

## SIMILARITY-TRANSFORMED HAMILTONIANS BY MEANS OF GAUSSIAN-DAMPED INTERELECTRONIC DISTANCES

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A method is presented to improve the description of electron correlation in configuration interaction (CI) calculations. In this method, the standard CI expansion  $\psi$  is multiplied by a correlation function  $\phi = \exp(F)$  with

$$F = \sum_{m=1}^M c_m \sum_{i<j} r_{ij} \exp(-\gamma_m r_{ij}^2).$$

With this correlation function, the total wavefunction  $\Psi = \phi\psi$  exhibits the right behavior when two electrons coalesce while  $F$  vanishes for large interelectronic distances. The correlation function is implemented using the methodology of similarity-transformed Hamiltonians and is applied to two-electron systems. A generalization to many-electron systems is indicated. The new method yields more accurate results than standard CI calculations of the energy and interelectronic distance of the He atom. The  $H_2$  molecule was chosen to study the long-range behavior of the correlation function.

**Keywords:** Hamiltonian; Gaussian; Wavefunctions; Configuration interaction; Correlation functions; *Ab initio* calculations.

In nonrelativistic quantum chemistry, much effort has been put forth to compute approximate solutions of the time-independent Schrödinger equation  $\hat{H}\Psi = E\Psi$ . The convergence of the calculation of accurate approximate solutions of the Hamiltonian is often hampered by electron correlation, a phenomenon related to the instantaneous repulsions among the electrons.

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Electron correlation cannot be taken into account by independent-particle models (*e.g.*, Hartree–Fock) where instantaneous repulsions are neglected. Although such models may yield acceptable results on many occasions, correlation effects need to be taken into account for various purposes, for example for the description of bond dissociation and dispersion forces. In the present study, an attempt is undertaken to enhance the description of electron correlation in order to improve the convergence and accuracy of configuration interaction (CI) calculations.

The exact nonrelativistic wavefunction satisfies Kato's correlation cusp condition<sup>1</sup>

$$\lim_{r_{ij} \rightarrow 0} \left( \frac{\partial \Psi}{\partial r_{ij}} \right)_{\text{av}} = \frac{1}{2} \Psi(r_{ij} = 0), \quad (1)$$

where "av" stands for spherical averaging. The description of the correlation cusp and the amount of electron correlation in CI calculations can be significantly enhanced if we add a correlation function to the wavefunction, that is, if we write the wavefunction as  $\Psi = \phi\psi$ , where  $\psi$  is a standard CI-type expansion (*i.e.*, a linear combination of orbital products) and  $\phi$  is a correlation function<sup>2–4</sup>. Since  $\partial\psi / \partial r_{ij} = 0$ , it follows that  $\phi$  should satisfy the cusp condition. This fact can be exploited to design appropriate correlation functions. Furthermore,  $\phi$  should remain finite when  $r_{ij}$  approaches infinity in order not to corrupt the standard CI-type expansion  $\psi$ . In the present study, therefore, we have decided to investigate the correlation function  $\phi = \exp F$  with

$$F = \sum_{m=1}^M c_m \sum_{i < j} G_{ij}^m \quad (2)$$

and

$$G_{ij}^m = r_{ij} \exp(-\gamma_m r_{ij}^2). \quad (3)$$

Note that  $\phi$  satisfies the cusp condition when

$$\sum_{m=1}^M c_m = 1/2, \quad (4)$$

irrespective of  $\psi$ . Moreover, the correlation function approaches unity when  $r_{ij}$  becomes large.

In this paper, we shall present a method to implement the above described correlation function using the transcorrelated method previously developed by Boys and Handy<sup>5-12</sup> and reviewed by one of us<sup>13,14</sup> as well as by Nooijen and Bartlett<sup>15</sup>. All of the formulae for the implementation are derived for any number of electrons but the method has thus far been applied only to two-electron systems.

Our present work is closely related to the very recent work by Ten-no and co-workers<sup>16-20</sup>. However, their method differs from ours since they use correlation functions with

$$\tilde{G}_{ij}^m = \exp(-\gamma_m r_{ij}^2), \quad (5)$$

that is, *without* the linear  $r_{ij}$  term. The Gaussian functions (5) do not satisfy the correlation cusp. Rather, they are used to fit the Coulomb hole. One motivation for the present work was to supplement the method of Ten-no and co-workers by linear  $r_{ij}$  terms.

