

# This paper is published as part of a PCCP Themed Issue on: Explicit- $r_{12}$ Correlation Methods and Local Correlation Methods

Guest Editors: Hans-Joachim Werner and Peter Gill

## Editorial

### Explicit- $r_{12}$ correlation methods and local correlation methods

*Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b808067b](https://doi.org/10.1039/b808067b)

## Papers

### Implementation of the CCSD(T)-F12 method using cusp conditions

Denis Bokhan, Seiichiro Ten-no and Jozef Noga, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803426p](https://doi.org/10.1039/b803426p)

### Analysis of non-covalent interactions in (bio)organic molecules using orbital-partitioned localized MP2

Stefan Grimme, Christian Mück-Lichtenfeld and Jens Antony, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803508c](https://doi.org/10.1039/b803508c)

### Tighter multipole-based integral estimates and parallel implementation of linear-scaling AO-MP2 theory

Bernd Doser, Daniel S. Lambrecht and Christian Ochsenfeld, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b804110e](https://doi.org/10.1039/b804110e)

### Local correlation domains for coupled cluster theory: optical rotation and magnetic-field perturbations

Nicholas J. Russ and T. Daniel Crawford, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b804119a](https://doi.org/10.1039/b804119a)

### Local and density fitting approximations within the short-range/long-range hybrid scheme: application to large non-bonded complexes

Erich Goll, Thierry Leininger, Frederick R. Manby, Alexander Mitrushchenkov, Hans-Joachim Werner and Hermann Stoll, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b804672q](https://doi.org/10.1039/b804672q)

### Equations of explicitly-correlated coupled-cluster methods

Toru Shiozaki, Muneaki Kamiya, So Hirata and Edward F. Valeev, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803704n](https://doi.org/10.1039/b803704n)

### Vanadium oxide compounds with quantum Monte Carlo

Annika Bande and Arne Lüchow, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803571q](https://doi.org/10.1039/b803571q)

### Second-order Møller–Plesset calculations on the water molecule using Gaussian-type orbital and Gaussian-type geminal theory

Pål Dahle, Trygve Helgaker, Dan Jonsson and Peter R. Taylor, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803577f](https://doi.org/10.1039/b803577f)

### The $\Sigma^-$ states of the molecular hydrogen

Jacek Komasa, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803548b](https://doi.org/10.1039/b803548b)

### Slater-type geminals in explicitly-correlated perturbation theory: application to $n$ -alkanols and analysis of errors and basis-set requirements

Sebastian Höfener, Florian A. Bischoff, Andreas Glöß and Wim Klopper, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803575j](https://doi.org/10.1039/b803575j)

### Accurate calculations of intermolecular interaction energies using explicitly correlated wave functions

Oliver Marchetti and Hans-Joachim Werner, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b804334e](https://doi.org/10.1039/b804334e)

### Variational formulation of perturbative explicitly-correlated coupled-cluster methods

Martin Torheyden and Edward F. Valeev, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803620a](https://doi.org/10.1039/b803620a)

### Resolution of the identity atomic orbital Laplace transformed second order Møller–Plesset theory for nonconducting periodic systems

Artur F. Izmaylov and Gustavo E. Scuseria, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803274m](https://doi.org/10.1039/b803274m)

### On the use of the Laplace transform in local correlation methods

Danylo Kats, Denis Usvyat and Martin Schütz, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b802993h](https://doi.org/10.1039/b802993h)

### Intracule densities in the strong-interaction limit of density functional theory

Paola Gori-Giorgi, Michael Seidl and Andreas Savin, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803709b](https://doi.org/10.1039/b803709b)

### Intracule functional models

#### Part III. The dot intracule and its Fourier transform

Yves A. Bernard, Deborah L. Crittenden and Peter M. W. Gill, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803919d](https://doi.org/10.1039/b803919d)

### Density matrix renormalisation group Lagrangians

Garnet Kin-Lic Chan, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b805292c](https://doi.org/10.1039/b805292c)

### The interaction of carbohydrates and amino acids with aromatic systems studied by density functional and semi-empirical molecular orbital calculations with dispersion corrections

Raman Sharma, Jonathan P. McNamara, Rajesh K. Raju, Mark A. Vincent, Ian H. Hillier and Claudio A. Morgado, *Phys. Chem. Chem. Phys.*, 2008, **10**, 2767

### The principle-quantum-number (and the radial-quantum-number) expansion of the correlation energy of two-electron atoms

Werner Kutzelnigg, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b805284k](https://doi.org/10.1039/b805284k)

# Implementation of the CCSD(T)-F12 method using cusp conditions

Denis Bokhan,<sup>ab</sup> Seiichiro Ten-no<sup>\*ab</sup> and Jozef Noga<sup>cd</sup>

Received 27th February 2008, Accepted 14th April 2008

First published as an Advance Article on the web 15th May 2008

DOI: 10.1039/b803426p

The explicitly-correlated coupled-cluster singles and doubles with perturbative triples method (CCSD(T)-F12) is implemented using the cusp conditions. Numerical tests for a set of 16 molecules have shown agreement of correlation energies within 1 mE<sub>h</sub> between the cusp-condition and fully-optimized CCSD(T)-F12 methods. Benchmark calculations on 13 chemical reactions with the cusp-condition CCSD(T)-F12 method reproduce experimental enthalpies within 2 kJ mol<sup>-1</sup>. It is also shown that regular unitary-invariant *ansatz* cannot exactly satisfy singlet and triplet cusp conditions in open-shell situations. We present an extended *ansatz* which can handle both conditions exactly.

