excited state equations, we get additional equations for the response amplitudes $E_{1'}$.

III. REMARKS ON THE IMPLEMENTATION

The generation of the explicit expressions and their numerical evaluation was achieved by automated techniques as implemented in the GECCO program. Starting from the definition of the cluster operator and the coupled-cluster Lagrange functional [including the rules for the (F12)-truncation], the code expands the explicit expressions for the Lagrangian and obtains all necessary equations by differentiation. After optimal factorization of the terms and the elimination of common intermediates, the expressions for the energy, residual or for matrix-vector products are evaluated using a string based approach, comparable to that of Kállay and Surján.²⁴ The code has previously been applied to the implementation of the full CCSD-F12 model,²⁰ further details will be published elsewhere. The basic integrals have been imported from a special version of the DALTON code.²⁵

As mentioned above, we employ the truncated CCSD(F12) model in the present work. The present version of GECCO supports ansatz 3 (modified ansatz 2) (Ref. 26) and approximations B and C. Auxiliary basis sets are used to better represent the resolution of the identity, employing the CABS approach.²⁶

The correctness of the implementation has been checked by comparison to the DALTON implementation of CCSD(F12) for both optimized occupied-occupied pair rotations c_{ij}^{kl} and the SP ansatz. Likewise we could check the correctness of our implementation for the excitation energies by solving both the right-hand and left-hand eigenvalue equations, which lead to identical eigenvalues.

The overall scaling of all the XSP methods is N^6 , with N being a measure for system size. More specific, the computationally most expensive noniterative terms scale with $O^2V^2X^2$ and OV^5 , where O is the number of occupied, V is the number of virtual orbitals, and X is the number of auxiliary functions in the CABS. The most expensive terms which are evaluated in each iteration scale O^2V^4 and $O^3V^2X^1$. Thus, the iterative effort of the XSP approaches has the same scaling as the SP ansatz. The noniterative terms scale somewhat worse (SP, for comparison: O^2X^2 and $O^3V^1X^1$) due to the presence of geminals with virtual-occupied pairs in the XSP approach. For the XSP+ T_1 approach, the additional single excitations into the CABS add terms scaling with at most N^5 to the iterative effort. The most worrisome term is probably one that scales like $O^1V^1X^2$, as this is a quadratic scaling with auxiliary basis set size, however, with a low prefactor (only N^4 overall scaling).

IV. NUMERICAL EXAMPLES

A. Calculation details

The presented examples comprise of boron hydride, BH, at a distance of $R=2.328\ 898\ 31\ a_0$, singlet carbene, CH₂, with nuclei at the Cartesian coordinates (in a_0): C (0.0, 0.0, 0.189 234 24) and H (0.0, 1.625 690 44, -1.126 589 82); the second H is at the appropriate position for C_{2v} point group symmetry. For lithium fluoride, LiF, an artificially stretched bond ($4.0a_0$) was employed, as explained below. We have used the augmented series of Dunning's correlation consistent basis sets,^{27,28} aug-cc-pVXZ, as this has become a kind of standard in F12 calculations. We note, however, that attempts exist to create new basis sets which are specially suited for explicitly correlated basis sets.²² It is not clear, however, in how far these are suited for excited states, or response properties and a test of this is not the scope of the present work. As auxiliary basis, to better represent the resolution of the identity in orbital space, we used an uncontracted aug-cc-pV6Z basis. In case of lithium fluoride, a special $21s14p7d6f5g4h3i$ basis was constructed for both lithium and fluorine, starting from the well-tempered basis sets²⁹ and adding one further diffuse function. The exponents ζ^l for higher angular momentum functions were generated by the formula $\zeta^l = \zeta^0(l+3)/3$, and always the largest exponents were discarded.

The Slater correlation factor is fitted by a linear combination of six Gaussian geminals, with the exponents and coefficients given in Ref. 5. For all examples, we used the modified ansatz 2 (=ansatz 3) for the strong-orthogonality projector and approximation C for the evaluation of the B and C intermediates; no extended or generalized Brillouin

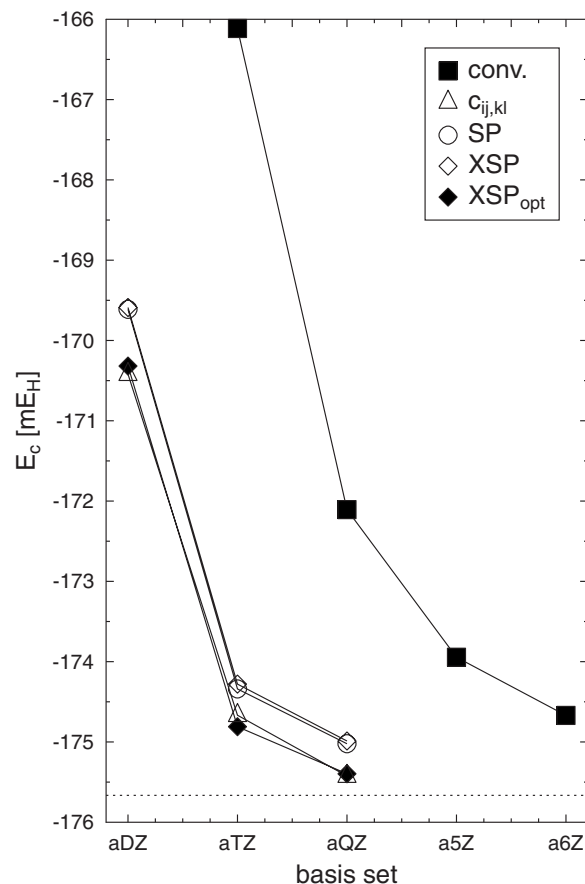


FIG. 2. CH₂: Convergence of the CCSD correlation energy. The aug-cc-pVXZ basis sets are abbreviated as "aXZ." All explicitly correlated models use a Slater exponent $\gamma=1.4$. The basis set limit extrapolated from the conventional calculations is indicated by a horizontal line.

condition was enforced. Likewise, no hybrid scheme was applied, i.e., the exchange contributions to the B intermediate were fully evaluated.

As mentioned before, a special version of the DALTON code²⁵ was employed in order to generate the reference wave function and the basic integrals. Conventional coupled-cluster calculations were performed using the C FOUR package.³⁰ For all calculations the frozen-core approximation was used.

B. Ground state energies

In this section, we have chosen singlet CH₂ to discuss the behavior of the various CCSD(F12) schemes for ground state energy calculations. In Fig. 2, the convergence of the CCSD correlation energy with increasing basis set size is plotted. For orientation, we extrapolated to the limit using the two-point X^{-3} formula of Helgaker *et al.*³¹ The conventional calculation shows the expected slowly convergent behavior, even for an aug-cc-pV6Z basis set an error of more than 1 mE_h remains. All explicitly correlated models improve the results significantly. For an aug-cc-pVTZ basis both the SP and XSP approaches recover a larger fraction of the correlation energy than the conventional aug-cc-pV5Z result does. For an aug-cc-pVQZ basis, the deviation from the (conventionally estimated) basis set limit is below 1 mE_h. The increased flexibility, either by the usual intro-

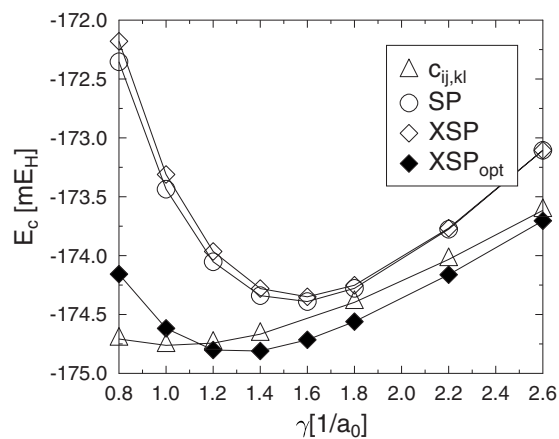


FIG. 3. CH_2 : Dependence of the CCSD correlation energy on the Slater exponent γ . The aug-cc-pVTZ basis set was used.

duction of occupied-occupied pair rotations or by including optimized virtual-occupied pairs (XSP_{opt} approach), seems to further improve the results.³²

A crucial question in all explicitly correlated approaches using a single Slater-type geminal is the dependence of the result on the Slater exponent γ , cf. Eq. (1). In Fig. 3 we have plotted the γ dependence of the two new approaches XSP and XSP_{opt} and compare to the γ dependence of the usual c_{ij}^{kl} and SP ansätze. Obviously, the XSP approach performs nearly equivalent to the original SP method, as the two curves run nearly parallel to each other, the energies obtained for the XSP ansatz are only slightly shifted up. As observed before,^{4,19} the optimum γ for the latter methods is considerably larger than for the c_{ij}^{kl} ansatz. Compared to that, the optimum γ for XSP_{opt} is slightly shifted to lower values, but still the length scale is shorter than for the c_{ij}^{kl} ansatz.

