Application of the transcorrelated Hamiltonian to the linearized coupled cluster singles and doubles model

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Abstract

Explicitly correlated calculations using the transcorrelated Hamiltonian are performed at the level of linearized coupled cluster (LCC) theory. Two different reference functions are employed in the calculations and the results are compared with those of the conventional LCC. The application to the water molecule shows a markedly better convergence of the correlation energies when the transcorrelated Hamiltonian is used than in the conventional approach. We also present results for some other ten-electron systems, Ne, HF, NH_3, and CH_4. © 2002 Published by Elsevier Science B.V.

1. Introduction

Continuous developments of computers and theoretical methods are making ab initio calculations including electron correlation increasingly available for larger molecules. However, there remains a problem that a large one-electron basis set is required to obtain reliable energetics with chemical accuracy. This is due to the difficulty in expanding many-electron wavefunctions as a linear combination of Slater determinants i.e., the slow convergence in describing the correlation cusp by the products of one-electron functions [1]. This difficulty is dramatically ameliorated by the use of two-electronic functions (geminals) [2–4], which more appropriately describe the correlation cusp. Gaussian-type geminal (GTG) methods [5–9,17,18] and R12 [11–14] methods have been implemented for many-electron calculations. Although the Rayleigh–Ritz variational method combined with the use of explicitly correlated basis functions gives excellent accuracy [15–18], it becomes impractical for systems with large number of electrons. To remedy this, the coupled cluster (CC) approach was applied to the GTG method [8,9] and the pair functions were expressed in terms of the explicitly correlated functions. Also the R12 method which includes the linear r_{12} dependence in the pair functions [10–12] was combined with the CC method and has been applied in highly accurate calculations of some atoms and molecules [13,14].

Recently, we proposed another explicitly correlated method [19–22] using the transcorrelated Hamiltonian [23] which was defined as a similarity-transformed Hamiltonian with the correlation factor expanded in terms of GTGs. We chose the correlation factor to compensate for the Coulomb interaction at short inter-electronic distances. We implemented the second-order many-body perturbation theory (MBPT) with the transcorrelated Hamiltonian [19,21] and demonstrated that this led to better convergence of the correlation energies with the expansion of the one-electronic basis than in the conventional MBPT method. In this Letter, we implement the linearized coupled cluster (LCC) [27,28] method within the framework of the transcorrelated approach to determine higher-order correlation corrections and examine their convergence with the basis set expansion.

In Section 2, we briefly describe the transcorrelated Hamiltonian used in this work. In Section 3, we review the pseudo-orbital method [19] and the biorthogonal self-consistent field (SCF) method [21]. In that section, we also formulate the LCC equations. In Section 4, we present and discuss the numerical results for some atoms and molecules. The conclusions are presented in Section 5.

2. Transcorrelated Hamiltonian

The transcorrelated Hamiltonian is defined as [23]

$$\tilde{H} = e^{-F} H e^{F}. \tag{2.1}$$

The exponent, F, used in the present work is a sum of geminals [19–22], which depend on inter-electronic distances

$$F = \sum_{i<j} f(r_{ij}). \tag{2.2}$$

$\tilde{H}$ is rewritten as

$$\tilde{H} = H + [H,F] + \tfrac{1}{2}[[H,F],F]$$
$$= H + K + L, \tag{2.3}$$

where the operators K and L are given by

$$K = \frac{1}{2} \sum_{ij} K_{ij}, \tag{2.4}$$

$$L = \frac{1}{6} \sum_{ijk} L_{ijk}, \tag{2.5}$$

$$K_{12} = -\nabla_1^2 f(r_{12}) - \nabla_1 f(r_{12}) \cdot (\nabla_1 - \nabla_2)$$
$$\quad - \nabla_1 f(r_{12}) \cdot \nabla_1 f(r_{12}), \tag{2.6}$$

$$L_{123} = -3\nabla_1 f(r_{12}) \cdot \nabla_1 f(r_{13}). \tag{2.7}$$

We represent the geminal as a linear combination of Gaussian functions

$$f(r_{12}) = -\sum_{G=1}^{N_G} c_G \exp\left(-\zeta_G r_{12}^2\right). \tag{2.8}$$