## I. Introduction

The basic idea of explicitly-correlated methods<sup>1-9</sup> is to include pair functions directly dependent upon the inter-electronic distance into the calculation of wave function. This can significantly accelerate the convergence of standard methods, which scales as  $(L_{\max} + 1)^{-3}$ ,<sup>10</sup> where  $L_{\max}$  is the highest angular momentum involved in the partial wave expansion. Indeed, by the inclusion of linear- $r_{12}$ <sup>11</sup> terms the convergence starts to go as  $(L_{\max} + 1)^{-7}$ .<sup>12</sup> Such an acceleration is possible not only because of the correct behaviour of wave functions at the inter-electronic coalescence points,<sup>13,14</sup> but also because of the general improvement of the shape and size of the Coulomb hole.<sup>15</sup>

Explicitly correlated methods which transcend the limitation to tiny molecules have been developed since the introduction of the resolution of the identity (RI) approximation for many electron integrals. Recent advances in the field<sup>16</sup> have mainly focused on the accuracy and efficiency of the RI approximation by the use of auxiliary basis sets,<sup>17,18</sup> density fitting,<sup>19,20</sup> and numerical quadratures.<sup>21</sup> Another topic is the use of the exponential correlation factor  $\exp(-\gamma r_{12})$ <sup>22</sup> which is more suitable to model the Coulomb hole than the linear  $r_{12}$  function.<sup>22-27</sup> The F12 variants of such a correlation factor turned out to give very much improved results as compared to the original R12 methods, especially those with a small one-particle basis set, which is unable to describe the shape of the Coulomb hole in a broader region around the inter-electronic coalescence points. A two-point extrapolation scheme of the F12 method was also examined more recently.<sup>28</sup>

In addition to the advances of explicitly correlated methods in second-order Møller–Plesset perturbation theory (MP),

various R12/F12 approaches have been reported in conjunction with other correlated methods.<sup>29-37</sup> Coupled-cluster R12 (CC-R12) theory was put forward in early nineties by one of us (JN) and coworkers.<sup>29,30</sup> More recently, the full CCSD(T)-F12 method has been implemented within the standard approximation.<sup>38</sup> Even though the latter method provides very accurate results and is unitary invariant, its applicability to large systems (similarly as for CCSD(T)-R12) has its own limitations: (i) there is an unpleasantly scaling overhead involving  $\propto n_{\text{occ}}^5 n_{\text{bas}}^2$  ( $n$  is the number of the pertinent orbitals) and several other  $\propto n_{\text{occ}}^4 n_{\text{bas}}^2$  steps prior to the iterative solving of the CC equations; (ii) the computations may suffer from the numerical instabilities due to the linear dependencies among the geminals.<sup>39,40</sup>

A simplified unitary invariant *ansatz* with fixed amplitudes has been used in the single- and multi-reference MP2-F12 methods.<sup>21,27,36</sup> The same *ansatz* has been employed in approximate explicitly correlated CCSD(T) methods.<sup>41,42</sup> These approaches do not have any convergence problem and are significantly cheaper than the methods which optimize the geminal amplitudes.

In this article, we present an implementation of the full CCSD(T)-F12 method using the cusp-conditions. In what follows, the cusp conditions with the intermediate normalization are formulated. The open-shell situation is also considered and a suitable *ansatz* in CCSD(T)-F12 is derived. It is shown that the regular unitary invariant *ansatz*<sup>43</sup> cannot exactly satisfy the cusp conditions. Numerical results for the total energies of 16 closed-shell molecules are presented in section III. We also report reaction enthalpies of 16 isogyric reactions. Conclusions will be presented in section IV.

## II. Cusp conditions

The cusp conditions with intermediate normalization are introduced from many-body perturbation theory. In the following formulae, we shall use  $i, j, \dots, \alpha, \beta, \dots$ , and  $p, q, \dots$  for occupied, virtual, and general orbitals in the complete basis set, respectively.

<sup>a</sup> Graduate School of Information Science, Nagoya University, Chikusa-ku, Nagoya, 464-8601, Japan.  
E-mail: tenno@is.nagoya-u.ac.jp

<sup>b</sup> CREST, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama, 332-0012, Japan

<sup>c</sup> Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina CH1, Bratislava, SK-84215, Slovakia

<sup>d</sup> Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, SK-84536, Slovakia

## A The Hartree–Fock conditions

The spin-free singlet ( $S$ ) and triplet ( $T$ ) pair functions are defined as:

$$\begin{aligned} \{pq\}^{(S)}(\vec{r}_1, \vec{r}_2) &= \delta_{pq} \varphi_p(\vec{r}_1) \varphi_q(\vec{r}_2) \\ &+ \frac{1}{\sqrt{2}}(1 - \delta_{pq})(\varphi_p(\vec{r}_1) \varphi_q(\vec{r}_2) + \varphi_p(\vec{r}_2) \varphi_q(\vec{r}_1)) \end{aligned} \quad (2.1)$$

$$\{pq\}^{(T)}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}(\varphi_p(\vec{r}_1) \varphi_q(\vec{r}_2) - \varphi_p(\vec{r}_2) \varphi_q(\vec{r}_1)). \quad (2.2)$$

Representation of the pair functions in the Jacobi coordinates,

$$\vec{R} = \frac{\vec{r}_1 + \vec{r}_2}{2}, \quad (2.3)$$

$$\vec{r} = \vec{r}_1 - \vec{r}_2, \quad (2.4)$$

implies the following relations:

$$\{pq\}^{(S)}(\vec{R}, \vec{r}) = \{pq\}^{(S)}(\vec{R}, -\vec{r}), \quad (2.5)$$

$$\{pq\}^{(T)}(\vec{R}, \vec{r}) = -\{pq\}^{(T)}(\vec{R}, -\vec{r}). \quad (2.6)$$

Using the spherical harmonics basis for the relative coordinates,

$$\vec{r} = (r, \theta, \phi), \quad (2.7)$$

the pair functions can be expanded as

$$\{pq\}^{(S)}(\vec{R}, \vec{r}) = \sum_{l,m} \{pq\}_{lm}^{(S)}(r, \vec{R}) Y_{lm}(\theta, \phi), \quad (2.8)$$

$$(l = 0, 2, \dots, 2n, \dots),$$

$$\{pq\}^{(T)}(\vec{R}, \vec{r}) = \sum_{l,m} \{pq\}_{lm}^{(T)}(r, \vec{R}) Y_{lm}(\theta, \phi), \quad (2.9)$$

$$(l = 1, 3, \dots, 2n + 1, \dots).$$

As the Hartree–Fock (HF) potential has no singularity at the coalescence, the Schrödinger equation for the non-interacting pair functions in the vicinity of  $r = 0$  can be rewritten as

$$\left[ -\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{l(l+1)}{r^2} + O(r^0) \right] \{pq\}_{lm}^{(*)}(\vec{R}, r) = 0, \quad (2.10)$$

where the asterisk stands for  $S$  and  $T$ . The result of the action of non-local exchange operator on the pair functions also contains a leading term, proportional to  $r^0$ . Eqn (2.10) is fulfilled if

$$\{pq\}_{lm}^{(*)}(\vec{R}, r) = \{PQ\}_{lm}^{(*)}(\vec{R}) r^l + O(r^{l+2}). \quad (2.11)$$