As observed in previous publications,^{4,18,19} the γ -dependence diminishes for larger basis set, as shown for the XSP approaches in Fig. 4. The double-zeta basis sets are obviously too inflexible, but starting from triple zeta, we obtain satisfactory results for a broad range of γ values. As a general trend, the minimum shifts to larger γ for increasing basis set level, less pronounced, however, for the XSP_{opt} approach. It should be noted, that the optimum γ is dependent on the molecular system. However, it must be chosen *globally*, like a basis set parameter, in order to obtain consistent results. In so far, there is no point in choosing an optimum γ based on Fig. 4, and we will (somewhat arbitrarily) use $\gamma = 1.4$ in all further examples, unless stated otherwise.

As discussed in Sec. II D, the F12 approaches only give a correction to the correlation energy. In Fig. 5, we have plotted the convergence of the total ground state energy of CH_2 . In fact, we observe for both XSP and XSP_{opt} that the basis set incompleteness error for the reference energy diminishes the overall improvement of the results. E.g. for the aug-cc-pVTZ basis set, the total XSP_{opt} energy is (in terms of deviation from the limit) only as good as the conventional aug-cc-pVQZ result. Including single excitations into the CABS basis, significantly enhances the values. As for correlation energies, an improvement by two zeta levels is now

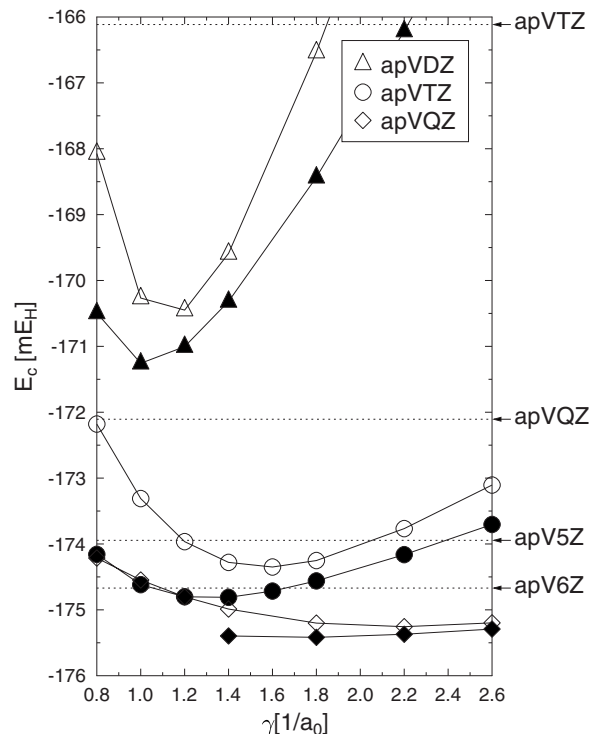


FIG. 4. CH_2 : Dependence of the CCSD correlation energy on the Slater exponent γ . The curves with open symbols refer to the XSP model, those with filled symbols to the XSP_{opt} model. The horizontal lines indicate the correlation energies from the conventional calculation.

observed for the total energy. In the following sections, we will investigate whether this result carries over to excitation energies and equilibrium geometries.

C. Vertical excitation energies

We start with the vertical $A^1\Pi \leftarrow X^1\Sigma^+$ transition of BH. In Fig. 6 the basis set dependence of the various models is compared. The convergence of the conventional calculation is rather rapid, as ground state and excited state correlation effects largely cancel (*vide infra*). For the calculation of excitation energies with the SP approach, a tremendous basis set error occurs, in accordance with similar findings in Ref. 11. The XSP ansatz significantly improves on SP, but seemingly it does not straightly converge to the limit which obviously is reached for the conventional calculations. For the given Slater exponent of $\gamma=1.4$, the three values for XSP/aug-cc-pVXZ ($X=D, T, Q$) cluster about 0.01 eV above the apparent basis set limit. Including single excitations into the CABS does not seem to help in this case. If we optimize the additional singles parameters \tilde{T}_1 , however, we obtain a nice and—as compared to the conventional calculations—even improved convergence to the basis set limit.

To gain more insight into the properties of the discussed methods, we will now examine three issues: (a) the γ dependence of the excitation energies, (b) a break-down of the excitation energies into several contributions and the convergence of the latter, and (c) the convergence of energy differences between excited states.

In Fig. 7 the γ -dependence of XSP and XSP_{opt} excitation energies is shown for different basis sets. We notice that in

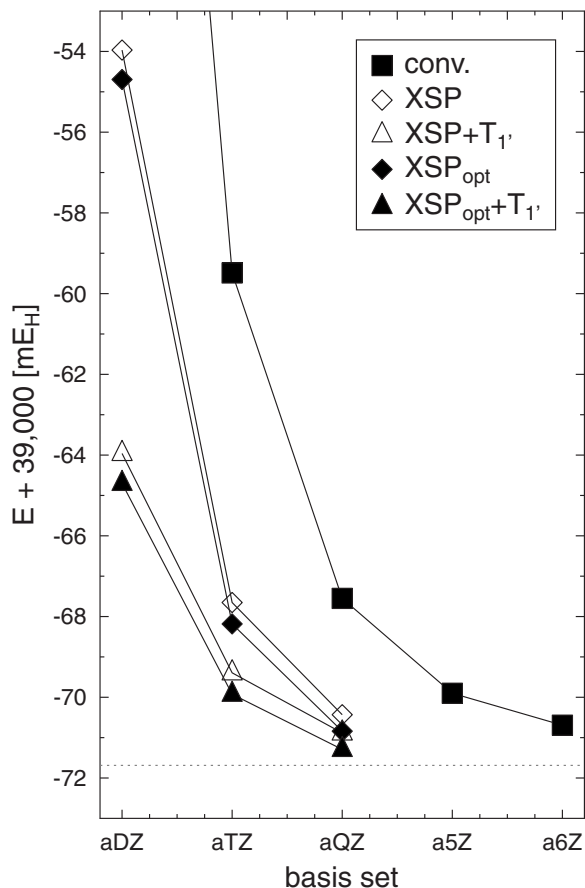


FIG. 5. CH₂: Convergence of the CCSD total energy. All explicitly correlated models use a Slater exponent $\gamma=1.4$. The basis set limit estimated from the conventional calculations (extrapolated correlation energy and aug-cc-pV6Z Hartree-Fock energy) is indicated by a horizontal line.

all cases the dependence decreases for larger basis sets and that—for $0.8 < \gamma < 1.4$ —the optimization of \tilde{T}_1 significantly reduces the dependence, as well. Apparently, the XSP approach prefers rather large values of γ for improved excitation energies which, however, runs counter the observations for the ground state correlation energy. There, values of 1.4–1.6 seem optimal, although for larger basis sets a somewhat

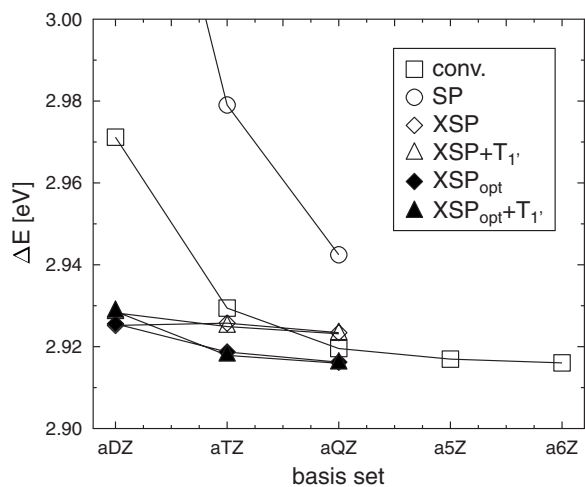


FIG. 6. BH: Convergence of the $B^1\Pi \leftarrow X^1\Sigma^+$ vertical CCSD excitation energy. All explicitly correlated models use a Slater exponent $\gamma=1.4$.