In this work, we employ an even-tempered sequence of 10 Gaussian functions with the range of exponents between 904000.0 and 0.12. The coefficients are determined by the least square fitting so that the relation

$$r_{12}^{-1} w(r_{12}) = \nabla_1^2 f(r_{12}) + \nabla_1 f(r_{12}) \cdot \nabla_1 f(r_{12}) \tag{2.9}$$

approximately holds for a short-range weight function, $w(r_{12})$, which localizes the correlation factor near $r_{12} = 0$. We chose the weight function as, $w(r_{12}) = \exp\left(-\zeta_w r_{12}^2\right)$, with the exponent $\zeta_w = 20.0$. The correlation factor, e^F, treats the short-range behavior of the correlation cusp explicitly, and its use excludes a large amount of Coulomb singularity from the Hamiltonian. This fact enables us to accurately expand the eigenfunction of $\tilde{H}$ using a smaller one-electronic basis than what is required for expanding the eigenfunction of H. The idea of eliminating the Coulomb singularity from the Hamiltonian has been previously proposed by Nooijen and Bartlett [24], and Jankowski [25,26]. It should be noted that the three-electron interaction L becomes small due to the localized nature of the correlation factor. We therefore can insert the resolution of identity in L and use this approximation to calculate the three-electron integrals [19–22]. The number of additional integrals increases only linearly with the system size.

3. Transcorrelated LCCSD method

We have performed LCC calculations using two types of reference functions, the usual Hartree–

Fock (HF) SCF wave function and the biorthogonal SCF wave functions. Henceforward, we use the notations, $i, j, \ldots$ and $a, b, \ldots$ for occupied and virtual orbitals, respectively. In the HF case, we treat the orbital relaxation induced by the operator K with the pseudo-orbital equation [19] prior to the LCC calculation,

$$\left\langle X_\mu^+ \psi_0 \right| (H + K) \exp\left(\bar{T}_1\right) |\psi_0\rangle_c = 0 \tag{3.1}$$
$$\forall \mu \in S,$$

$$\bar{T}_1 = \sum_{ai} \bar{t}_i^a a_a^+ a_i, \tag{3.2}$$

where X_μ^+ denotes excitation operators with respect to the HF vacuum, ψ_0. The three-body operator, L, is excluded from the above equation because its contribution is assumed to be small. The LCC singles and double (LCCSD) equations [27,28] are given by:

$$\langle \psi_0 | \hat{\tilde{H}}(1 + T) |\psi_0\rangle = E, \tag{3.3}$$

$$\left\langle X_\mu^+ \psi_0 \right| [H_0, T] |\psi_0\rangle$$
$$= -\left\langle X_\mu^+ \psi_0 \right| \hat{\tilde{V}} + [\hat{\tilde{V}}, T] |\psi_0\rangle \quad \forall \mu \in S, D, \tag{3.4}$$

where the operators are defined as

$$\hat{\tilde{H}} = \exp(-\bar{T}_1) \tilde{H} \exp(\bar{T}_1), \tag{3.5}$$

$$\hat{\tilde{V}} = \hat{\tilde{H}} - H_0, \tag{3.6}$$

$$T = T_1 + T_2$$
$$= \sum_{ai} t_i^a a_a^+ a_i + \frac{1}{2} \sum_{abij} t_{ij}^{ab} a_a^+ a_b^+ a_j a_i, \tag{3.7}$$

and H_0 is the usual HF model Hamiltonian.

The second method uses the biorthogonal sets of orbitals, $\lambda = \{\chi_1, \chi_2, \cdots\}$ and $\pi = \{\phi_1, \phi_2, \cdots\}$, which satisfy the relation

$$\langle \chi_p / \phi_q \rangle = \delta_{pq}. \tag{3.8}$$

The transcorrelated Hamiltonian, $\tilde{H}$, is rewritten in terms of the biorthogonal orbitals in the second quantized form [21,29–31]

$$\tilde{H} = \sum_{pq} \langle \chi_p | h | \phi_q \rangle b_p^+ c_q$$
$$+ \frac{1}{2} \sum_{pqrs} \langle \chi_p \chi_q | r_{12}^{-1} + K_{12} | \phi_r \phi_s \rangle b_p^+ b_q^+ c_s c_r$$
$$+ \frac{1}{6} \sum_{pqrstu} \langle \chi_p \chi_q \chi_r | L_{123} | \phi_s \phi_t \phi_u \rangle b_p^+ b_q^+ b_r^+ c_u c_t c_s, \tag{3.9}$$