Thus, we obtain the specific expressions of the singlet and triplet pairs as

$$\{pq\}^{(S)}(r, \vec{R}) = \{PQ\}_{00}^{(S)}(\vec{R}) Y_{00} + O(r^2), \quad (2.12)$$

$$\{pq\}^{(T)}(r, \vec{R}) = \sum_{m=-1}^1 \{PQ\}_{lm}^{(T)}(\vec{R}) r Y_{lm}(\theta, \phi) + O(r^3). \quad (2.13)$$

## B Cusp conditions with intermediate normalization

For the derivation of the cusp conditions of the exact  $N$ -electron wave function, it is convenient to use the exponential *ansatz*,

$$|\Psi(1, \dots, N)\rangle = e^{\hat{T}} |\text{HF}\rangle, \quad (2.14)$$

with

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_N + \hat{T}'_2, \quad (2.15)$$

where  $\hat{T}_m$  is the usual  $m$ -particle cluster excitation operator and the geminal operator  $\hat{T}'_2$  is defined as

$$\hat{T}'_2 = \frac{1}{2} \sum_{\alpha\beta ijkl} t'_{ij}{}^{kl} \langle \alpha\beta | r_{12} + O(r_{12}^2) | kl \rangle \hat{E}_{\alpha i} \hat{E}_{\beta j}. \quad (2.16)$$

$\hat{E}_{pq}$  denotes the unitary group generator,

$$\hat{E}_{pq} = a_{p\uparrow}^+ a_{q\uparrow} + a_{p\downarrow}^+ a_{q\downarrow}. \quad (2.17)$$

With this choice of  $\hat{T}$ , the intermediate normalization holds  $\langle \text{HF} | \Psi \rangle = 1$ , and the amplitudes are determined by

$$\langle \mu_n | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \text{HF} \rangle = 0, \quad (n = 1, \dots, N). \quad (2.18)$$

The equation for  $\mu'_2$  corresponding to  $\hat{T}'_2$  is not included in (2.18), since  $\mu'_2$  is a subset of  $\mu_2$  in the complete basis set. The equations are expanded order-by-order using the partitioning,

$$\hat{H} = \hat{H}_0 + \hat{V}. \quad (2.19)$$

The zeroth order Hamiltonian over the HF canonical orbitals reads

$$\hat{H}_0 = \sum_p \langle p | \hat{F}_1 | p \rangle \hat{E}_{pp} = \sum_p \varepsilon_p \hat{E}_{pp}. \quad (2.20)$$

The first order equation reduces to the pair function equation in the form,

$$\begin{aligned} & \sum_{kl} [t'_{ij}{}^{kl} (*) \langle \{\alpha\beta\}^{(*)} | \hat{F}_{12}(r_{12} + O(r_{12}^2)) | \{kl\}^{(*)} \rangle \\ & - \langle \{\alpha\beta\}^{(*)} | r_{12} + O(r_{12}^2) | \{ij\}^{(*)} \rangle t'_{ij}{}^{kl} (*) (\varepsilon_k + \varepsilon_l)] \\ & + \left\langle \{\alpha\beta\}^{(*)} \left| \frac{1}{r_{12}} \right| \{ij\}^{(*)} \right\rangle + \dots = 0, \end{aligned} \quad (2.21)$$

where  $\hat{F}_{12} = \hat{F}_1 + \hat{F}_2$ , and the  $\hat{T}'_2$  amplitudes for singlet and triplet pairs are

$$t'_{ij}{}^{kl}(S) = t'_{ij}{}^{kl} + t'_{ij}{}^{lk}, \quad (2.22)$$

$$t'_{ij}{}^{kl}(T) = t'_{ij}{}^{kl} - t'_{ij}{}^{lk}. \quad (2.23)$$

It is noted that the generalized Brillouin condition<sup>12</sup> is needed for (2.21) in the finite basis case. Consider the singlet component first. Decomposing pair functions into spherical harmonics and taking the condition (2.12) into account, it is possible to rewrite (2.21) into the form,

$$\begin{aligned} & \sum_{kl} t'_{ij}{}^{kl}(S) \langle \{\alpha\beta\}_{00}^{(S)}(\vec{R}) | \left[ -\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + O(r^0) \right] \\ & (r + O(r^2)) | \{kl\}_{00}^{(S)}(\vec{R}) \rangle \\ & + \left\langle \{\alpha\beta\}_{00}^{(S)}(\vec{R}) \left| \frac{1}{r} \right| \{ij\}_{00}^{(S)}(\vec{R}) \right\rangle + \dots = 0. \end{aligned} \quad (2.24)$$

The singularity in the perturbation is eliminated if

$$t'_{ij}{}^{kl}(S) = 1/2 \delta_{ik} \delta_{jl}, \quad (2.25)$$

which corresponds to the  $s$ -wave cusp condition. The equation for triplet pairs is

$$\sum_m \sum_{kl} t'_{ij}(T) \langle \{\alpha\beta\}_{1m}^{(T)}(\vec{R}) | r \left[ -\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{2}{r^2} + O(r^0) \right] (r + O(r^2)) | r \{kl\}_{1m}^{(T)}(\vec{R}) \rangle + \langle \{\alpha\beta\}_{1m}^{(T)}(\vec{R}) | r | \{ij\}_{1m}^{(T)}(\vec{R}) \rangle + \dots = 0, \quad (2.26)$$

which leads to the  $p$ -wave cusp condition,

$$t'^{kl}_{ij}(T) = \frac{1}{4} \delta_{ik} \delta_{jl}. \quad (2.27)$$

It is noted that the leading terms cancel individually for each value of  $m$  since  $\{kl\}_{1m}^{(T)}$  is not a function of  $r$ . The cusp conditions are varied for the exact wave function if a new term proportional to  $\langle \alpha\beta | \frac{1}{r_{12}} | ij \rangle$  does not arise from the connected terms of  $(\hat{V}e^{\hat{T}})_c$  in higher-order  $\mu_2$  equations. Especially, the type of the summations,  $\sum_{\delta\gamma} \langle \alpha\beta | \frac{1}{r_{12}} | \delta\gamma \rangle t'_{ij}^{\delta\gamma}$ , does not break off. Nevertheless, the undesirable component,  $\langle \delta\gamma | O(r_{12}^0) | ij \rangle$ , does not participate in  $\hat{T}'_2$  due to the orthogonality between virtual and occupied orbitals, and the conditions (2.25) and (2.27) are likely to be valid for the exact wavefunction.