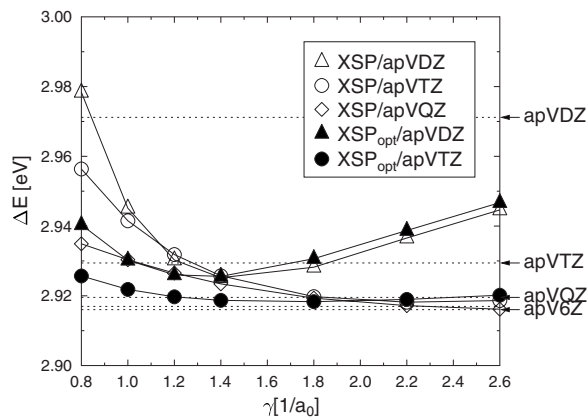


FIG. 7. BH: Dependence of the $B^1\Pi \leftarrow X^1\Sigma^+$ vertical CCSD excitation energy on the Slater exponent γ .

larger γ would do no harm, see Fig. 4. We have not pursued that issue further, noting that first, the XSP_{opt} approach has a much less problematic behavior (in fact, Fig. 7 suggests that with $\gamma=1.4$ we have obtained the best results), and that second, the remaining error for XSP is rather small (<0.01 eV in this case). Rather, we have the “unfortunate” situation that the convergence of excitation energies in BH seems not to be dominated by correlation effects such that the benefits of the XSP approach are smaller than its deficiencies. We will below give a different example, LiF, where correlation effects are much stronger and where both XSP and XSP_{opt} significantly improve the convergence.

Next, we will analyze the BH excitation energies by splitting them into the following three contributions:

$$\Delta E_S = \langle 0 | \bar{E}_1 [e^{T_1} H e^{T_1}, E_1] | 0 \rangle, \quad (26)$$

$$\Delta E_{D,GS} = \langle 0 | \bar{E}_1 [e^S H e^S, E_1] | 0 \rangle - \Delta E_S, \quad (27)$$

$$\Delta E_{D,XS} = \Delta E - \Delta E_S - \Delta E_{D,GS}. \quad (28)$$

The first one is the pure one-electron contribution, the second is interpreted as ground state correlation contribution, and the remainder will be addressed as excited state correlation contribution. The analysis is similar to that presented in Refs. 11 and 12.

In analogy to the mentioned work, we consider two states of BH, which illustrate the two situations: convergence of the excitation energy of a rather compact valence state ($A^1\Pi$ state) and a semidiffuse state ($B^1\Sigma^+$). The first state is analyzed in Table III. The one-electron contribution is very fast convergent, beyond the triple-zeta level it changes by less than 0.005 eV. The ground and excited state correlation contributions to the excitation energy converge slower, but they always have different signs and thus cancel to a large extent. As already mentioned in the discussion of Fig. 6, this leads to a much diminished basis set dependence of the excitation energy.

Comparing the conventional result and the result from the SP approach, we directly find the reason for the failure of the latter. The SP ansatz only improves the ground state correlation, whereas the excited state correlation is nearly the same as in the orbital expansion case. As a consequence, an

TABLE III. Analysis of the contributions to the CCSD $A \ ^1\Pi \leftarrow X \ ^1\Sigma^+$ vertical transition energy of BH. The contributions are defined by Eqs. (26)–(28).

Basis	ΔE	ΔE_S	$\Delta E_{D,GS}$	$\Delta E_{D,XS}$	$\Delta E_{D,GS} + \Delta E_{D,XS}$
Conventional					
apVDZ	2.9712	2.7224	1.4886	-1.2399	0.2487
apVTZ	2.9294	2.7299	1.6104	-1.4109	0.1995
apVQZ	2.9195	2.7316	1.6404	-1.4524	0.1880
apV5Z	2.9170	2.7320	1.6493	-1.4644	0.1849
SP					
apVDZ	3.0886	2.7194	1.5926	-1.2234	0.3691
apVTZ	2.9790	2.7287	1.6542	-1.4039	0.2503
apVQZ	2.9424	2.7309	1.6606	-1.4490	0.2116
XSP					
apVDZ	2.9252	2.7258	1.5986	-1.3992	0.1994
apVTZ	2.9257	2.7325	1.6568	-1.4636	0.1932
apVQZ	2.9234	2.7329	1.6616	-1.4711	0.1906
XSP+ $T_{1'}$					
apVDZ	2.9283	2.7303	1.5970	-1.3990	0.1979
apVTZ	2.9249	2.7316	1.6566	-1.4633	0.1933
apVQZ	2.9231	2.7326	1.6616	-1.4711	0.1905
XSP _{opt}					
apVDZ	2.9256	2.7262	1.6127	-1.4133	0.1994
apVTZ	2.9187	2.7323	1.6518	-1.4654	0.1864
apVQZ	2.9162	2.7326	1.6571	-1.4734	0.1836
XSP _{opt} + $T_{1'}$					
apVDZ	2.9286	2.7307	1.6111	-1.4132	0.1979
apVTZ	2.9179	2.7314	1.6516	-1.4651	0.1865
apVQZ	2.9159	2.7324	1.6570	-1.4734	0.1836

imbalance between of ground and excited state contributions occurs. This is the same finding as described for the response of the c_{kl}^{ij} ansatz in Ref. 11, although for the latter approach one could have expected that the response of the c_{kl}^{ij} remedies the problem. However, this was found to be not the case, in the particular example of the $^1\Pi$ state of BH for the obvious reason that no response amplitudes with appropriate symmetry exist, as all occupied orbitals have Σ symmetry.¹¹

Turning to the XSP ansatz, we find that the balanced description of ground and excited state correlation is largely restored: not only the ground state contribution is improved (the values are comparable to that of the SP approach), also the excited state values lie—for all three basis sets—much closer to the apparent basis set limit. The one-electron part remains nearly unaffected for XSP. Inclusion of the single excitations into the CABS slightly improves the convergence of the one-electron contribution, most noticeably for the aug-cc-pVDZ basis, although the total excitation energy seems to become worse in this case. In fact, the result without $T_{1'}$ was only fortuitously better due to error cancellation, as one-electron and correlation contributions approach the limit from different sides.

The introduction of optimized singles amplitudes for the explicit correlation part, \tilde{T}_1 (XSP_{opt} ansatz), leads to nearly no changes in the one-electron contribution. The major ef-

fects are a slight increase of the ground state correlation contribution and a slight decrease of the excited state correlation contribution, which finally results in an improved balance and a faster convergence. Comparison to the XSP result suggests that the latter model slightly overestimates the differential correlation effect.