Calculations on the He atom were performed in large basis sets of Gaussian atomic orbitals (AOs) to assess the quality of the description of short-range correlation by the new wavefunctions. The H<sub>2</sub> molecule (with different internuclear distances) was used as a model system to investigate the long-range behavior of the correlation function and to optimize the parameter  $\gamma$ , which determines the range of correlations. We furthermore indicate how to calculate expectation values using the new wavefunctions and, finally, we investigate the convergence behavior of the new method in comparison with traditional CI.

## THEORY

### *Similarity-Transformed Hamiltonians*

In atomic units, the molecular electronic Hamiltonian is written as

$$\hat{H} = V_{\text{nuc}} + \sum_i \hat{h}_i + \sum_{i < j} \frac{1}{r_{ij}}, \quad (6)$$

where  $V_{\text{nuc}}$  is the nuclear repulsion energy

$$V_{\text{nuc}} = \sum_{K < L} \frac{Z_K Z_L}{r_{KL}}, \quad (7)$$

$\hat{h}_i$  is the one-electron Hamiltonian

$$\hat{h}_i = -\frac{1}{2}\Delta_i - \sum_K \frac{Z_K}{r_{iK}} \quad (8)$$

and  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$  is the interelectronic distance. The sums over  $i$  and  $j$  run over the electrons and the sums over  $K$  and  $L$  run over the nuclei in the molecule.

We write the molecular electronic wavefunction as

$$\Psi = \phi\psi_R = \exp(F)\psi_R = \phi^{-1}\psi_L = \exp(-F)\psi_L, \quad F = \sum_{i<j} f_{ij}, \quad (9)$$

where  $f_{ij}$  is a symmetric two-electron function (geminal), which in the present work is chosen as a linear combination of *Gaussian-damped interelectronic distances*

$$f_{ij} = \sum_{m=1}^M c_m G_{ij}^m, \quad G_{ij}^m = r_{ij} \exp(-\gamma_m r_{ij}^2). \quad (10)$$

The  $c_m$  and  $\gamma_m$  are adjustable parameters.

We multiply the molecular electronic Schrödinger equation  $\hat{H}\Psi = E\Psi$  from the left by the operator  $\exp(-F)$  to obtain

$$\exp(-F)\hat{H}\exp(F)\psi_R = E\psi_R, \quad (11)$$

which may be regarded as a Schrödinger equation with an effective, non-Hermitian *similarity-transformed Hamiltonian* (STH)

$$\hat{H}^F = \exp(-F)\hat{H}\exp(F), \quad (12)$$

which corresponds to the Hirschfelder Hamiltonian<sup>2</sup>

$$\hat{H}^F = \hat{H} + \phi^{-1}[\hat{H}, \phi] = \hat{H} - \frac{1}{2}\phi^{-1}\sum_i \{(\Delta_i \phi) + 2(\nabla_i \phi) \cdot \nabla_i\}. \quad (13)$$

The nested-commutator expansion of  $\hat{H}^F$  yields

$$\hat{H}^F = \hat{H} + [\hat{H}, F] + \frac{1}{2} [[\hat{H}, F], F]. \quad (14)$$

$[\hat{H}, F]$  constitutes the two-electron operator

$$[\hat{H}, F] = -\frac{1}{2} \sum_i \sum_{j \neq i} \{(\Delta_i f_{ij}) + 2(\nabla_i f_{ij}) \cdot \nabla_i\}, \quad (15)$$

while the double commutator gives rise to the three-electron operator

$$\frac{1}{2} [[\hat{H}, F], F] = -\frac{1}{2} \sum_i \sum_{j \neq i} \sum_{k \neq i} (\nabla_i f_{ij}) \cdot (\nabla_i f_{ik}). \quad (16)$$

Since  $[[[\hat{H}, F], F], F] = 0$ , there are no terms beyond the double commutator in the nested-commutator expansion.