The diagonal orbital-invariant *ansatz* from the  $s$ - and  $p$ -wave cusp conditions (SP *ansatz*) was introduced in ref. 21 and 27. Eqn (2.22) and (2.23) lead to the  $\hat{T}'_2$  amplitudes in the SP *ansatz* as

$$t'^{ij}_{ij}(SP) = 3/8, \quad (2.28)$$

$$t'^{ij}_{ij}(SP) = 1/8, \quad (2.29)$$

$$t'^{ii}_{ii}(SP) = 1/2. \quad (2.30)$$

The resulting cluster operator can be expressed in the rational generator form<sup>21</sup> as

$$\hat{T}'_2(SP) = \frac{1}{2} \sum_{\alpha\beta ij} \langle \alpha\beta | \bar{G}_{12} | ij \rangle \hat{E}_{\alpha i} \hat{E}_{\beta j}, \quad (2.31)$$

where  $\bar{G}_{12}$  is

$$\bar{G}_{12} = \left( \frac{3}{8} + \frac{p_{12}}{8} \right) (r_{12} + O(r_{12}^2)), \quad (2.32)$$

and  $p_{12}$  is the permutation operator over the position vectors,  $\vec{r}_1$  and  $\vec{r}_2$ . Two-body correlation factors of spatial spin coordinates<sup>48</sup> have been widely used in the quantum Monte Carlo method. Nevertheless, the presence of the permutation operator in the rational generator indicates that electron correlation effects are strictly nonlocal, and the parity distinction between singlet and triplet pairs is important for a rapid convergence.

### C Open-shell case

For open-shell systems, the cluster operator (2.31) needs to be considered in terms of spin-orbitals. Particularly, for UHF,

it becomes

$$\begin{aligned} \hat{T}'_2(SP) &= \frac{1}{2} \sum_{\alpha\beta ij} \langle \alpha_{\uparrow} \beta_{\uparrow} | \bar{G}_{12} | i_{\uparrow} j_{\uparrow} \rangle \{ a_{\alpha_{\uparrow}}^+ a_{\beta_{\uparrow}}^+ a_{j_{\uparrow}} a_{i_{\uparrow}} \} \\ &+ \frac{1}{2} \sum_{\alpha'\beta' i'j'} \langle \alpha'_{\downarrow} \beta'_{\downarrow} | \bar{G}_{12} | i'_{\downarrow} j'_{\downarrow} \rangle \{ a_{\alpha'_{\downarrow}}^+ a_{\beta'_{\downarrow}}^+ a_{j'_{\downarrow}} a_{i'_{\downarrow}} \} \\ &+ \sum_{\alpha\beta' i'j'} \langle \alpha_{\uparrow} \beta'_{\downarrow} | \bar{G}_{12} | i_{\uparrow} j'_{\downarrow} \rangle \{ a_{\alpha_{\uparrow}}^+ a_{\beta'_{\downarrow}}^+ a_{j'_{\downarrow}} a_{i_{\uparrow}} \}, \end{aligned} \quad (2.33)$$

where the spatial parts of the up and down spin orbitals are distinguished by a prime. It is important to note that spin-flipped geminal basis appears in the last term due to the permutation operator in the rational generator,

$$\begin{aligned} (r_{12} + O(r_{12}^2)) p_{12} | i_{\uparrow} j'_{\downarrow} \rangle a_{j'_{\downarrow}} a_{i_{\uparrow}} \\ = (r_{12} + O(r_{12}^2)) | j'_{\uparrow} i_{\downarrow} \rangle a_{j'_{\uparrow}} a_{i_{\downarrow}}. \end{aligned} \quad (2.34)$$

Since the original unitary-invariant (IJKL) *ansatz* does not contain such a term,<sup>43</sup> the *ansatz* cannot satisfy the cusp conditions exactly for different occupied orbitals for different spins. This problem can be fixed by the use of the generalized unitary-invariant *ansatz* (from now on, we shall use  $f_{12}$  for the correlation factor  $[r_{12} + O(r_{12}^2)]$ )

$$\begin{aligned} \hat{T}'_2(IJKL) &= \frac{1}{2} \sum_{\alpha\beta ijkl} t'^{k_{\uparrow} l_{\uparrow}}_{i_{\uparrow} j_{\uparrow}} \langle \alpha_{\uparrow} \beta_{\uparrow} | f_{12} | k_{\uparrow} l_{\uparrow} \rangle \{ a_{\alpha_{\uparrow}}^+ a_{\beta_{\uparrow}}^+ a_{j_{\uparrow}} a_{i_{\uparrow}} \} \\ &+ \frac{1}{2} \sum_{\alpha'\beta' i'j'k'l'} t'^{k'_{\downarrow} l'_{\downarrow}}_{i'_{\downarrow} j'_{\downarrow}} \langle \alpha'_{\downarrow} \beta'_{\downarrow} | f_{12} | k'_{\downarrow} l'_{\downarrow} \rangle \{ a_{\alpha'_{\downarrow}}^+ a_{\beta'_{\downarrow}}^+ a_{j'_{\downarrow}} a_{i'_{\downarrow}} \} \\ &+ \sum_{\alpha\beta' i'j'k'l'} t'^{k_{\uparrow} l'_{\downarrow}}_{i_{\uparrow} j'_{\downarrow}} \langle \alpha_{\uparrow} \beta'_{\downarrow} | f_{12} | k_{\uparrow} l'_{\downarrow} \rangle \{ a_{\alpha_{\uparrow}}^+ a_{\beta'_{\downarrow}}^+ a_{j'_{\downarrow}} a_{i_{\uparrow}} \} \\ &+ \sum_{\alpha\beta' i'j'k'l'} t'^{l'_{\uparrow} k_{\downarrow}}_{i'_{\downarrow} j_{\uparrow}} \langle \alpha_{\uparrow} \beta'_{\downarrow} | f_{12} | l'_{\uparrow} k_{\downarrow} \rangle \{ a_{\alpha_{\uparrow}}^+ a_{\beta'_{\downarrow}}^+ a_{j_{\downarrow}} a_{i'_{\uparrow}} \}. \end{aligned} \quad (2.35)$$

The corresponding diagonal (IIJ) *ansatz* can be obtained by setting  $k = i$  and  $l = j$ .