The excitation into the ($B \ ^1\Sigma^+$) state is analyzed in Table IV. With the singly augmented basis set series, we observe slow convergence even for the one-electron contribution. Obviously, the introduction of correlation factors cannot amend this shortcoming of the basis, as the results for XSP and XSP_{opt} show. The introduction of the extended singles $T_{1'}$ does not significantly improve the results, either. This does not arise from a deficiency in the CABS, as including further diffuse functions in the *auxiliary* basis does not change results. Rather, the reason is that the $T_{1'}$ enter perturbatively only. In the present case, however, the principal configuration needs to be described by a basis function that is not included in the orbital basis set, which cannot be amended by a perturbative correction. If we move to the doubly augmented basis sets, the problems in the one-electron terms vanish, and the convergence properties of the approaches are similar to the $A \ ^1\Pi$ case, see Tables III and IV.

So far, we have reached the conclusion that the major

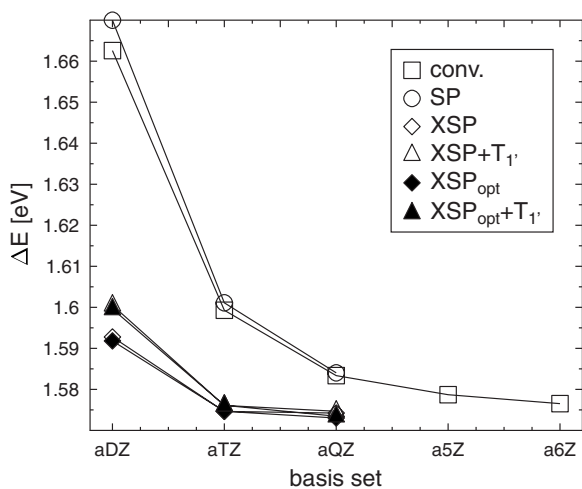
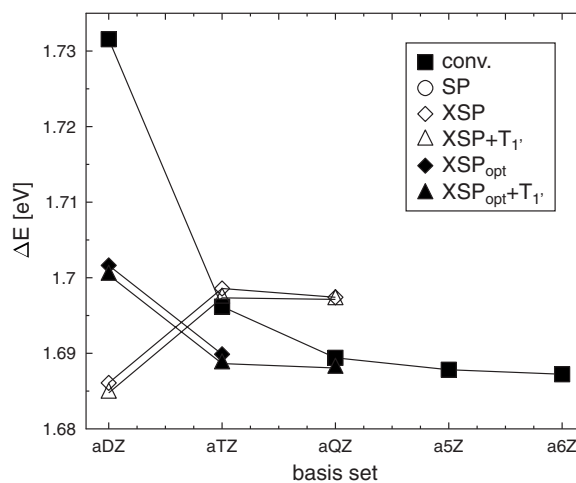
TABLE IV. Analysis of the contributions to the CCSD $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ vertical transition energy of BH. The contributions are defined by Eqs. (26)–(28).

Basis	ΔE	ΔE_S	$\Delta E_{D,GS}$	$\Delta E_{D,XS}$	$\Delta E_{D,GS} + \Delta E_{D,XS}$
Conventional					
apVDZ	6.5021	6.0041	1.2740	-0.7760	0.4980
apVTZ	6.5463	5.9472	1.3911	-0.7920	0.5991
apVQZ	6.5537	5.9313	1.4198	-0.7973	0.6225
apV5Z	6.5516	5.9196	1.4284	-0.7964	0.6320
dapVTZ	6.5186	5.9139	1.3914	-0.7866	0.6047
dapVQZ	6.5383	5.9122	1.4199	-0.7938	0.6261
dapV5Z	6.5452	5.9112	1.4284	-0.7944	0.6340
XSP					
apVDZ	6.5856	6.0050	1.3846	-0.8039	0.5806
apVTZ	6.5861	5.9486	1.4387	-0.8012	0.6375
apVQZ	6.5754	5.9327	1.4418	-0.7991	0.6427
dapVTZ	6.5584	5.9146	1.4384	-0.7945	0.6438
dapVQZ	6.5599	5.9134	1.4416	-0.7952	0.6464
XSP _{opt}					
apVDZ	6.5991	6.0022	1.3967	-0.7999	0.5968
apVTZ	6.5779	5.9449	1.4326	-0.7996	0.6330
apVQZ	6.5677	5.9302	1.4366	-0.7992	0.6374
dapVTZ	6.5493	5.9110	1.4315	-0.7931	0.6384
dapVQZ	6.5514	5.9109	1.4358	-0.7952	0.6405
XSP _{opt} +T ₁ '					
apVDZ	6.5839	5.9834	1.3870	-0.7865	0.6005
apVTZ	6.5662	5.9318	1.4290	-0.7945	0.6344
apVQZ	6.5622	5.9183	1.4337	-0.7810	0.6526
dapVTZ	6.5525	5.9141	1.4314	-0.7931	0.6383
dapVQZ	6.5521	5.9117	1.4357	-0.7953	0.6404

problem of explicitly correlated calculations for excitation energies lies in the balance between ground and excited state. For coupled-cluster response theory the problem is even more evident, than, e.g., for configuration interaction-type calculations, as ground and excited state are not treated equally by construction. In fact, if we look at energy differences *between* excited states, most of the above problems (in particular for XSP) seem to cancel. In Fig. 8 we have plotted

the energy difference between the $A^1\Pi$ state and the corresponding $^3\Pi$ state. Now, both XSP and XSP_{opt} behave nearly identically, and quickly converge to the limit. For the SP approach, on the other hand the same behavior as for a conventional calculation is observed, as the improvements for the ground state wave function completely cancel.

These effects are seen in other examples as well. In Fig. 9 we have plotted the excitation energy of the 1^1B_1

FIG. 8. BH: Convergence of the $B^1\Pi \leftarrow X^3\Sigma^+$ vertical CCSD excitation energy. All explicitly correlated models use a Slater exponent $\gamma=1.4$.FIG. 9. CH₂: Convergence of the $1^1B_1 \leftarrow 1^1A_1$ vertical CCSD excitation energy. All explicitly correlated models use a Slater exponent $\gamma=1.4$.

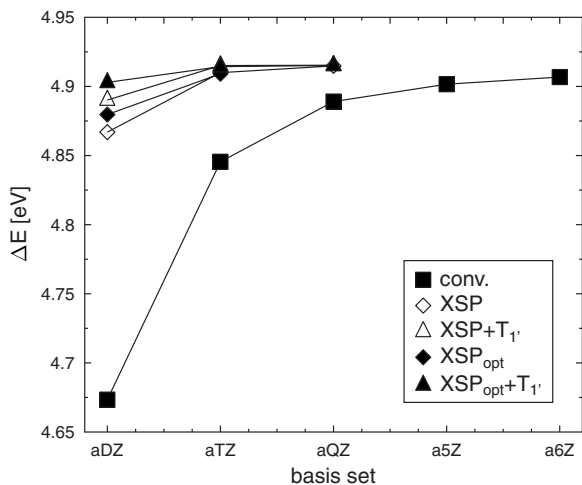


FIG. 10. CH_2 : Convergence of the $1^3A_1 \leftarrow 1^1B_1$ vertical CCSD excitation energy. All explicitly correlated models use a Slater exponent $\gamma = 1.4$.

$\leftarrow 1^1A_1$ transition of CH_2 , where 1^1A_1 is treated as ground state in the coupled-cluster calculation. We obtain the same picture as in the case of the transition to the $1^1\Pi$ state of BH: at the aug-cc-pVQZ level an error of ~ 0.01 eV remains for the XSP approach, whereas XSP_{opt} nicely converges to the limit. If we instead consider the difference between, e.g., 1^1B_1 and 1^3A_1 , all XSP approaches nicely converge to the limit and clearly improve upon the conventional calculation, see Fig. 10.

As a last example for vertical excitation energies, we want to discuss the LiF molecule. The choice was motivated by the fact that the above examples lack strong differential correlation effects. The low-lying excited states of LiF, however, are charge-transfer excitations which feature a strong change in the electron density upon excitation, and consequently significant differential correlation energies can be expected. We artificially enhanced the charge-transfer character by choosing a somewhat enlarged bond distance of $4.0a_0$.