The similarity-transformed Hamiltonian has right and left eigenfunctions  $\Psi_R$  and  $\Psi_L$ , respectively. In particular,

$$\hat{H}^F \Psi_R = E \Psi_R, \quad (\hat{H}^F)^\dagger \Psi_L = E \Psi_L \quad (17)$$

with

$$(\hat{H}^F)^\dagger = \exp(F) \hat{H} \exp(-F) = \hat{H}^F - 2[\hat{H}, F]. \quad (18)$$

Finally, the expectation value of an operator  $\hat{O}$  is computed according to

$$\langle \hat{O} \rangle = \langle \Psi | \hat{O} | \Psi \rangle \langle \Psi | \Psi \rangle^{-1} = \langle \Psi_L | \hat{O}^F | \Psi_R \rangle \langle \Psi_L | \Psi_R \rangle^{-1}. \quad (19)$$

### Two-Electron Systems

For a system with only two electrons, we obtain the following expression for the single commutator:

$$[\hat{H}, F] = \sum_{m=1}^M c_m [\hat{H}, G_{12}^m] \quad (20)$$

with

$$[\hat{H}, G_{12}^m] = -\frac{1}{2}(\Delta_1 G_{12}^m) - \frac{1}{2}(\Delta_2 G_{12}^m) - (\nabla_1 G_{12}^m) \cdot \nabla_1 - (\nabla_2 G_{12}^m) \cdot \nabla_2. \quad (21)$$

Noting that

$$(\nabla_1 G_{12}^m) = \mathbf{r}_{12} r_{12}^{-1} (1 - 2\gamma_m r_{12}^2) \exp(-\gamma_m r_{12}^2), \quad (22)$$

$$(\Delta_1 G_{12}^m) = r_{12}^{-1} (2 - 10\gamma_m r_{12}^2 + 4\gamma_m^2 r_{12}^4) \exp(-\gamma_m r_{12}^2), \quad (23)$$

we rewrite Eq. (21) as

$$[\hat{H}, G_{12}^m] = -r_{12}^{-1} \exp(-\gamma_m r_{12}^2) \{2 - 10\gamma_m r_{12}^2 + 4\gamma_m^2 r_{12}^4 + (1 - 2\gamma_m r_{12}^2) \mathbf{r}_{12} \cdot (\nabla_1 - \nabla_2)\}. \quad (24)$$

Similarly, for the double commutator, we obtain

$$\frac{1}{2} [[\hat{H}, F], F] = \frac{1}{2} \sum_{m=1}^M \sum_{m'=1}^M c_m c_{m'} [[\hat{H}, G_{12}^m], G_{12}^{m'}] \quad (25)$$

with

$$\begin{aligned} \frac{1}{2} [[\hat{H}, G_{12}^m], G_{12}^{m'}] &= -\frac{1}{2} (\nabla_1 G_{12}^m) \cdot (\nabla_1 G_{12}^{m'}) - \frac{1}{2} (\nabla_2 G_{12}^m) \cdot (\nabla_2 G_{12}^{m'}) \\ &= -(1 - 2\gamma_m r_{12}^2)(1 - 2\gamma_{m'} r_{12}^2) \exp\{-(\gamma_m + \gamma_{m'}) r_{12}^2\}. \end{aligned} \quad (26)$$

If we restrict the sum in Eq. (10) to only one term with  $\gamma_1 = 0$ , the commutators reduce to the expressions

$$[\hat{H}, r_{12}] = -\frac{2}{r_{12}} - \frac{\mathbf{r}_{12}}{r_{12}} \cdot (\nabla_1 - \nabla_2), \quad \frac{1}{2} [[\hat{H}, r_{12}], r_{12}] = -1 \quad (27)$$

and the similarity-transformed Hamiltonian in this special case becomes

$$\hat{H}^F = V_{\text{nuc}} + \hat{h}_1 + \hat{h}_2 + (1 - 2c_1) \frac{1}{r_{12}} - c_1 \frac{\mathbf{r}_{12}}{r_{12}} \cdot (\nabla_1 - \nabla_2) - c_1^2. \quad (28)$$

In Eq. (28), the Coulomb singularity in  $(1 - 2c_1)/r_{12}$  vanishes when  $c = 1/2$ . Thus, for this value of  $c_1$ , a much improved convergence rate is expected for the CI expansion of  $\hat{H}^F$  in comparison with  $\hat{H}$ .

### Many-Electron Systems

It was shown above that three-electron integrals are the most involved integrals to be computed for  $n$ -electron systems. Still, these integrals can be computationally quite demanding, especially in the multicenter case. Ten-no and co-workers<sup>16-20</sup> have derived methods to compute the three-electron integrals in Eq. (16) by means of resolution-of-identity approximations (closure approximations) to reduce the cost of the calculation.