where the new creation and annihilation operators are defined as

$$b_p^+ = \int \phi_p(1) \Psi^+(1) d1, \tag{3.10}$$

$$c_q = \int \chi_p(1) \Psi(1) d1, \tag{3.11}$$

using the field operators, $\Psi^+(1)$ and $\Psi(1)$. The biorthogonal relations (3.8) assure the anti-commutation relations

$$\{b_p^+, c_q\} = \delta_{pq}, \tag{3.12}$$

$$\{b_p, c_q\} = \{b_p^+, c_q^+\} = 0, \tag{3.13}$$

and enable us to use the Wick theorem and the diagrammatic techniques in the usual second quantization formulation. We determine the biorthogonal orbitals self-consistently as

$$\langle \chi_p | f | \phi_q \rangle = \langle \chi_p | h | \phi_q \rangle$$
$$+ \sum_i \langle \chi_p \chi_i | r_{12}^{-1} + K_{12} | \phi_q \phi_i \rangle_A$$
$$= \varepsilon_p \delta_{pq}, \tag{3.14}$$

where the subscript A denotes anti-symmetrized integrals. We also omit the contributions to the Fock operator from the three-body operator, L, in the SCF calculations. The use of the biorthogonal orbitals is necessary because the Fock operator, f, is nonhermitian. The biorthogonal model Hamiltonian is then written as

$$\tilde{H}_0^{(BO)} = \sum_p \varepsilon_p b_p^+ c_p. \tag{3.15}$$

The LCC equations based on the biorthogonal reference become:

$$\langle X | \tilde{H}(1 + T_b) | \Phi \rangle = E, \tag{3.16}$$

$$\langle Z_\mu^+ X | [H_0^{(BO)}, T_b] | \Phi \rangle$$
$$= -\langle Z_\mu^+ X | \tilde{V} + [\tilde{V}, T_b] | \Phi \rangle \quad \forall \mu \in S, D, \qquad (3.17)$$

where the perturbation and the cluster operator are given by:

$$\tilde{V} = \tilde{H} - H_0^{(BO)}, \qquad (3.18)$$

$$T = T_1 + T_2$$
$$= \sum_{ai} t_i^a b_a^+ c_i + \frac{1}{2} \sum_{abij} t_{ij}^{ab} b_a^+ b_b^+ c_j c_i. \qquad (3.19)$$

Z_μ denotes a deexcitation operator with respect to the right-hand vacuum,

$$Z_\mu = \{ b_i^+ b_j^+ \ldots c_b c_a \}, \qquad (3.20)$$

and X and Φ are the determinants composed of the biorthogonal occupied orbitals

$$X = \| \chi_1 \chi_2 \cdots \chi_n \|, \quad \Phi = \| \phi_1 \phi_2 \cdots \phi_n \|. \qquad (3.21)$$

These determinants are the left- and right-hand ground states of $\tilde{H}_0^{(BO)}$. For later analysis, we define the first-order corrections of the transcorrelated Hamiltonian as

$$\Delta E^{(1)} = \begin{cases} \langle \psi_0 | \hat{\tilde{H}} | \psi_0 \rangle - E_{HF} & \text{(pseudo-orbital)} \\ \langle X | \tilde{H} | \Phi \rangle - E_{HF} & \text{(biorthogonal).} \end{cases}$$
$$(3.22)$$

Our preliminary results imply that the contributions of the two- and three-body operators of the normal-ordered L with respect to both vacuums are very small. In the calculations we omit the terms that are derived from the contractions of T with the normal-ordered three-body operator in the LCCSD equations.

It should be noted that the present scheme maintains the scaling properties of the standard ab initio theory. Let us denote by N, V and O the numbers of basis functions, virtual orbitals, and occupied orbitals, respectively. The pseudo-orbital and biorthogonal SCF calculations scale as N^4 when we exclude the expensive, but less important, contribution of L from the iterative process. The most demanding steps in the LCCSD method are the double contractions of T_2 with two-electron operators in the transcorrelated Hamiltonian. These scale as $V^4 O^2$ at most as they do in the conventional LCCSD methods.