Indeed, the results presented Fig. 11 indicate a strong basis set effect for the conventional calculations. We have extrapolated the excitation energy to the complete basis set limit from the aug-cc-pVQZ and aug-cc-pV5Z results using the two-point X^{-3} formula.³¹ With respect to this procedure, a word of caution is appropriate, as we did not separate out the one-electron contribution; rather, we assume that the change in the one-electron contribution is negligible for the two basis sets. In fact, the fast convergence of the F12 results confirms the assumption that the major part of the basis set effect is due to correlation. The XSP_{opt} results nicely converge to the same limit as estimated from the conventional calculations, whereas the XSP ansatz deviates for the aug-cc-pVQZ basis by ~ 0.02 eV from the limit. Compared to the conventional calculation, this still is a significant improvement and we will show in the following section that for other properties XSP and XSP_{opt} work equally well.

D. Spectroscopic parameters

In this section, we want to examine the possible benefits for the calculation of potential energy surfaces, in particular, for excited state structures and harmonic frequencies. We

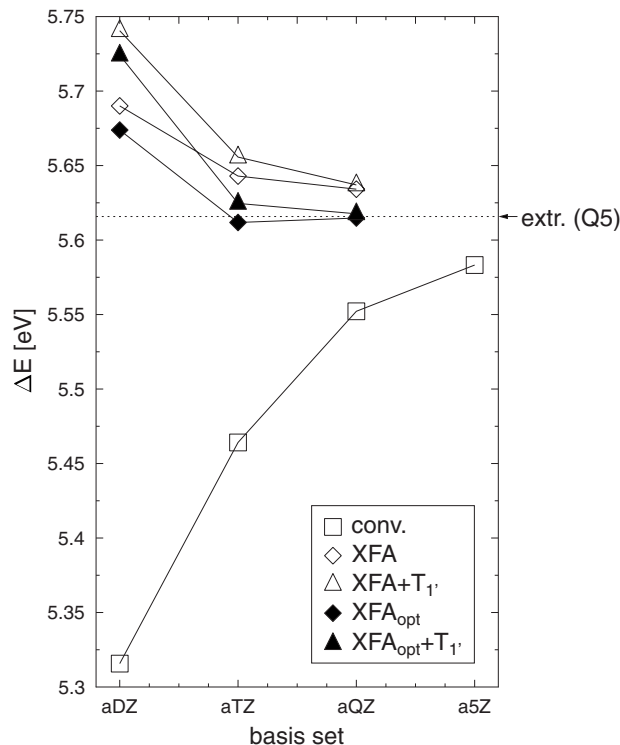


FIG. 11. LiF: Convergence of the $2^1\Sigma^+ \leftarrow 1^1\Sigma^+$ vertical CCSD excitation energy. All explicitly correlated models use a Slater exponent $\gamma = 1.4$.

will investigate the improvements due to the new XSP approaches for the $1^1\Pi$ states of two diatomics—BH and CO—and compare these to the improvements gained for the electronic ground state.

The potential energy curves were calculated around the presumed minima, with increments of $0.01a_0$. The actual minima (total energy and r_e) and the harmonic frequencies were obtained by interpolation with fourth-order polynomials. The accuracy of the obtained values was checked by comparison to analytical results using CF_{OUR},³⁰ which also was used to calculate the grid points for conventional CCSD. The extrapolated results were obtained by a two-point X^{-3} extrapolation scheme for each single point energy,³¹ either for the ground state correlation energy, or for the ground state correlation plus excitation energy. The Hartree–Fock contribution was taken from the aug-cc-pV6Z calculations.

The results for BH are presented in Table V. As benchmark we use the conventionally obtained basis set limit, as described above. However, it should be pointed out that the extrapolation scheme is purely empirical, and in case of excitation energies it is not well established. Thus, the extrapolated results should rather be regarded as orientation, a more reliable basis set limit may be available from F12 calculations with large basis sets, once the properties of the latter are better understood.

Comparison of the entries of Table V for aug-cc-pVTZ with and without correction of the Hartree–Fock contribution illustrates the importance of that correction: Particularly the errors in the equilibrium distance and the harmonic frequency are significantly reduced for both the electronic ground and excited states. Thus, the XSP and XSP_{opt} results

TABLE V. BH: CCSD spectroscopic parameters using conventional orbital expansions and the XSP approach (Slater exponent $\gamma=1.4$).

Method	Basis	T_e (eV)		r_e (pm)		ω_e (cm^{-1})	
		Value	$\Delta_{5/6}^a$	Value	$\Delta_{5/6}^a$	Value	$\Delta_{5/6}^a$
$X^1\Sigma^+$							
Conventional	5/6 extr			123.13		2371	
	apVTZ			123.42	+0.29	2359	-12
	apVTZ+HF/apV6Z ^b			123.27	+0.14	2363	-8
	apVQZ+HF/apV6Z ^b			123.19	+0.06	2369	-2
	apV5Z+HF/apV6Z ^b			123.15	+0.02	2370	-1
	apV6Z			123.14	+0.01	2371	+0
XSP	apVTZ+HF/apV6Z			123.11	-0.02	2372	+1
XSP _{opt}	apVTZ+HF/apV6Z			123.11	-0.02	2372	+1
XSP+ T_1'	apVTZ			123.11	-0.02	2373	+2
XSP _{opt} + T_1'	apVTZ			123.11	-0.02	2372	+1
$A^1\Pi$							
Conventional	5/6 extr.	2.914		122.11		2325	
	apVTZ	2.929	+0.015	122.44	+0.33	2303	-22
	apVTZ+HF/apV6Z ^b	2.929	+0.015	122.27	+0.16	2309	-16
	apVQZ+HF/apV6Z ^b	2.919	+0.005	122.18	+0.07	2321	-4
	apV5Z+HF/apV6Z ^b	2.916	+0.002	122.13	+0.02	2323	-2
	apV6Z	2.915	+0.001	122.12	+0.01	2324	-1
XSP	apVTZ+HF/apV6Z ^b	2.925	+0.011	122.07	-0.04	2325	+0
XSP _{opt}	apVTZ+HF/apV6Z ^b	2.917	+0.004	122.07	-0.04	2326	+1
XSP+ T_1'	apVTZ	2.924	+0.010	122.09	-0.02	2325	+0
XSP _{opt} + T_1'	apVTZ	2.917	+0.003	122.09	-0.02	2325	+0

^aDifference to 5/6 extrapolated value.^bHartree-Fock reference state energy from aug-cc-pV6Z basis was used.

(which do not include the single excitations into the CABS) are only meaningful, if the Hartree-Fock energy is corrected for the aug-cc-pV6Z result.

Including this correction, rather encouraging results are obtained: For both states, $X^1\Sigma^+$ and $A^1\Pi$, the XSP models using the triple-zeta basis sets are as close to the estimated basis set limit as the conventional aug-cc-pV5Z calculation. Only the outcome for the XSP excitation energy is somewhat too high which is improved by optimized \tilde{T}_1 amplitudes. Apart from the slight shift in the energetics, however, both XSP and XSP_{opt} yield nearly the same results.

The results for the T_1' -augmented models demonstrate that the Hartree-Fock contributions are rather well corrected by that approach. This means that the XSP+ T_1' and XSP_{opt}+ T_1' approaches allow to obtain results close to the basis set limit from a single calculation.

A very similar picture emerges for CO, see Table VI. Again the Hartree-Fock correction turns out to be highly important. The correlation corrections due to the geminals incorporated through the XSP approach seem to work extremely well, in this case we even surpass the aug-cc-pV6Z result for r_e and ω_e . Only for the adiabatic excitation energy, a slight deviation occurs, the value obtained with the XSP_{opt}+ T_1' approach is 0.012 eV above the conventionally estimated limit. As noted above, however, the extrapolation needs not necessarily be optimal for excitation energies.

