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Cluster expansion of the wavefunction

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Numerical examples illustrate the SAC and SAC-CI results for correlatioin energies compared to those from full CI calculations of Bauschlicher and Taylor.

Key words: Cluster Expansion — SAC — SAC — CI

There are three approaches to electron correlation. The first method is based on the variational principle. The most commonly used variational method is the method of configuration interaction, so called CI method. The CI has conceptual simplicity and generality. However, it suffers from one significant weakness, the slow convergence of the wavefunction. The CI expansion becomes progressively less compact and less efficient as the number of electrons in the system grows. The second approach is the perturbation theory. It is a size-consistent theory. The introduction of diagrammatic analysis is a powerful way of handling and summing various types of terms in a perturbation expansion. However, the use of a diagram is only an aid; it does not essentially alter the fact that we are doing a CI calculation, whose convergence is basis-set dependent and is normally rather slow. Moreover it is often not appropriate to assume that the usual fluctuational potential is small, i.e., to assume convergence of the perturbation series. Finally, there is an approach which is neither variational nor perturbational. It possesses some features of both. The theory is based on the cluster expansion of the exact wavefunction [1-6]. It is a size-consistent theory. The cluster expansion of the wavefunction converges faster than the CI expansion through the exponential. We have developed symmetry-adapted-cluster (SAC) theory [7, 8] for the ground state and SAC-CI theory [9] for excited states as a rapid convergent method. The method has successfully been applied to study the correlation problems in the ground and excited states.

Recently full CI calculations are reported by Bauschlicher and Taylor, on Ne, H_2O, F, F^- and HF [10]. Unlike previous full CI calculations [11, 12] and subsequent tests of methods [13-16], double zeta plus polarization or larger basis sets were used. Such results are very useful from the methodical point of view, since they can serve as a convenient reference point for the testing of quality of various approximate methods with the basis set and with the weight of a SCF reference in the CI expansion. So we performed SAC and SAC-CI calculations on these molecules and results are compared with their full CI and limited CI calculations.

Table 1 shows results on Ne. Calculations were performed using Gaussian basis sets of up to triple zeta plus double polarization quality. In this calculation we have included all single and double excitations as a connected cluster. In the first approximatioin (SAC-A) we have included the disconnected tetraexcited clusters $(1/2)S_2S_2$. In the second approximation (SAC-B) we consider explicitly the disconnected triexcited clusters of the type of S_1S_2 in addition to tetraexcited clusters $(1/2)S_2S_2$ of the approximation A.

Since the SCF reference is a good zero-order description of the ground state of Ne atom, the correlation energy is dominated by the double excitations. The SAC-A and SAC-B theories account for over 98.5% of the total correlation energy and can compare well with the SDTQ-CI results. Table 2 summarizes the breakdown of the correlation contribution by excitation level. The SAC convergent results correspond to summing all diagrams that contain double and products of double excitations through infinite order. Thus, the disconnected contributions of SAC theory is close to the contribution from the quadruple and higher excitations. Note here that the contribution from triple excitations is rather significant. The connected terms of triple excitations are not included in the present theory. If we take triple excitations into account, then it is expected that we can reproduce the full CI results to high order.

Table 1. Comparison of correlation energies of Ne atom[a]

Basis	[4s2p]	[5s3p]	[6s4p]	[4s2p1d]
SD-CI	−0.099530 (96.22)	−0.134751 (96.25)	−0.138889 (96.07)	−0.174133 (96.68)
SDTQ-CI	−0.103265 (99.83)	−0.139863 (99.90)	−0.144426 (99.90)	−0.179912 (99.89)
Full CI	−0.103437 (100.00)	−0.139998 (100.00)	−0.144576 (100.00)	−0.180108 (100.00)
SAC-A	−0.102295 (98.90)	−0.138254 (98.75)	−0.142630 (98.65)	−0.178312 (99.00)
SAC-B	−0.102045 (98.65)	−0.138019 (98.59)	−0.142365 (98.47)	−0.178120 (98.90)
	[5s3p1d]	[6s4p1d]	[4s2p2d]	[5s3p2d]
SD-CI	−0.210989 (96.60)	−0.216032 (96.41)	−0.196771 (96.46)	−0.235733 (96.27)
SDTQ-CI	−0.218155 (99.93)	−0.223882 (99.92)	−0.203767 (99.89)	−0.244661 (99.92)
Full CI	−0.218418 (100.00)	−0.224066 (100.00)	−0.203990 (100.00)	−0.244864 (100.00)
SAC-A	−0.216073 (98.93)	−0.221412 (98.82)	−0.201536 (98.80)	−0.241496 (98.62)
SAC-B	−0.215919 (98.86)	−0.221248 (98.74)	−0.201342 (98.70)	−0.241340 (98.65)