4. Results and discussion

We have applied the transcorrelated LCCSD methods in calculations of the 10-electronic systems, Ne, HF, H_2O, NH_3, and CH_4. The geometrical parameters used in this work are listed in Table 1. For the atoms, Ne, F, O, N, and C, we use the primitive functions derived from the cc-pVQZ basis sets [32] augmented with the p-, d-, and f-core polarization functions taken from the cc-pCVQZ basis sets [33]. The primitive functions of the cc-pVQZ basis set are adopted for the hydrogen atom. Table 2 shows the correlation energies obtained using the transcorrelated methods along with those obtained with the conventional and R12 methods for comparison. The first-order energy difference between the pseudo-orbital and biorthogonal SCF methods becomes large as the charge of the first row atom increases. The difference between the single excitation energies shows similar behaviors; absolute values of the single excitation energies obtained with the pseudo-orbital method are about 30 times larger than those with the biorthogonal SCF method. This is because the elements in the half-block of the approximate Fock matrix, $\langle \psi_0 | \tilde{H} | a_a^+ a_i \psi_0 \rangle$, do not vanish in the pseudo-orbital method. The corresponding matrix is entirely diagonal in the biorthogonal SCF method. The differences in the first-order and single excitation energies contribute oppositely in sign and compensate each other. The differences of the total energies are at most 3.6 mE_h. Only the pseudo-orbital LCCSD energy of the Ne atom is lower than the R12-CCSD(T) one by 1.66 mE_h due to the inadequacy of the HF reference for the heavy element. All other transcorrelated LCCSD energies are in the range between the R12-CCSD and R12-CCSD(T).

Table 1
Geometrical parameters for the systems HF, H_2O, NH_3 and CH_4 (E = F, O, N and C)

	HF	H_2O	NH_3	CH_4
R_{EH}	1.733	1.809	1.913	2.050
$\angle$HEH		104.52	106.67	109.47

Units for the bond length and angle are Bohr and degree, respectively.

Table 2
LCCSD energies (-mE_h) of Ne, HF, H_2O, NH_3 and CH_4 molecules with 12s6p5d3f1g/6s3p2d1f basis set

	Ne	HF	H_2O	NH_3	CH_4
HF	128543.47	100067.71	76064.89	56223.14	40216.34
Conventional LCCSD	365.27	366.36	352.55	325.52	287.61
Pseudo-orbital					
$\Delta E^{(1)}$	222.47	158.84	112.55	79.55	55.84
E_S[a]	−28.67	−17.39	−10.59	−6.36	−3.64
E_D[b]	197.92	244.02	263.89	261.22	241.82
LCCSD	391.72	385.47	365.85	334.13	294.02
Biorthogonal					
$\Delta E^{(1)}$	184.14	138.06	102.13	74.70	53.77
E_S	1.07	0.53	0.38	0.27	0.16
E_D	202.95	245.05	262.87	259.65	240.47
LCCSD	388.15	383.63	365.38	334.62	294.39
R12[c]					
CCSD	383.53	378.99	359.91	327.83	288.56
CCSD(T)	390.06	387.91	369.88	337.25	295.95

[a] Contributions of the single excitations.
[b] Contributions of the double excitations.
[c] Reference [14].

Table 3
Basis set dependence of correlation energies (-mE_h) of H_2O

Basis set	9s4p1d	10s5p3d1f	12s6p5d3f1g	14s8p7d5f3g
HF	76 030.43	76 057.31	76 064.89	76 066.87
Conventional				
Second	257.74	318.46	341.90	348.89
Third	263.61	323.38	344.43	350.14
Fourth	268.58	329.65	351.14	357.11
LCCSD	270.20	331.14	352.55	358.50
CCSD	266.34	325.06	345.74	351.48
CCSD(T)	271.24	333.40	355.27	361.36
Pseudo-orbital				
Second	325.38	354.54	362.20	363.11
Third	323.40	352.19	358.86	359.24
Fourth	328.08	357.78	364.70	365.18
LCCSD	329.34	358.95	365.85	366.34
Biorthogonal				
Second	317.76	347.34	355.47	356.54
Third	322.82	351.37	357.89	358.17
Fourth	327.38	356.97	363.89	364.38
LCCSD	329.02	358.53	365.38	365.87

The second-, third- and fourth-order perturbation energies within the LCCSD model are presented as well as LCCSD energies. The R12-MBPT(2)- A, R12-MP3, R12-MP4, R12-CCSD and R12-CCSD(T) energies are −362.69, −358.84, 371.54, 359.91 and −369.88 mE_h, respectively with 301 basis functions [14].