V. CONCLUSIONS

We have presented a modification of the cluster operator that enables explicitly correlated coupled-cluster calculations of electronically excited states. The new term in the cluster operator comprises of a geminal function acting on a virtual-occupied orbital pair. The present approach can be viewed as an extension of the SP approach pioneered by Ten-no,^{16,4} and we term it XSP approach. Two models are discussed in the scope of the coupled-cluster singles and doubles model, in one of them the virtual-occupied orbital pair is associated with the usual T_1 operator, in the other an additional \tilde{T}_1 operator is introduced (XSP_{opt} approach). Both models have been implemented using the GECCO program, which automatically expands the explicit expressions and evaluates them using a string based approach.

The numerical examples suggest that both XSP ansätze improve on the standard F12 approaches, which fail for excitation energies.¹¹ The first XSP approach, in which the excited pair geminal operator is contracted with the usual T_1 operator is slightly too inflexible and gives an *apparent* limit for excitation energies that is incorrect by 0.01–0.02 eV in the present examples. We note that this error is guaranteed to vanish if the orbital basis approaches completeness due to the strong-orthogonality projector. The source of the error seems to be a slight bias between the ground and excited state correlation contributions, as differences between excited states do not show this problem.

TABLE VI. CO: CCSD spectroscopic parameters using conventional orbital expansions and the XSP approach (Slater exponent $\gamma=1.4$).

Method	Basis	T_e (eV)		r_e (pm)		ω_e (cm ⁻¹)	
		Value	$\Delta_{5/6}^a$	Value	$\Delta_{5/6}^a$	Value	$\Delta_{5/6}^a$
$X^1\Sigma^+$							
Conventional	5/6 extr.			112.30		2238	
	apVTZ			112.88	+0.58	2215	-23
	apVTZ+HF/apV6Z			112.63	+0.33	2221	-17
	apVQZ+HF/apV6Z			112.44	+0.14	2232	-6
	apV5Z+HF/apV6Z			112.37	+0.07	2235	-3
	apV6Z			112.34	+0.04	2237	-1
XSP	apVTZ+HF/apV6Z			112.31	+0.01	2239	+1
XSP+ $T_{1'}$	apVTZ			112.32	+0.02	2239	+1
XSP _{opt} + $T_{1'}$	apVTZ			112.33	+0.03	2238	0
$A^1\Pi$							
Conventional	5/6 extr.	8.258		122.28		1592	
	apVTZ	8.211	-0.047	123.16	+0.88	1560	-32
	apVTZ+HF/apV6Z	8.236	-0.022	122.86	+0.58	1565	-27
	apVQZ+HF/apV6Z	8.246	-0.011	122.51	+0.23	1581	-11
	apV5Z+HF/apV6Z	8.252	-0.006	122.39	+0.11	1587	-5
	apV6Z	8.254	-0.004	122.34	+0.06	1589	-3
XSP	apVTZ+HF/apV6Z	8.294	+0.036	122.31	+0.03	1591	-1
XSP+ $T_{1'}$	apVTZ	8.289	+0.031	122.31	+0.03	1592	0
XSP _{opt} + $T_{1'}$	apVTZ	8.270	+0.012	122.33	+0.05	1591	-1

^aDifference to 5/6 extrapolated value.

Introducing new amplitudes \tilde{T}_1 (XSP_{opt} ansatz) resolves the problem, and highly accurate results are possible for triple-zeta basis sets, already. As an aside, the improvement comes at the cost of lower numerical stability due to near-linear dependencies in the geminal basis which determines the metric for the \tilde{T}_1 amplitudes and their response. This might pose a problem when going to larger molecules and warrants further investigation.

As shown by a detailed analysis of the contributions to the excited states, the improvement gained by the XSP models only affects the correlation. In order to improve the one-electron description, additional single excitations into the CABS space $T_{1'}$ are introduced, thereby extending the idea of Adler *et al.*²³ This correction was shown to work successfully for the total energy of CH₂ and the ground and excited state structure constants of BH and CO. However, the correction does not work, if the underlying orbital basis set does not properly describe the primary configuration of a state. This particularly may be the case for states with admixture of Rydberg character if the orbital basis is not sufficiently diffuse.

We conclude that the suggested approaches lead to very promising results and open the perspective for evaluating highly accurate excitation energies and response properties from explicitly correlated coupled-cluster response calculations. Of course, the improvements come at the price of a significantly increased complexity of the resulting equations and a higher prefactor in their numerical evaluation, although the scaling remains the same as for conventional CCSD. In fact, it is a major challenge in F12 theory to reduce the

overhead due to the additional terms, such that the improved basis set convergence directly maps to a reduced computational effort. Progress in this direction has been reported for ground state methods,^{6,23} and equivalent approaches need to be transferred to excited state and response calculations.

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APPENDIX: LAGRANGE FUNCTIONS OF THE DISCUSSED CCSD MODELS

The formulae in this section are automatically generated by GECCO. We use the Einstein summation convention over repeated upper and lower indices. In addition, restricted summation over equivalent indices is implied, e.g., $G_{ij}^{ab}t_{ab}^{ij}$ has two pairs of equivalent indices (ij, ab); without assumption of a restricted summation, an additional prefactor of $(\frac{1}{2})^2$ arises (for the present example). For index conventions see Table I; intermediates are defined in Table II.

The four Lagrangians presented in the following form a series of subsets. We start with the conventional contributions, which equal the usual CCSD-Lagrange function,

$$\begin{aligned}
\mathcal{L}_{\text{CCSD}} = & E_0 + F_i^a t_a^i + G_{ij}^{ab} t_{ab}^{ij} + \frac{1}{2} G_{ij}^{ab} t_a^i t_b^j + \Lambda_i^a F_a^i - \Lambda_i^a F_j^i t_a^j + \Lambda_i^a F_a^b t_b^i - \Lambda_i^a G_{ja}^{ib} t_b^j + F_i^a \Lambda_j^b t_{ab}^{ij} + \Lambda_k^b G_{ij}^{ka} t_{ab}^{ij} + \Lambda_j^c G_{ic}^{ab} t_{ab}^{ij} - F_i^b \Lambda_j^a t_a^i t_b^j \\
& + \Lambda_j^b G_{ik}^{ja} t_a^i t_b^k + \Lambda_j^b G_{ic}^{ab} t_a^i t_c^c + G_{ij}^{ab} t_a^i \Lambda_k^{jk} - G_{ij}^{ab} \Lambda_k^{ca} t_b^k t_c^c - G_{ij}^{ab} \Lambda_k^{ca} t_b^k t_c^c - G_{ij}^{ab} \Lambda_k^{ca} t_b^k t_c^c + \Lambda_{ij}^{ab} G_{ij}^{ij} + \Lambda_{ij}^{ab} G_{ka}^{ik} t_b^k + \Lambda_{ij}^{ab} G_{ic}^{ic} t_b^k \\
& - \Lambda_{ij}^{ab} F_j^i t_a^i t_b^k + \Lambda_{ij}^{ab} F_b^c t_{ac}^{ij} + \Lambda_{ij}^{ab} G_{kl}^{ij} t_{ab}^{kl} - \Lambda_{ij}^{ab} G_{ka}^{ic} t_b^k t_c^c + \Lambda_{ij}^{ab} G_{ab}^{cd} t_{cd}^{ij} + \frac{1}{2} \Lambda_{ij}^{ab} G_{kl}^{ij} t_a^i t_b^k t_c^c + \Lambda_{ij}^{ab} G_{ka}^{ib} t_b^k t_c^c + \frac{1}{2} \Lambda_{ij}^{ab} G_{ab}^{cd} t_{cd}^{ij} - F_k^c \Lambda_{ij}^{ab} t_a^i t_b^k t_c^c \\
& - F_k^c \Lambda_{ij}^{ab} t_a^i t_b^k t_c^c + \Lambda_j^b G_{ik}^{ka} t_a^i t_b^j + \Lambda_k^b G_{ij}^{kl} t_a^i t_b^j + \Lambda_k^b G_{ij}^{kl} t_a^i t_b^j + \Lambda_k^b G_{ij}^{kl} t_a^i t_b^j + \Lambda_k^b G_{ij}^{kl} t_a^i t_b^j + \Lambda_k^b G_{ij}^{kl} t_a^i t_b^j - G_{kl}^{cd} \Lambda_{ij}^{ab} t_a^i t_b^k t_c^c t_d^d \\
& + G_{ij}^{cd} \Lambda_{kl}^{ab} t_{ab}^{cd} - G_{kl}^{bc} \Lambda_{ij}^{ad} t_{ac}^{kl} + \frac{1}{2} G_{ik}^{ac} \Lambda_{jl}^{bd} t_{ab}^{ij} t_{cd}^{kl} + \frac{1}{2} \Lambda_{ij}^{bc} G_{kl}^{ia} t_a^i t_b^k t_c^c + \frac{1}{2} \Lambda_{ij}^{ad} G_{ka}^{bc} t_a^i t_b^k t_c^c - G_{il}^{ad} \Lambda_{jk}^{bc} t_a^i t_b^k t_c^c t_d^d + \frac{1}{2} G_{ij}^{cd} \Lambda_{kl}^{ab} t_a^i t_b^k t_c^c t_d^d \\
& - G_{ik}^{ad} \Lambda_{jl}^{bc} t_a^i t_b^k t_c^c t_d^d - G_{il}^{ad} \Lambda_{jk}^{bc} t_a^i t_b^k t_c^c t_d^d + \frac{1}{2} G_{kl}^{ab} \Lambda_{ij}^{cd} t_a^i t_b^k t_c^c t_d^d + \frac{1}{4} G_{ij}^{cd} \Lambda_{kl}^{ab} t_a^i t_b^k t_c^c t_d^d.
\end{aligned}$$