[a] The total SCF energies are [4s2p] = −128.522354, [5s3p] = 128.524013, and [6s4p] = −128.543823 hartree

Table 2. Comparison of percent correlation energy contribution of Ne atom

Basis	[4s2p]	[5s3p]	[6s4p]	[4s2p1d]	[5s3p1d]	[6s4p1d]	[4s2p2d]	[5s3p2d]
Singles and doubles	96.22	96.25	96.07	96.68	96.60	96.41	96.46	96.27
Triples	1.36	1.31	1.41	1.05	1.03	1.12	1.25	1.33
Quadruples	2.25	2.34	2.41	2.15	2.30	2.38	2.18	2.32
Quadruples and higher excitations	2.42	2.44	2.51	2.26	2.37	2.46	2.29	2.40
Disconnected terms in SAC-A	2.68	2.50	2.58	2.32	2.33	2.41	2.34	2.35
Disconnected terms in SAC-B	2.43	2.34	2.40	2.22	2.26	2.33	2.24	2.29

Correlation energies of the H_2O calculations are summarized in Table 3. Calculations were performed with a double zeta plus polarization quality at three geometries, corresponding to stretching of the two OH bonds to r_e (equilibrium bond distance), $1.5 * r_e$ and $2.0 * r_e$. A stretched water molecule was studied already with a smaller basis set [13–16]. In general the SCF reference function would certainly not be expected to give a balanced description at both the equilibrium and distorted geometires of a molecule. Thus it is a good example to examine the effects of the disconnected clusters when the SCF configuration does not have a dominant coefficient. The SAC approximation recovers about 98% of the full CI correlation energy at the equilibrium geometry. Although the SD-CI only picks up 80% of the correlation energy in the case of $2.0 * r_e$, 93% is recovered by SAC-A and 95% by SAC-B. The number of parameters of the full CI method is 6740280 and 31096 is used in the multi-reference CI. But the number of parameters to be determined in our theory equals the number of connected terms, namely only 926. This is one of the advantages of the cluster expansion approach. However, the accuracy of the SAC theory with single and double excitations does not compare well with the full CI results with the two bonds elongation. Of course, in this case of simultaneously stretching two bonds, the effects of triple and quadruple excitations are expected to increase substantially. That is, the SAC theory based on a single reference cannot overcome the

Table 3. SAC and CI calculations on H_2O with double zeta plus polarization basis, three OH bond lengths. Energies are relative to the SCF energy[a]

		Geometry	
Calculation	r_e	$1.5 * r_e$	$2.0 * r_e$
SD-CI	−0.203230 (94.05)	−0.240490 (88.77)	−0.294320 (79.55)
CAS	−0.089334 (41.34)	−0.152647 (56.35)	−0.257630 (69.63)
MRCI	−0.213566 (98.83)	−0.213566 (98.83)	−0.368231 (99.53)
Full CI	−0.216082 (100.00)	−0.270911 (100.00)	−0.369983 (100.00)
SAC-A	−0.212077 (98.15)	−0.260383 (96.11)	−0.344148 (93.02)
SAC-C	−0.212006 (98.11)	−0.260989 (96.34)	−0.350668 (94.78)

[a] SCF energies are $r_e = -76.040542$, $1.5 * r_e = -75.800494$. and $2.0 * r_e = -75.582286$ hartree

Table 4. SAC and CI energies for F^- ion. Energies are relative to the SCF energy in hartree[a]

	[4s3p]	[4s3p1d]	[4s3p2d]	[5s4p2d]
SD-CI	−0.132219 (93.66)	−0.197820 (93.98)	−0.220160 (93.75)	−0.245405 (93.31)
SDT-CI	−0.134132 (95.01)	−0.201061 (95.52)	−0.224457 (95.58)	−0.251774 (95.73)
SDTQ-CI	−0.140690 (99.66)	−0.209909 (99.72)	−0.234164 (99.72)	−0.262254 (99.72)
Full CI	−0.141176 (100.00)	−0.210493 (100.00)	−0.234828 (100.00)	−0.262994 (100.00)
SAC-A	−0.139198 (98.60)	−0.206639 (98.17)	−0.229827 (97.87)	−0.255868 (97.29)
SAC-B	−0.138702 (98.25)	−0.206477 (98.09)	−0.229667 (97.80)	−0.255625 (97.20)

[a] SCF energies are [4s3p] = −99.442848 and [5s4p] = −99.443696 hartree

poorness of the Hartree–Fock reference function. Laidig and Bartlett [15] have reported the linealized multi-reference coupled cluster calculations of H_2O at symmetric displacements and showed that the error is nearly constant as a function of displacement.