These resolution-of-identity approximations should also be invoked in all of the formulae that occur with the correlation functions of the present work. All of the two-electron integrals are available to do so.

### COMPUTATIONAL DETAILS

The two-electron integrals required for the present study were implemented into the DALTON program<sup>21</sup>. This implementation is described in detail elsewhere<sup>22</sup>.

The 19s16p14d12f10g8h6i4k Gaussian basis for He was derived from the 17s set of Huzinaga and Miguel<sup>23,24</sup> in two steps. First, functions of angular symmetry  $\ell$  were added whose exponents were obtained by multiplying the respective number of smallest exponents of the 17s set with the factor  $(2\ell + 1)/3$ . Second, two diffuse s functions were added with exponents 0.043 and  $0.0215 a_0^{-2}$ .

The calculations on  $H_2$  were carried out in the 5s4p subset of the aug-cc-pVQZ basis<sup>24,25</sup>.

### RESULTS

Figure 1 as well as Tables I-III demonstrate that the STH method yields a more accurate total energy and interelectronic distance than standard CI calculations of the He atom ground state. Furthermore, the error decreases

much faster with the STH method than with standard CI when the number of basis functions is increased. More is gained by the STH method in a larger basis. When only s-type functions are used, the standard CI method appears to be superior in accuracy to the STH. This might be due to the

TABLE I

He atom ground-state energy, obtained from calculations with the similarity-transformed Hamiltonian of Eq. (28) with  $c_1 = 1/2$ , in comparison with standard CI calculations

Basis set <sup>a</sup>	$E(\hat{H}^F) / E_h$	$\delta(\hat{H}^F)^b / \mu E_h$	$E(\hat{H}) / E_h$	$\delta(\hat{H})^b / \mu E_h$
19s	-3.010 772 36	-107 048	-2.879 027 61	24 697
19s16p	-2.904 831 30	-1107	-2.900 513 53	3211
19s16p14d	-2.904 061 41	-337	-2.902 762 12	963
19s16p14d12f	-2.903 805 89	-82	-2.903 314 21	410
19s16p14d12f10g	-2.903 751 43	-27	-2.903 509 63	215
19s16p14d12f10g8h	-2.903 735 20	-11	-2.903 594 60	130
19s16p14d12f10g8h6i	-2.903 729 33	-5	-2.903 634 64	90
19s16p14d12f10g8h6i4k	-2.903 727 45	-3	-2.903 647 06	77

<sup>a</sup> Subsets of the 19s16p14d12f10g8h6i4k basis. <sup>b</sup> Error with respect to the exact value of  $E = -2.903 724 377 E_h$  from ref.<sup>26</sup> See also ref.<sup>27</sup>

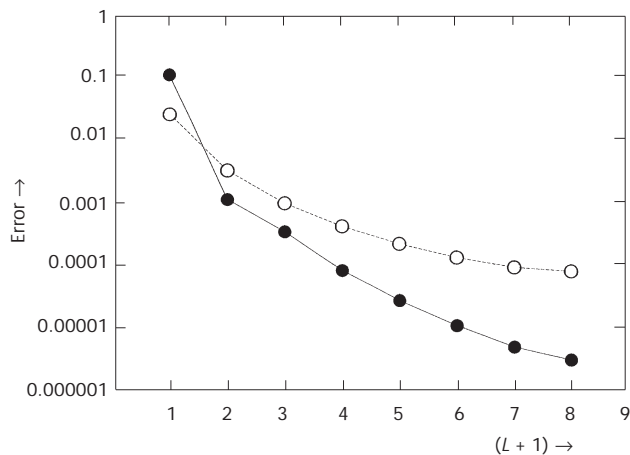


FIG. 1

Absolute error (in  $E_h$ ) in the He ground-state energy of the standard CI expansion (○) and of the similarity-transformed Hamiltonian of Eq. (28) with  $c_1 = 1/2$  (●) as a function of the basis set



TABLE II

He atom ground-state kinetic energy, potential energy, virial, and expectation values of  $r_{12}$ , obtained from standard CI calculations