### III. CCSD(T)-F12 with CUSP conditions

The SP *ansatz* derived from the cusp conditions has been employed by Tew *et al.*<sup>41</sup> and independently by Adler *et al.*<sup>42</sup> in their approximated CCSD(T)-F12 methods. Henceforth, we discuss the CCSD(T)-F12 method with the *ansatz* in detail. For the finite orbital expansion, we are using an additional notation,  $a, b, \dots$  for virtual orbitals in the given basis set to distinguish from those in the complete basis set,  $\alpha, \beta, \dots$

The energy functional of CCSD-F12 is

$$E_{\text{CCSD-F12}} = \langle \text{HF} | (1 + \hat{\Lambda}) e^{-\hat{T}} \hat{H} e^{-\hat{T}} | \text{HF} \rangle, \quad (3.36)$$

with the cluster operator restricted to

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}'_2, \quad (3.37)$$

$$\hat{T}_1 = \sum_{ai} t_{ai}^a \hat{E}_{ai}, \quad (3.38)$$

$$\hat{T}_2 = \frac{1}{2} \sum_{abij} t_{ij}^{ab} \hat{E}_{ai} \hat{E}_{bj}, \quad (3.39)$$

$$T'_2 = \frac{1}{2} \sum_{ijkl} t'_{kl}{}^{ij} \left( \sum_{\alpha\beta} \langle \alpha\beta | f_{12} | kl \rangle \hat{E}_{\alpha i} \hat{E}_{\beta j} - \sum_{ab} \langle ab | f_{12} | kl \rangle \hat{E}_{ai} \hat{E}_{bj} \right), \quad (3.40)$$

and  $f_{12}$  is the short-range Slater-type geminal<sup>22,27</sup> for our purpose,

$$f_{12} = -\frac{1}{\gamma} \exp(-\gamma r_{12}). \quad (3.41)$$

It is noted that the second term of (3.40) was absent in (2.16). Nevertheless, both expressions give the same result with the same geminal amplitudes if the distinct term is representable by the regular  $\hat{T}_2$  operator in such away that  $\hat{T}_2 + \hat{T}'_2$  is conserved. The corresponding de-excitation operator is

$$\hat{\Lambda} = \hat{\Lambda}_1 + \hat{\Lambda}_2 + \hat{\Lambda}'_2, \quad (3.42)$$

$$\hat{\Lambda}_1 = \sum_{ai} \lambda_a^i \hat{E}_{ia}, \quad (3.43)$$

$$\hat{\Lambda}_2 = \frac{1}{2} \sum_{abij} \lambda_{ab}^{ij} \hat{E}_{ia} \hat{E}_{jb}, \quad (3.44)$$

$$\Lambda'_2 = \frac{1}{2} \sum_{ijkl} \lambda'_{ij}{}^{kl} \left( \sum_{\alpha\beta} \langle \alpha\beta | f_{12} | kl \rangle \hat{E}_{\alpha i} \hat{E}_{\beta j} - \sum_{ab} \langle ab | f_{12} | kl \rangle \hat{E}_{ia} \hat{E}_{jb} \right). \quad (3.45)$$

Equations for the  $\hat{T}_1$ ,  $\hat{T}_2$  and  $\hat{T}'_2$  can be obtained by differentiation of the CCSD-F12 energy functional (3.36) with respect to the  $\hat{\Lambda}$  amplitudes. On the other hand, the corresponding  $\hat{\Lambda}$  equations can be obtained by the differentiation of the functional (3.36) with respect to  $t_a^a$ ,  $t_{ij}^{ab}$  and  $t'_{ij}{}^{kl}$ .

One of the most important properties of the energy functional (3.36) is the insensitivity of the energy functional to the small deviations in  $\hat{T}$  and  $\hat{\Lambda}$ . Let us suppose the approximate operators,

$$\tilde{\hat{T}} = \hat{T} + \delta\hat{T}, \quad (3.46)$$

$$\tilde{\hat{\Lambda}} = \hat{\Lambda} + \delta\hat{\Lambda}, \quad (3.47)$$

with the errors,  $\delta\hat{T}$  and  $\delta\hat{\Lambda}$ . Substituting the approximate operators into (3.36), we have

$$\begin{aligned} \tilde{E}_{\text{CCSD-F12}} &= E_{\text{CCSD-F12}} + \langle \text{HF} | (1 + \tilde{\hat{\Lambda}}) [\tilde{\hat{H}}, \delta\tilde{\hat{T}}] | \text{HF} \rangle \\ &\quad + \langle \text{HF} | \delta\tilde{\hat{\Lambda}} \tilde{\hat{H}} | \text{HF} \rangle + O(\delta^2), \end{aligned} \quad (3.48)$$

where  $\tilde{\hat{H}} = e^{-\tilde{\hat{T}}} \hat{H} e^{\tilde{\hat{T}}}$ . The second and third term on the right-hand side of eqn (3.48) vanish because of the  $\Lambda$  and cluster operator equations. So far, small deviations of  $\delta\hat{T}$  and  $\delta\hat{\Lambda}$  in (3.36) cause only a quadratic error in the correlation energy. The presence of the  $\Lambda$ -term in (3.36) is essential for the cancellation of the linear error.

The usual explicitly correlated CC methods do not require  $\hat{\Lambda}$  amplitudes for the energy since the cluster operator is fully optimized. However, since equations for the  $\hat{T}'_2$  can be numerically unstable,<sup>40</sup> it is more convenient to use the cusp conditions for  $\hat{T}'_2$  and  $\hat{\Lambda}'_2$  instead of the full optimization of the geminal amplitudes. Consequently, for optimized  $\hat{T}_1$  and  $\hat{T}_2$ , the energy functional (3.36) becomes

$$E_{\text{CCSD-F12}} = \langle \text{HF} | (1 + \hat{\Lambda}'_2) e^{-\hat{T}} \hat{H} e^{\hat{T}} | \text{HF} \rangle. \quad (3.49)$$

In our implementation we use the SP *ansatz* (2.28), (2.29), and (2.30) from the cusp conditions, and  $\hat{\Lambda}'_2$  in the SP *ansatz* is simply given by

$$\hat{\Lambda}'_2(\text{SP}) = \hat{T}'_2(\text{SP}). \quad (3.50)$$

In the order-by-order expansion of the working equations, the first-order operator is  $\hat{\Lambda}^{(1)} = \hat{T}^{(1)}$ , and the second order component of the present method is reduced to the MP2-F12 energy of the Hylleraas functional with the SP *ansatz*.<sup>21,27</sup> Moreover, the method makes the computational-cost significantly cheaper excluding the estimates of laborious intermediates involving geminal amplitudes from the coupled-cluster iteration. This feature has been discussed by Tew *et al.*<sup>41</sup> and Adler *et al.*<sup>42</sup> in their implementations of more approximate CCSD(T)-F12 methods, which retain terms at most linear to  $\hat{T}'_2$ . The use of the SP *ansatz* becomes even more effective for the inclusion of the quadratic terms as it is in our case.