For the explicitly correlated CCSD(F12) model in the SP approach, the CCSD Lagrangian is extended by the following terms:

$$\begin{aligned}
\mathcal{L}_{\text{SP}} = & \mathcal{L}_{\text{CCSD}} + 2V_0 + \tilde{B}_0 + B_0 - [\mathcal{R}^\dagger]_{ij}^{ap''} G_{kp}^{ij} t_a^i t_b^k + [V^\dagger]_{ij}^{a_i} t_a^i + [C^\dagger]_{ij}^{ab} t_{ab}^{ij} + [\mathcal{R}^\dagger]_{ij}^{ap''} G_{kp}^{ib} t_a^i t_b^k + [V^\dagger]_{ij}^{ab} t_{ab}^{ij} - [\mathcal{R}^\dagger]_{ij}^{bp''} G_{kp}^{ia} t_a^i t_b^k \\
& + \frac{1}{2} [V^\dagger]_{ij}^{ab} t_a^i t_b^k + [\mathcal{R}^\dagger]_{ij}^{bp''} G_{ip}^{ac} t_a^i t_b^k + [\mathcal{R}^\dagger]_{ij}^{ap''} G_{jp}^{bc} t_a^i t_b^k - [\mathcal{R}^\dagger]_{ij}^{cp''} G_{kp}^{ab} t_a^i t_b^k - \frac{1}{2} [\mathcal{R}^\dagger]_{ij}^{cp''} G_{kp}^{ab} t_a^i t_b^k - F_i^p \Lambda_j^a \mathcal{R}_{ap}^{ij} - \Lambda_k^a G_{kp}^{ij} \mathcal{R}_{ap}^{ij} \\
& + \Lambda_i^a V_a^i - \Lambda_i^a t_a^i t_j^j - G_{ij}^{ap''} \Lambda_k^a \mathcal{R}_{bp}^{ij} - G_{ij}^{ap''} t_a^i \Lambda_k^b \mathcal{R}_{bp}^{jk} + \Lambda_{ij}^{ab} C_{ij} - \Lambda_{ij}^{ab} G_{ka}^{ip''} \mathcal{R}_{bp}^{jk} + \Lambda_{ij}^{ab} V_{ij} - F_k^p \Lambda_{ij}^{ab} \mathcal{R}_{ap}^{ij} + \Lambda_{ik}^{ab} G_{jl}^{kp} t_b^l \mathcal{R}_{ap}^{ij} \\
& + \Lambda_{ij}^{ab} V_{ka}^{ij} - \Lambda_{ik}^{ab} G_{jb}^{cp''} t_c^c \mathcal{R}_{ap}^{ij} + \Lambda_{jk}^{bc} G_{ic}^{ap''} t_a^i \mathcal{R}_{bp}^{jk} - \Lambda_{ij}^{ab} V_{kl}^{ij} + \Lambda_{ij}^{ab} V_{kl}^{ij} - G_{kl}^{bp''} \Lambda_{ij}^{ac} t_{ab}^{ij} \mathcal{R}_{cp}^{kl} - G_{ik}^{ap''} \Lambda_{jl}^{bc} t_{ab}^{ij} \mathcal{R}_{cp}^{kl} \\
& - G_{ij}^{ap''} \Lambda_{kl}^{bc} t_{ac}^{ij} \mathcal{R}_{bp}^{kl} + \frac{1}{2} \Lambda_{ij}^{ab} V_{kl}^{ij} t_a^i t_b^k t_c^c - G_{ik}^{cp''} \Lambda_{jl}^{ab} t_b^l \mathcal{R}_{ap}^{ij} - G_{il}^{ap''} \Lambda_{jk}^{bc} t_a^i t_b^k t_c^c \mathcal{R}_{bp}^{ij}.
\end{aligned}$$