Basis set <sup>a</sup>	$\langle \hat{T} \rangle / E_h$	$\langle V \rangle / E_h$	$-\frac{1}{2} \langle V \rangle / \langle \hat{T} \rangle$	$\langle r_{12} \rangle / a_0$
19s	2.879 027	-5.758 055	1.000 000	1.387 999
19s16p	2.900 513	-5.801 026	1.000 000	1.424 184
19s16p14d	2.902 761	-5.805 523	1.000 000	1.422 838
19s16p14d12f	2.903 313	-5.806 627	1.000 000	1.422 413
19s16p14d12f10g	2.903 508	-5.807 017	1.000 000	1.422 254
19s16p14d12f10g8h	2.903 595	-5.807 189	1.000 000	1.422 182
19s16p14d12f10g8h6i	2.903 623	-5.807 257	1.000 002	1.422 149
19s16p14d12f10g8h6i4k	2.903 614	-5.807 261	1.000 006	1.422 141
$\infty^b$	2.903 724	-5.807 449	1.000 000	1.422 070

<sup>a</sup> Cf. Table I. <sup>b</sup> From ref.<sup>28</sup>

TABLE III

He atom ground-state kinetic energy, potential energy, virial, and expectation values of  $r_{12}$ , obtained from calculations with the similarity-transformed Hamiltonian of Eq. (28) with  $c_1 = 1/2$

Basis set <sup>a</sup>	$\langle \hat{T} \rangle / E_h$	$\langle V \rangle / E_h$	$-\frac{1}{2} \langle V \rangle / \langle \hat{T} \rangle$	$\langle r_{12} \rangle / a_0$
19s	2.747 273	-5.758 046	1.047 956	1.386 425
19s16p	2.902 073	-5.806 904	1.000 475	1.416 121
19s16p14d	2.901 593	-5.805 654	1.000 425	1.421 608
19s16p14d12f	2.902 853	-5.806 659	1.000 164	1.421 953
19s16p14d12f10g	2.903 273	-5.807 025	1.000 082	1.422 036
19s16p14d12f10g8h	2.903 454	-5.807 189	1.000 048	1.422 060
19s16p14d12f10g8h6i	2.903 538	-5.807 268	1.000 033	1.422 068
19s16p14d12f10g8h6i4k	2.903 567	-5.807 294	1.000 028	1.422 071
$\infty^b$	2.903 724	-5.807 449	1.000 000	1.422 070

<sup>a</sup> Cf. Table I. <sup>b</sup> From ref.<sup>28</sup>

choice of basis functions, which were optimized for standard CI calculations and not for the similarity-transformed Hamiltonian. However, although the total energy is very accurate, the individual STH expectation values for kinetic and potential energy are less accurate than their counterparts from standard CI calculations (Tables II, III). Again, this might be due to the choice of basis set, which is nearly optimal for standard CI calculations. A better basis set for the STH calculations could perhaps be generated by scaling all basis-set exponents by a certain factor, but this has not yet been attempted.

When the quality of the calculation is tested as a function of  $\gamma$ , it is observed that the error is increased for intermediate values of  $\gamma$  (Table IV and Fig. 2). The reason for the deterioration is unknown. We conclude that  $\gamma$  should be kept small to describe short-range correlation effectively.

On the other hand, the calculations of the stretched  $H_2$  molecule indicate that  $\gamma$  should be sufficiently large to maintain convergence in the calculation when the interelectronic distance is very long. Because of this controversy, it is impossible to make conclusive statements about the optimal value of parameter  $\gamma$ . The choice of  $\gamma$  obviously depends on the mutual distances between the electrons in the system. An STH calculation of a large  $n$ -electron molecule should perhaps be preceded by an inexpensive CI or even Hartree–Fock calculation in a small basis to estimate the average inter-

