

The Analytic Gradient with a Reduced Molecular Orbital Space for the Equation-of-Motion Coupled-Cluster Theory: Systematic Study of the Magnitudes and Trends in Simple Molecules

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The analytic gradient method for the equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) energy has been extended to employ a reduced molecular orbital (MO) space. Not only the innermost core MOs but also some of the outermost virtual MOs can be dropped in the reduced MO space, and a substantial amount of computation time can be reduced without deteriorating the results. In order to study the magnitudes and trends of the effects of the dropped MOs, the geometries and vibrational properties of the ground and excited states of BF, CO, CN, N₂, AlCl, SiS, P₂, BCl, AlF, CS, SiO, PN and GeSe are calculated with different sizes of molecular orbital space. The 6-31G* and the aug-cc-pVTZ basis sets are employed for all molecules except GeSe for which the 6-311G* and the TZV+f basis sets are used. It is shown that the magnitudes of the drop-MO effects are about 0.005 Å in bond lengths and about 1% on harmonic frequencies and IR intensities provided that the dropped MOs correspond to (1s), (1s,2s,2p), and (1s,2s,2p,3s,3p) atomic orbitals of the first, the second, and the third row atoms, respectively. The geometries and vibrational properties of the first and the second excited states of HCN and HNC are calculated by using a drastically reduced virtual MO space as well as with the well defined frozen core MO space. The results suggest the possibility of using a very small MO space for qualitative study of valence excited states.

Introduction

The equation-of-motion coupled-cluster (EOM-CC) method¹⁻³ and its analytic gradient^{4,5} are now considered as one of the most accurate and reliable method for studying potential energy surface (PES) of an electronically excited state of a molecule.⁶⁻⁸ The large demand on computational resources of the methods, however, is severely restricting their actual applications for a wider range of molecular systems.

In an effort to reduce the computational demands in the EOM-CC and its analytic gradient, Stanton and Gauss has developed a simplified EOM-MBPT(2)⁹ method based on the expansion of similarity transformed Hamiltonian through second order. An even more approximate method, P-EOM-MBPT(2)¹⁰ and its analytic gradient,¹¹ has been also developed based on the partitioning scheme of the EOM-MBPT(2) equation. Their performance and reliability are compared with other methods, such as CIS and CIS(D).^{8,11}

Meanwhile, analytic energy gradients for coupled-cluster methods¹² for a ground state have been generalized to use a reduced MO space, which permit dropping not only the innermost core MOs but also the outermost virtual MOs.¹³ We are going to refer to the extended method as the 'drop-MO method', and the original method, with all molecular orbitals participating in electron correlation, as the 'all-MO method'. Because the computation time of coupled-cluster methods depend on the high power of the number of MOs, a large portion of computation time can be reduced by dropping just a few chemically inert core MOs. The performance and usefulness of the drop-MO gradient method for the ground state have been systematically studied in the previous work.¹³ The

theoretical studies for the photoelectron spectra of Al₃ and Ag₃ as well as the stability of BCl₂⁻ and AlCl₂⁻ by using the drop-MO method have demonstrated its usefulness and reliability for a ground or low-lying electronic states.^{14,15}

The similar efficiency in studying PES of an excited state can be expected if the analytic gradient of the equation-of-motion coupled-cluster energy⁴ is extended to permit using a reduced molecular orbital space. The extension is now implemented in the ACES-II suits of programs.¹⁶ A preliminary result of the method for the first excited state of formaldehyde has already been presented in the previous paper.¹⁷ The present work is to provide some more details about the extension of the method and the results of systematic studies on the several aspects of the extended method.

The basic theoretical problems behind the extension and the ideas used in solving the problems are described in the next section of 'Theoretical considerations'. A systematic study about the magnitude and trends of the effects of the reduced MO space on geometries, vibrational properties, and excitation energies are conducted by calculating the properties of the ground and excited states of BF, CO, CN, N₂, AlCl, SiS, P₂, BCl, AlF, CS, SiO, PN, and GeSe. Another aspect of the present extension, *i.e.*, the possibility of applying the EOM-CCSD method for valence excited state of larger molecules with drastically reduced small MO space, is also examined by calculating the first and the second excited singlet states of HCN and HNC.

Theoretical Considerations

Because the present work is a rather straightforward

extension of the previous drop-MO work for a ground state,¹³ only a brief description about the main theoretical problem encountered in the modification of the all-MO analytic gradient for CCSD and EOM-CCSD energies will be described here first, and then the actual problems encountered in implementing the extended method and the strategy used in solving the problems will follow.