SAC and CI correlation energies for F^- ion are given in Table 4. Both SAC-A and SAC-B theories reproduce about 98% of total correlation energies for the smaller basis set. If the basis set is improved to [5s4p2d], the contribution of the higher than double excitation, especially triple excitation, increases and SAC theory recover 97% of the full CI correlation energy.

Next we performed SAC-CI calculations on the ionized state of F^- and calculated the electron affinity (EA) of F. The results are summarized in Table 5. In the SAC-CI calculations, disconnected triple (S_2T_1) and quadruple (S_2T_2) excitations are considered in addition to the connected T_1 and T_2 terms. Since the importance of higher than double excitations is more important for F^- than F, a very high percentage of the correlation must obtained to accurately compute the EA. For the largest basis set the SCF EA is in error by 1.71 eV, which is reduced by 1.45 eV with the inclusion of SD-CI correlation, but the full CI EA is sitll larger by 0.26 eV. The EA in the SAC-CI approximation agrees exceedingly well with the full CI EA. The same tendency is found in the results with the smaller basis sets. The success of the calculations of these transition energies implies that our theory can account for the proper differences in correlation energy between two states involved.

The results for ${}^1\Sigma^+$ state of HF at three geometries are summarized in Table 6. Higher excitations become more important when the HF bond is stretched and the SCF reference becomes a poorer zeroth-order description of the wavefunction.

Table 5. A comparison of the computed electron affinity of F, in eV

	[4s3p1d]	[4s3p2d]	[5s4p2d]
SCF	1.32	1.32	1.33
SD-CI	2.69	2.79	2.78
Full CI	2.90	3.03	3.04
SAC-CI	2.84	2.98	3.04

Table 6. SAC and CI calculations on HF with double zeta plus polarization basis. Energies are relative to the SCF energy.[a]

Calculation	Geometry r_e	$1.5 * r_e$	$2.0 * r_e$
SD-CI	−0.194503 (95.40)	−0.212294 (93.45)	−0.235961 (89.54)
SDT-CI	−0.196871 (96.56)	−0.216047 (95.11)	−0.244383 (92.73)
SDTQ-CI	−0.203600 (99.86)	−0.226670 (99.78)	−0.262618 (99.65)
Full CI	−0.203882 (100.00)	−0.227164 (100.00)	−0.263536 (100.00)
SAC-A	−0.201171 (98.67)	−0.222306 (97.86)	−0.251756 (95.53)
SAC-B	−0.201015 (98.59)	−0.222612 (98.00)	−0.257984 (97.89)

[a] SCF energies are $r_e = -100.047087$, $1.5 * r_e = -99.933229$, and $2.0 * r_e = -99.817572$ hartree

However, the SAC theory yields a very good approximation for the calculation of the correlation energy. Especially, SAC-B approximation recovers 98% of the full CI correlation energy at three geometries. Although the SD-CI only picks up 90% of the correlation energy in the case of $2.0 * r_e$ 95.5% is recovered by SAC-A and 97.9% by SAC-B. The difference between SAC-A and SAC-B results of 2.4% of total correlation energy comes mainly from the disconnected triply excited clusters, S_1S_2. When a molecule is at a distorted geometry, the orbital optimization, S_1, becomes important and the disconnected triple excitation of S_1S_2 also becomes important. These results indicate that the SAC theory is a good approximation for moderate variation of nuclear separation of a single bond.

To conclude our SAC and SAC-CI results give fairly good agreement with the full CI calculations with much fewer parameters. The SAC theory with single and double excitations can be quite accurate in dealing with dynamical correlation effects. However, it is based on a single reference and has difficulty in handling the nondynamical correlation effects in the case of degeneracies. Extension of the SAC theory to multiconfigurational reference functions must be the most promising approach to treat dynamical and nondynamical correlation effects. This would be worth further study and we are now continuing work in line with this subject.

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