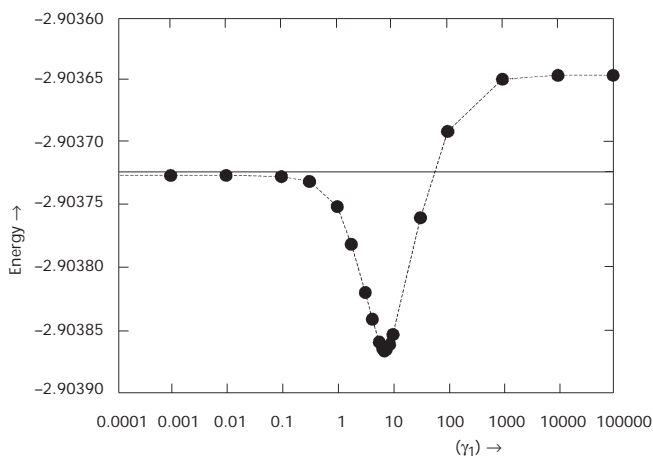


FIG. 2

He atom ground-state energy obtained from calculations with the similarity-transformed Hamiltonian of Eq. (12) in the 19s16p14d12f10g8h6i4k basis with  $M = 1$  and  $c_1 = 1/2$ , as a function of the damping parameter  $\gamma_1$ . The horizontal line indicates the exact energy

TABLE IV

He atom ground-state energy obtained from calculations with the similarity-transformed Hamiltonian of Eq. (12) in the 19s16p14d12f10g8h6i4k basis with  $M = 1$  and  $c_1 = 1/2$

$\log(\gamma_1)$	$-E/E_h$
$-\infty$	-2.903 727
-3.000 00	-2.903 727
-2.000 00	-2.903 727
-1.000 00	-2.903 728
-0.500 00	-2.903 732
0.000 00	-2.903 752
0.250 00	-2.903 782
0.500 00	-2.903 820
0.625 00	-2.903 841
0.750 00	-2.903 859
0.812 50	-2.903 864
0.843 75	-2.903 866
0.875 00	-2.903 865
0.937 50	-2.903 861
1.000 00	-2.903 853
1.500 00	-2.903 761
2.000 00	-2.903 692
3.000 00	-2.903 650
4.000 00	-2.903 647
$\infty$	-2.903 647

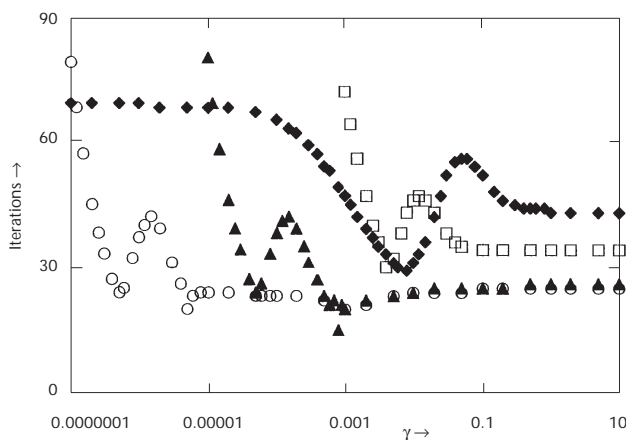


FIG. 3

Number of iterations needed to solve the CI equations for the  $H_2$  molecule as a function of the damping parameter  $\gamma$ . Results are shown for internuclear H-H distances of 5.0 ( $\blacklozenge$ ), 10.0 ( $\square$ ), 100.0 ( $\blacktriangle$ ), and 1000.0 ( $\circ$ )  $a_0$

electronic distance  $\langle r_{12} \rangle$ . The damping parameters  $\gamma_m$  could perhaps be chosen accordingly.

The optimal value of  $\gamma$  seems to be a certain threshold value  $\gamma^{\text{thr}}$ , which is small but just large enough so that the calculation still converges. It is observed from Fig. 3 that the threshold to convergence is  $\gamma^{\text{thr}} \propto \langle r_{12} \rangle$ .

Finally, we note that Ten-no and co-workers<sup>16-20</sup> have developed a useful fitting procedure for obtaining the  $\gamma_m$  in the expansion (2) in terms of their correlation functions given in Eq. (5). It would therefore be interesting to see how the same procedure would perform with our correlation functions given in Eq. (3).

## CONCLUSIONS

The newly developed STH method outshines the standard CI method in the description of the He atom. The error in the total energy is smaller and decreases much faster when the number of basis functions is increased. It has been shown that the STH method is also successful in calculating expectation values (*e.g.*,  $\langle r_{12} \rangle$ ).

The STH method with the here presented correlation function is also capable of describing systems with large interelectronic distances, provided that the damping parameter  $\gamma$  is large enough. In future work, the method should be extended to many-electron systems using closure approximations in order to apply this and similar techniques to general molecules.

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