## IV. Results and discussion

### A Correlation energies

Correlation energies of selected 16 molecules were calculated using the uncontracted basis set derived from the augmented cc-pCVQZ set.<sup>49–51</sup> The molecular geometries are taken from the ref. 45. We have implemented the SP *ansatz* based on the CCSD(T)-F12 approach within the standard approximation.<sup>38</sup> The approximation C<sup>46</sup> has been used for matrix evaluations. In all calculations, the exponent of the Slater-type geminal is  $\gamma = 1.5$ . As shown in ref. 30, corresponding perturbative triples correction in CCSD(T)-F12 using the standard approximation only contains regular terms from the conventional CCSD(T).<sup>44</sup>

The SCF and correlation energies are listed in the Table 1. For most of the molecules, CCSD(T)-F12 results for the fully optimized (IJKL *ansatz*) and cusp conditions (SP *ansatz*) approaches differ less than by 1 mE<sub>h</sub>. This is reasonable since CCSD(T)-F12 approaches with the SP and IJKL *ansätze* become equivalent in the limit of complete basis set. As mentioned above, its main advantage with respect to the full IJKL *ansatz* lays in its numerical stability and favorable scaling which designates this approach for a use with more extended molecular systems. Current results show that such calculations are without significant loss in accuracy.

### B Reaction enthalpies

In addition to the absolute energies, we have also investigated the performance of cusp-condition CCSD(T)-F12 method on reaction enthalpies for the set of 13 reactions, studied by Bak *et al.*<sup>47</sup> The calculated enthalpies are listed in Table 2.



**Table 1** Hartree–Fock and correlation energies from different methods (in a.u.)

	SCF	MP2		CCSD		CCSD(T)	
		IJKL	SP	IJKL	SP	IJKL	SP
H <sub>2</sub>	-1.334629	-0.034220	-0.034197	-0.040813	-0.040747		
HF	-100.069492	-0.385476	-0.384944	-0.379659	-0.379359	-0.388095	-0.387794
H <sub>2</sub> O	-76.066515	-0.362688	-0.362215	-0.360413	-0.360186	-0.369914	-0.369687
NH <sub>3</sub>	-56.224135	-0.323233	-0.322785	-0.328733	-0.328517	-0.337793	-0.337573
CH <sub>4</sub>	-40.216468	-0.274394	-0.274016	-0.289418	-0.289229	-0.296564	-0.296371
CO <sub>2</sub>	-187.723173	-0.866081	-0.864473	N.a. <sup>a</sup>	-0.840214	N.a. <sup>a</sup>	-0.872466
CH <sub>2</sub>	-38.895616	-0.210067	-0.209658	-0.230698	-0.230495	-0.236434	-0.236219
CH <sub>2</sub> O	-113.921987	-0.565561	-0.564648	N.a. <sup>a</sup>	-0.564842	N.a. <sup>a</sup>	-0.583367
F <sub>2</sub>	-198.770561	-0.743301	-0.741891	-0.732910	-0.731767	-0.754919	-0.753776
N <sub>2</sub>	-108.991679	-0.538622	-0.537430	-0.526606	-0.526079	-0.547480	-0.546952
CO	-112.789504	-0.521174	-0.520141	N.a. <sup>a</sup>	-0.513954	N.a. <sup>a</sup>	-0.533174
HCN	-92.914774	-0.500708	-0.499662	-0.495387	-0.494906	-0.515420	-0.514943
C <sub>2</sub> H <sub>2</sub>	-76.854879	-0.455774	-0.454785	-0.459453	-0.459110	-0.477774	-0.477434
HNO	-129.848153	-0.616594	-0.615235	N.a. <sup>a</sup>	-0.608992	N.a. <sup>a</sup>	-0.631717
C <sub>2</sub> H <sub>4</sub>	-78.069798	-0.483230	-0.482387	-0.498786	-0.498420	-0.515629	-0.515259
H <sub>2</sub> O <sub>2</sub>	-150.849224	-0.693375	-0.692183	-0.686448	-0.685643	-0.708325	-0.707521

<sup>a</sup> Not available due to the numerical instability in the  $\mu'_2$  equation.

Experimental electronic contributions to reaction enthalpies in last column of Table 2 are obtained by subtracting from the experimental values the harmonic and unharmonic zero-point vibrational energy contributions and first-order one-electron Darwin and mass-velocity scalar relativistic energy contribution.<sup>47</sup>

In Fig. 1, we show the normal distribution functions,

$$\rho(P) = \frac{1}{\Delta_{\text{std}}\sqrt{2\pi}} \exp\left(-\frac{1}{2}\left(\frac{P - \bar{\Delta}}{\Delta_{\text{std}}}\right)^2\right) \quad (4.51)$$

calculated from the statistical measures, *i.e.* the maximum absolute error ( $\Delta_{\text{abs}}^{\text{max}}$ ), the mean error ( $\bar{\Delta}$ ), the mean absolute error  $\bar{\Delta}_{\text{abs}}$ , and the standard deviation ( $\Delta_{\text{std}}$ ) displayed in Table 3. The errors are relative to the experimental values.

From Table 3 and Fig. 1 one can see a systematic improvement in the accuracy by enhancing the perturbational level as SCF, MP2, CCSD, and CCSD(T). On the other hand, the chemical accuracy is provided only with the CCSD(T)-F12 method, and the non-iterative inclusion of the triple excitation

contributions to the correlation energy is crucial in describing reaction enthalpies even in explicitly correlated methods.

For all of the explicitly correlated methods, the differences between the standard deviations of fully optimized (IJKL) and cusp-condition versions (SP) are negligibly small. Although the statistical measures for the SP *ansatz* involves reactions unavailable in the IJKL *ansatz*, the selection does not alter the conclusion. So far, it is likely that the CCSD(T)-F12 (SP) method can be used without serious compromise in accuracy for predictive reaction enthalpies.