Basis set dependence of the correlation energies for H_2O is shown in Table 3. For the oxygen atom, we use the primitive functions derived from the cc-pVXZ (X = D, T, Q and 5) basis sets augmented with the d-, f-, and g-core polarization functions of the corresponding cc-pCVXZ basis sets. This gives rise to 9s4p1d, 10s5p3d1, 12s6p5d3f1g, and 14s8p7d5f3g sets. The corresponding primitive functions of the cc-pVXZ basis sets are used for the hydrogen atom except that the cc-pVQZ functions are used with the 14s8p7d5f3g set. Although the second-order correlation energies depend on the choice of the reference, the differences of the correlation energies quickly decrease as the perturbation order increases. Both transcorrelated energies almost coincide at the infinite order (LCCSD) for each basis set. An important feature is that the transcorrelated energies are almost saturated with the 12s6p5d3f1g set in each order, while there is still about 6 mE_h difference between the conventional energies obtained with the 12s6p5d3f1g and 14s8p7d5f3g sets. In Fig. 1, the transcorrelated LCCSD ene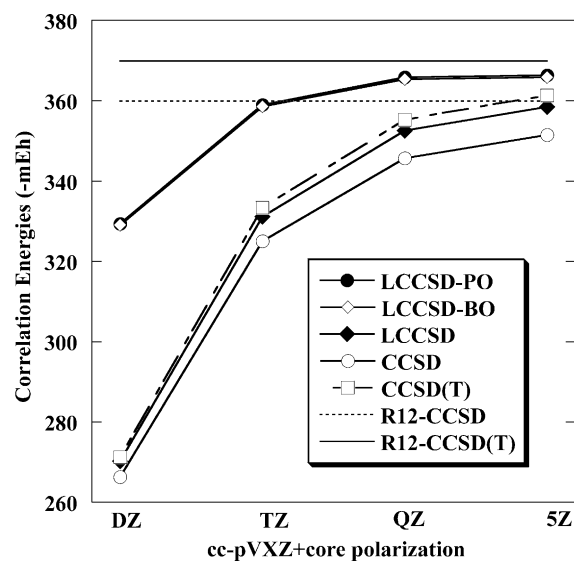rgies and the conventional LCCSD, CCSD, and CCSD(T) energies are plotted against the cardinal number X of the parent cc-pVXZ basis sets. The R12-CCSD and R12-CCSD(T) energies with 301 basis functions [14] are also depicted by the horizontal lines. The transcorrelated LCCSD methods, the correlation energies of which lie between the R12-CCSD and R12-CCSD(T), recover more correlation energies than the conventional LCCSD, CCSD, and CCSD(T). The best transcorrelated energy is higher than the R12-CCSD(T) one by ca. 4 mE_h. The fourth-order triples and quadruples contributions, which are absent in the present treatment, should recover most of the remaining correlation error.

5. Conclusions

We developed the LCC method using the transcorrelated Hamiltonian. It was shown that the transcorrelated Hamiltonian improves the basis set convergence of the dynamic correlation effects. This is because the correlation factor is chosen to cancel the Coulomb singularity at short inter-electronic distances. In other words, the eigenfunction of the transcorrelated Hamiltonian is almost free from the cusp behavior near the coalescence of two electrons. Our choice of the localized geminal (1) leads to favorable scaling properties concerning the additional integrals in the transcorrelated Hamiltonian, (2) makes the contribution of the three-electron operator L small, and (3) conforms the transcorrelated Hamiltonian to the original Hamiltonian at large inter-electronic distances and maintains the ordinary molecular orbital picture. Especially, the second feature allows us to use the approximate resolution of identity to adequately represent the secondary operator L. The computational requirements of the transcorrelated calculations are similar to the conventional methods. We used spherically symmetric geminals in this work. Although the introduction of geminals, which are explicitly dependent on the electronic positions, might improve the accuracy of the transcorrelated method, the present treatment seems adequate as long as we deal with molecules composed of the atomic elements lighter than Ne.

Fig. 1. The transcorrelated LCCSD energies for H_2O are plotted with those of the conventional LCCSD, CCSD, and CCSD(T) methods. LCCSD-PO and LCCSD-BO indicate the transcorrelated LCCSD energies by the pseudo-orbital and biorthogonal SCF methods, respectively. The horizontal dotted and solid lines indicate the R12-CCSD and R12-CCSD(T) energies with 301 basis functions [14].

Multireference treatments will be required to accurately describe excited states and potential energy surfaces. These applications of the transcorrelated Hamiltonian are straightforward and we are planning to proceed with such development.

Acknowledgements

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