The additional terms for the CCSD(F12) extended SP approach read

$$\begin{aligned}
\mathcal{L}_{\text{XSP}_{\text{opt}}} = & \mathcal{L}_{\text{SP}} + V_i^a t_a^i + \tilde{B}_i^a t_a^i - X_i^a F_j^i t_a^j + B_i^a t_a^i + F_j^p \Lambda_i^a \mathcal{R}_{ap}^{ib} t_a^i - F_i^p \Lambda_j^a \mathcal{R}_{ap}^{ib} t_b^j - \Lambda_j^a G_{ik}^{jp} \mathcal{R}_{ap}^{ib} t_b^j + \Lambda_i^a V_{ja}^{ib} t_b^j \\
& + \Lambda_j^b V_{ik}^{ja} t_a^i t_b^k - \Lambda_j^b V_{ia}^{jk} t_b^k - G_{ik}^{ap''} \Lambda_j^b t_a^i \mathcal{R}_{bp}^{jk} + G_{ik}^{ap''} t_a^i \Lambda_j^b \mathcal{R}_{bp}^{jk} - G_{ij}^{ap''} t_a^i \Lambda_k^b \mathcal{R}_{bp}^{jk} + \Lambda_{ij}^{ab} C_{ab}^{ic} t_b^k + \Lambda_{ik}^{ab} G_{ja}^{ip''} \mathcal{R}_{bp}^{jk} \\
& - \Lambda_{ij}^{ab} G_{ka}^{ip''} \mathcal{R}_{bp}^{jk} + \Lambda_{ij}^{ab} V_{ab}^{ic} t_b^k - F_j^p \Lambda_{ik}^{ab} t_b^k \mathcal{R}_{ap}^{ij} - \Lambda_{jl}^{ab} G_{ik}^{jp} t_a^i \mathcal{R}_{bp}^{jk} - \Lambda_{ij}^{ab} G_{kl}^{jp} t_b^k \mathcal{R}_{ap}^{ij} + \Lambda_{ik}^{ab} V_{ja}^{ic} t_b^k \\
& + \Lambda_{jk}^{ac} G_{ia}^{bp''} t_b^k \mathcal{R}_{cp}^{id} - \Lambda_{ij}^{ab} G_{kb}^{cp''} t_c^c \mathcal{R}_{ap}^{id} + \Lambda_{jk}^{bc} G_{ic}^{ap''} t_a^i \mathcal{R}_{bp}^{jd} + \Lambda_{ik}^{ab} V_{jl}^{kc} t_{ab}^{ij} - \Lambda_{ik}^{ab} V_{j}^{c} t_{ab}^{ij} + \Lambda_{kl}^{ab} V_{ij}^{kc} t_{ab}^{ij} \\
& - G_{kl}^{bp''} \Lambda_{ij}^{ac} t_{ab}^{ij} \mathcal{R}_{cp}^{kl} + G_{il}^{ap''} \Lambda_{jk}^{bc} t_{ab}^{ij} \mathcal{R}_{cp}^{kl} - G_{ik}^{ap''} \Lambda_{jl}^{bc} t_{ab}^{ij} \mathcal{R}_{cp}^{kl} - G_{ij}^{ap''} \Lambda_{kl}^{bc} t_{ab}^{ij} \mathcal{R}_{cp}^{kl} + \frac{1}{2} \Lambda_{il}^{ab} V_{jk}^{ic} t_a^i t_b^k t_c^c \\
& - G_{jl}^{cp''} \Lambda_{ik}^{ab} t_b^k \mathcal{R}_{ap}^{id} - G_{ij}^{bp''} \Lambda_{kl}^{ac} t_a^i t_b^k \mathcal{R}_{cp}^{id} - G_{ik}^{ap''} \Lambda_{jl}^{bc} t_a^i \mathcal{R}_{bp}^{jd} + \tilde{\Lambda}_i^a [V^\dagger]_a^i + \tilde{\Lambda}_i^a \tilde{B}_i^a - \tilde{\Lambda}_i^a F_j^i X_j^a + \tilde{\Lambda}_i^a \tilde{B}_i^a t_b^j \\
& + \tilde{\Lambda}_j^b F_j^i X_{ib}^a t_a^i + \tilde{\Lambda}_i^a X_{ja}^{ib} F_j^i t_b^j - \tilde{\Lambda}_i^a F_j^i X_{ab}^j + \tilde{\Lambda}_i^a B_i^a + \tilde{\Lambda}_i^a B_{ab}^j - \tilde{\Lambda}_i^a B_{ja}^{ib} - \tilde{\Lambda}_j^a [\mathcal{R}^\dagger]_{ia}^{bp''} G_{kp}^{ij} t_a^i t_b^k + \tilde{\Lambda}_i^a [V^\dagger]_{a_i}^i t_a^i - \tilde{\Lambda}_i^a [V^\dagger]_{ja}^{ib} t_b^j \\
& + \tilde{\Lambda}_j^b [C^\dagger]_{ic}^{ab} t_{ab}^{ij} + \tilde{\Lambda}_k^b [\mathcal{R}^\dagger]_{ib}^{cp''} G_{jp}^{ia} t_a^i t_b^k - \tilde{\Lambda}_k^b [\mathcal{R}^\dagger]_{ic}^{ap''} G_{jp}^{kb} t_a^i t_b^k + \tilde{\Lambda}_j^b [V^\dagger]_{ic}^{ab} t_{ab}^{ij} - \tilde{\Lambda}_k^b [\mathcal{R}^\dagger]_{ia}^{bp''} G_{jp}^{ic} t_a^i t_b^k + \tilde{\Lambda}_i^a [\mathcal{R}^\dagger]_{ja}^{cp''} G_{kp}^{ib} t_a^i t_b^k \\
& + \tilde{\Lambda}_j^b [V^\dagger]_{ib}^{ac} t_a^i t_b^k + \tilde{\Lambda}_k^b [\mathcal{R}^\dagger]_{jc}^{bp''} G_{ip}^{ad} t_a^i t_b^k - \tilde{\Lambda}_k^b [\mathcal{R}^\dagger]_{jb}^{dp''} G_{ip}^{ad} t_a^i t_b^k + \tilde{\Lambda}_k^b [\mathcal{R}^\dagger]_{ic}^{ap''} G_{jp}^{bd} t_a^i t_b^k + \tilde{\Lambda}_j^b [\mathcal{R}^\dagger]_{kc}^{dp''} G_{ip}^{ad} t_a^i t_b^k \\
& - \tilde{\Lambda}_k^a [\mathcal{R}^\dagger]_{ia}^{cp''} G_{jp}^{bd} t_a^i t_b^k t_c^c.
\end{aligned}$$

The additional terms for the inclusion of extended T_1 amplitudes are as follows:

$$\begin{aligned}
\mathcal{L}_{\text{XSP}_{\text{opt}}+T_1} = & \mathcal{L}_{\text{XSP}_{\text{opt}}} + F_i^p t_p^i + G_{ij}^{ap''} t_a^i t_p^j + \Lambda_i^a F_a^p t_p^i - \Lambda_i^a G_{ja}^{ip''} t_p^j - F_i^p \Lambda_j^a t_a^i t_p^j + \Lambda_j^a G_{ik}^{jp} t_a^i t_p^k + \Lambda_j^b G_{ib}^{ap''} t_a^i t_p^j - \Lambda_j^a G_{ib}^{bp''} t_a^i t_p^j \\
& - G_{ij}^{ap''} t_p^i \Lambda_k^b t_{ab}^{jk} - G_{ij}^{ap''} \Lambda_k^b t_{ab}^{jk} + G_{ij}^{bp''} \Lambda_k^a t_a^i t_b^j t_p^k - G_{ij}^{ap''} \Lambda_k^b t_a^i t_b^j t_p^k + \Lambda_i^p F_i^p + F_i^a \Lambda_j^p \mathcal{R}_{ap}^{ij} - F_j^a \Lambda_i^p \mathcal{R}_{ap}^{ij} \\
& + F_i^a \Lambda_j^p \mathcal{R}_{ap}^{ij} + F_i^p \Lambda_j^q \mathcal{R}_{p,q}^{ij} + F_j^q \Lambda_i^p \mathcal{R}_{p,q}^{ia} + F_i^p \Lambda_j^q \mathcal{R}_{p,q}^{ia} + \Lambda_i^p F_a^p t_a^i - \Lambda_i^p G_{jp}^{ia} t_a^i - \Lambda_i^p F_j^i t_p^j + \Lambda_i^p F_p^q t_p^q \\
& + \Lambda_j^p G_{ip}^{ab} t_{ab}^{ij} + \Lambda_j^p G_{ip}^{ab} t_a^i t_b^j + \Lambda_{ij}^{ab} G_{ab}^{ip''} t_p^i + \Lambda_{ik}^{ab} G_{ja}^{ip''} t_b^k t_p^i + \Lambda_{ij}^{ab} G_{ab}^{cp''} t_c^c t_p^i - F_k^p \Lambda_{ij}^{ab} t_p^i t_{ab}^{jk} + \Lambda_{jk}^{ab} G_{il}^{kp} t_p^i t_{ab}^{jl} \\
& + \Lambda_{kl}^{ab} G_{ij}^{cp''} t_p^i t_{ab}^{ij} - \Lambda_{jk}^{ab} G_{ib}^{cp''} t_p^i t_{ac}^{jk} + \Lambda_{ik}^{ac} G_{jc}^{bp''} t_p^i t_{ab}^{ij} + \frac{1}{2} \Lambda_{il}^{ab} G_{jk}^{ip''} t_a^i t_b^k t_p^l + \Lambda_{ik}^{ac} G_{ja}^{bp''} t_b^k t_c^c t_p^i - G_{il}^{ap''} t_a^i \Lambda_{jk}^{bc} t_p^j t_{bc}^{kl} \\
& + G_{il}^{cp''} \Lambda_{jk}^{ab} t_c^c t_p^i t_{ab}^{ij} + G_{ij}^{cp''} \Lambda_{kl}^{ab} t_c^c t_p^i t_{ab}^{ij} + G_{il}^{cp''} \Lambda_{jk}^{ab} t_b^k t_p^i t_{ac}^{jk} - G_{ik}^{ap''} \Lambda_{jl}^{bc} t_c^c t_p^i t_{ab}^{ij} + \frac{1}{2} G_{ij}^{cp''} \Lambda_{kl}^{ab} t_a^i t_b^k t_c^c t_p^l.
\end{aligned}$$

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