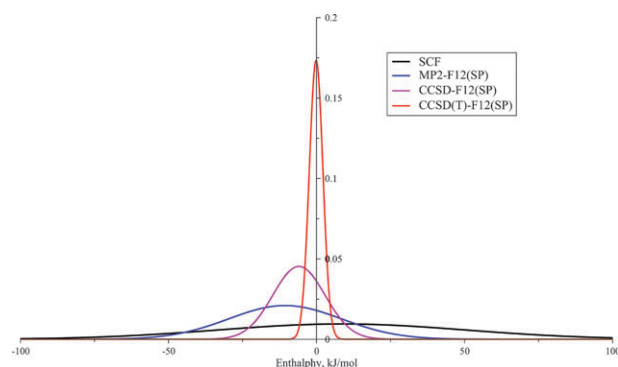
## V. Conclusions

In this paper, we have studied the performance of the CCSD(T)-F12 (SP) method based on the cusp conditions. For this purpose, we have investigated the total energies of 16 molecules and the reaction enthalpies of 13 isogyric reactions. All the considered molecules are closed-shell systems with the domination of a single determinant and containing

**Table 2** Reaction enthalpies (in kJ mol<sup>-1</sup>) for a set of 13 isogyric reactions involving molecules from Table 1

Reaction	MP2			CCSD		CCSD(T)		Exp
	SCF	IJKL	SP	IJKL	SP	IJKL	SP	
CO + H <sub>2</sub> → CH <sub>2</sub> O	2.57	-24.10	-24.49	N.a. <sup>a</sup>	-22.73	N.a. <sup>a</sup>	-22.24	-21.85
N <sub>2</sub> + 3H <sub>2</sub> → 2NH <sub>3</sub>	-147.56	-161.17	-162.13	-169.66	-170.44	-162.43	-163.16	-165.38
C <sub>2</sub> H <sub>2</sub> + H <sub>2</sub> → C <sub>2</sub> H <sub>4</sub>	-213.86	-196.10	-196.54	-209.97	-210.09	-206.09	-206.19	-203.95
CO <sub>2</sub> + 4H <sub>2</sub> → CH <sub>4</sub> + 2H <sub>2</sub> O	-242.78	-234.41	-235.39	N.a. <sup>a</sup>	-259.59	N.a. <sup>a</sup>	-243.55	-245.29
CH <sub>2</sub> O + 2H <sub>2</sub> → CH <sub>4</sub> + H <sub>2</sub> O	-246.98	-255.07	-255.35	N.a. <sup>a</sup>	-256.38	N.a. <sup>a</sup>	-250.13	-251.95
CO + 3H <sub>2</sub> → CH <sub>4</sub> + H <sub>2</sub> O	-244.41	-279.20	-279.85	N.a. <sup>a</sup>	-279.13	N.a. <sup>a</sup>	-272.35	-273.80
HCN + 3H <sub>2</sub> → CH <sub>4</sub> + NH <sub>3</sub>	-329.34	-313.39	-315.03	-330.19	-330.92	-320.14	-320.83	-320.35
H <sub>2</sub> O <sub>2</sub> + H <sub>2</sub> → 2H <sub>2</sub> O	-394.73	-388.89	-389.60	-377.83	-378.92	-370.46	-371.37	-365.63
HNO + 2H <sub>2</sub> → H <sub>2</sub> O + NH <sub>3</sub>	-460.96	-463.29	-464.56	N.a. <sup>a</sup>	-456.28	N.a. <sup>a</sup>	-445.33	-445.59
C <sub>2</sub> H <sub>2</sub> + 3H <sub>2</sub> → 2CH <sub>4</sub>	-466.47	-441.14	-441.93	-458.44	-458.87	-447.86	-448.26	-446.71
CH <sub>2</sub> + H <sub>2</sub> → CH <sub>4</sub>	-491.98	-571.03	-571.17	-539.00	-539.21	-542.70	-542.93	-544.23
F <sub>2</sub> + H <sub>2</sub> → 2HF	-616.89	-599.39	-600.36	-578.82	-580.41	-565.33	-566.92	-564.93
2CH <sub>2</sub> → C <sub>2</sub> H <sub>4</sub>	-731.37	-897.03	-896.96	-829.54	-829.64	-843.64	-843.79	-845.71

<sup>a</sup> Not available.



**Fig. 1** Normal distribution functions for the errors of the reaction enthalpies listed in Table 2.

**Table 3** Statistical measures (in  $\text{kJ mol}^{-1}$ ) for errors of the reaction enthalpies listed in Table 2

	MP2		CCSD		CCSD(T)		
	SCF	IJKL	SP	IJKL	SP	IJKL	SP
$\Delta_{\text{abs}}^{\text{max}}$	114.34	51.32	51.28	16.17	16.07	4.83	5.74
$\Delta$	8.51	-9.91	-10.62	-4.57	-5.94	-0.22	-0.13
$\Delta_{\text{abs}}$	29.29	15.37	15.28	9.92	9.18	1.91	1.77
$\Delta_{\text{std}}$	41.86	19.23	19.03	10.37	8.81	2.52	2.30

only the first row elements, however, a variety of different chemical bonds is provided.

The calculated total energies of the cusp-condition-based method are very close to those from the fully-optimized CCSD(T)-F12 method, that is, the corresponding differences are less than  $1 \text{ mE}_h$  in most cases. Results for the 13 investigated isogyric reactions suggest that the cusp-condition CCSD(T)-F12 method has a potential for providing reaction enthalpies within chemical accuracy (*ca.*  $4 \text{ kJ mol}^{-1}$ ). A statistical analysis of the calculated enthalpies has been carried out to estimate the predictive power of the methods. It has been proven that the standard deviations from the fully-optimized and cusp-condition based CCSD(T)-F12 methods are almost identical. Concerning the applicability of the SP *ansatz* in highly accurate calculations for larger molecular systems, the aforementioned results are especially encouraging. This is strengthened by the fact that the method is orbital invariant, free from possible numerical instabilities, and much cheaper than the fully optimized CCSD(T)-F12.

Theoretical analysis for the open-shell systems revealed that the standard unitary-invariant *ansatz* cannot satisfy the singlet and the triplet cusp conditions exactly. An extended *ansatz* proposed in this work can fix this problem retaining the orbital-invariance. We intend to implement the method to check the effect of the spin-flipped geminal basis in open-shell molecules.

## Acknowledgements

This work has been supported by the Grant Agency of the Ministry of Education of the Slovak Republic and Slovak Academy of Sciences (VEGA project No. 2/6182) as well as by

the Slovak Research and Development Agency (APVV 20-018405) and a Centres of Excellence program of SAS (COMCHEM).

## References

- S. F. Boys, *Proc. R. Soc. London, Ser. A*, 1960, **258**, 402.
- K. Singer, *Proc. R. Soc. London, Ser. A*, 1960, **258**, 412.
- W. A. Lester and M. Krauss, *J. Chem. Phys.*, 1964, **41**, 1407.
- O. Sinanoglu, *Adv. Chem. Phys.*, 1965, **6**, 315.
- K.-C. Pan and H. F. King, *J. Chem. Phys.*, 1970, **53**, 4397.
- K.-C. Pan and H. F. King, *J. Chem. Phys.*, 1972, **56**, 4667.
- K. Szalewicz, B. Jeziorski, H. J. Monkhorst and J. G. Zabolitsky, *Chem. Phys. Lett.*, 1982, **91**, 169.
- K. Szalewicz, B. Jeziorski, H. J. Monkhorst and J. G. Zabolitsky, *J. Chem. Phys.*, 1983, **78**, 1420.
- K. Szalewicz, B. Jeziorski, H. J. Monkhorst and J. G. Zabolitsky, *J. Chem. Phys.*, 1983, **79**, 5543.
- W. Kutzelnigg and J. D. Morgan III, *J. Chem. Phys.*, 1992, **96**, 4484.
- W. Kutzelnigg, *Theor. Chim. Acta*, 1985, **68**, 445.
- W. Kutzelnigg and W. Klopper, *J. Chem. Phys.*, 1991, **94**, 1985.
- T. Kato, *Commun. Pure Appl. Math.*, 1957, **10**, 151.
- R. T. Pack and W. B. Brown, *J. Chem. Phys.*, 1966, **45**, 556.
- T. L. Gilbert, *Rev. Mod. Phys.*, 1963, **35**, 491.
- W. Klopper, F. R. Manby, S. Ten-no and E. F. Valeev, *Int. Rev. Phys. Chem.*, 2006, **25**, 427.
- W. Klopper and C. C. M. Samson, *J. Chem. Phys.*, 2002, **116**, 6397.
- E. F. Valeev, *Chem. Phys. Lett.*, 2004, **395**, 190.
- F. R. Manby, *J. Chem. Phys.*, 2003, **119**, 4607.
- S. Ten-no and F. R. Manby, *J. Chem. Phys.*, 2003, **119**, 5358.
- S. Ten-no, *J. Chem. Phys.*, 2004, **121**, 117.
- S. Ten-no, *Chem. Phys. Lett.*, 2004, **398**, 56.
- D. P. Tew and W. Klopper, *J. Chem. Phys.*, 2005, **123**, 074101.
- A. J. May, E. Valeev, R. Polly and F. R. Manby, *Phys. Chem. Chem. Phys.*, 2005, **7**, 2710.
- F. R. Manby, H.-J. Werner, T. B. Adler and A. J. May, *J. Chem. Phys.*, 2006, **124**, 094103.
- E. F. Valeev, *J. Chem. Phys.*, 2006, **125**, 244106.
- S. Ten-no, *J. Chem. Phys.*, 2007, **126**, 014108.
- D. Yamaki, H. Koch and S. Ten-no, *J. Chem. Phys.*, 2007, **127**, 144104.
- J. Noga, W. Klopper and W. Kutzelnigg, CC-R12: an explicitly correlated coupled-cluster theory, in *Recent Advances in Coupled-Cluster Methods*, ed. R. J. Bartlett, World Scientific, 1997.
- J. Noga and W. Kutzelnigg, *J. Chem. Phys.*, 1994, **101**, 7738.
- R. J. Gdanitz, *Chem. Phys. Lett.*, 1993, **210**, 253.
- R. J. Gdanitz, *Chem. Phys. Lett.*, 1998, **283**, 253.
- H. Fliegl, W. Klopper and C. Hättig, *J. Chem. Phys.*, 2005, **122**, 084107.
- H. Fliegl, C. Hättig and W. Klopper, *J. Chem. Phys.*, 2006, **124**(4), 084107.
- D. P. Tew, W. Klopper, C. Neiss and C. Hättig, *Phys. Chem. Chem. Phys.*, 2007, **9**, 1921.
- S. Ten-no, *Chem. Phys. Lett.*, 2007, **447**, 175.
- E. F. Valeev, *Phys. Chem. Chem. Phys.*, 2008, **10**, 106.
- J. Noga, S. Kedzuch, J. Šimunek and S. Ten-no, *J. Chem. Phys.*, 2008, **128**, 174103.
- J. Noga, W. Kutzelnigg and W. Klopper, in *Recent Advances in Computational Chemistry*, ed. R. J. Bartlett, World Scientific, Singapore, 1997, vol. 3, p. 1.
- W. Klopper, W. Kutzelnigg, H. Müller, J. Noga and S. Vogtner, *Top. Curr. Chem.*, 1999, **203**, 21.
- D. Tew, W. Klopper and C. Hättig, *Chem. Phys. Lett.*, 2008, **452**, 326.
- T. B. Alder, G. Knizia and H.-J. Werner, *J. Chem. Phys.*, 2007, **127**, 221106.
- W. Klopper, *Chem. Phys. Lett.*, 1991, **186**, 583.
- K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.*, 1989, **157**, 479.
- K. L. Bak, J. Gauss, P. Jorgensen, J. Olsen, T. Helgaker and J. F. Stanton, *J. Chem. Phys.*, 2001, **114**, 6548.

- 46 S. Kedžuch, M. Milko and J. Noga, *Int. J. Quantum Chem.*, 2005, **105**, 929.  
47 K. L. Bak, J. Gauss, P. Jorgensen, J. Olsen, T. Helgaker and W. Klopper, *J. Chem. Phys.*, 2000, **112**, 9229.  
48 R. Jastrow, *Phys. Rev.*, 1955, **98**, 1479.

- 49 T. H. Dunning Jr, *J. Chem. Phys.*, 1989, **90**, 1007.  
50 R. A. Kendall, T. H. Dunning Jr and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6769.  
51 D. E. Woon and T. H. Dunning Jr, *J. Chem. Phys.*, 1995, **103**, 4572.



9050/090

RSCPublishing

**Fast  
Publishing?  
Ahead of the field**

To find out more about RSC Journals, visit

**[www.rsc.org/journals](http://www.rsc.org/journals)**