The correlated wave function in the coupled-cluster singles and doubles (CCSD) method, starting from a reference Hartree-Fock wave function $|\Phi_0\rangle$, is defined by using excitation operators T as following.¹²

$$\Psi_{CCSD} = \exp(T)|\Phi_0\rangle, \quad T = T_1 + T_2$$

$$T_1 = \sum_{i,a} t_i^a \{a^+ i\}, \quad T_2 = \frac{1}{2!} \sum_{i,j,a,b} t_{ij}^{ab} \{a^+ i b^+ j\}$$

After making the normal ordered Hamiltonian by subtracting the ground state, $H_N = H - \langle\Phi_0|H|\Phi_0\rangle$, the equation for the correlation energy becomes the following.

$$H_N \exp(T)|\Phi_0\rangle = \Delta E_{ground}^{CCSD} \exp(T)|\Phi_0\rangle$$

The CCSD correlation energy and wave function are calculated by solving the coupled equations obtained by projecting the above equation with respect to $\langle\Phi_0|$, $\langle\Phi_i^a|$, $\langle\Phi_{ij}^{ab}|$ after the pre-multiplication by $\exp(-T)$.

On the other hand, the wave function for an excited state in the equation-of-motion coupled-cluster theory (EOM-CC) is defined by applying excitation operators R , which has the same form as T , on the coupled-cluster wave function for the ground state, and using the commutation relation between excitation operators.³

$$|\Psi_{EOM-CC}\rangle = R \exp(T)|\Phi_0\rangle = \exp(T)R|\Phi_0\rangle$$

The equation for the excitation energy can be written with the similarity transformed Hamiltonian as the following:

$$\exp(-T)H_N \exp(T)R|\Phi_0\rangle = \bar{H}R|\Phi_0\rangle$$

$$= \Delta E^{EOM-CC} R|\Phi_0\rangle$$

Then an eigenvalue of the similarity transformed normal ordered Hamiltonian, $\bar{H} = \exp(-T)H_N \exp(T)$, is the energy of the excited state.

When the correlation energy and excitation energy at a given geometry are the target of a calculation method, the calculation with a reduced MO space can be done just by restricting the i, j and a, b in the T_1 and T_2 operator to be within the reduced MO space, *i.e.*, just by dropping the selected core and/or virtual molecular orbitals in the transformation of two-electron integrals. That is why we often refer to the method as the drop-MO method.

Once the correlation and excitation energies are defined and calculated by using the reduced MO space, then the gradients of the energies are also defined within the same reduced MO space. The following equation for the analytic gradient in the reduced MO space is exactly the same form as in the all MO space, because nothing has been altered in all the equations and procedures for the analytic gradient of

the correlation and the excitation energies.

$$\frac{\partial(\Delta E^{CCSD} \text{ or } \Delta E^{EOM-CCSD})}{\partial\chi} = \sum_{p,q} D_{pq} \frac{\partial f_{pq}}{\partial\chi} +$$

$$\sum_{p,q,r,s} \Gamma(pq,rs) \frac{\partial \langle pq||rs\rangle}{\partial\chi}$$

The only difference is that the MO indices, p, q, r , and s , are now restricted to the MOs participating in the reduced MO space. The one-particle reduced density D_{pq} and the two-particle reduced $\Gamma(pq,rs)$ density are also defined within the reduced MO space, and their actual forms depend on the level of excitations, the reference function, and the target electronic state.^{4,18-24}

The derivatives in the above equation, however, lead to orbital response terms dependent on all MOs. Because active MOs ϕ_p are linear combinations of basis atomic orbitals ϕ_μ ,

$$\phi_p = \sum_{\mu} \phi_{\mu}$$

the orbital response, with respect to an external perturbation χ , is defined by using the coupled-perturbed Hartree-Fock (CPHF) coefficients U_{vp}^{χ} ,²⁵

$$\frac{\partial c_{\mu p}}{\partial\chi} = \sum_{\nu} U_{\nu p}^{\chi} c_{\mu\nu}$$

where the index ν now span over all MOs including frozen MOs. The important fact is that the response of each active MO is defined within all MO space including the dropped MOs even when some MOs are dropped in constructing the reduced MO space. This is the main problem for the analytic gradient with a reduced MO space.²⁶ The explicit development of the above equations into a computationally tractable form is given in our previous work.¹³ The only difference of the present work for an excited state from the previous one for a ground state is the explicit forms of D_{pq} and $\Gamma(pq,rs)$ which are defined by the Eqs. (38) and (39) of the original work.⁴ All other steps in the derivations are exactly the same as before.¹³ Instead of presenting details of the derivations once again, only the three important aspects of the derivations and implementations, distinctive in the drop-MO method, are worthy to be given here.

The first problem is the necessity of the following two-electron integrals,

$$\langle pI||qJ\rangle, \langle pI||qr\rangle, \langle pA||qJ\rangle, \langle pA||qr\rangle,$$

where the p, q, r , and s refer to the generic active occupied and virtual MOs. On the other hand, the I, J refer to dropped occupied MOs while the A stands for dropped virtual MOs. Inspection of Eq. (11) of the previous work¹³ shows that these integrals are indispensable for the construction of the one-particle intermediates, even though these integrals are not required to solve the CC and the equations. These additional integrals have to be generated by a separate integral transformation.

The second problem arises from the fact that the correla-

tion and excitation energies are not invariant to mixing the dropped and active MOs. It implies that the CPHF coefficient between the dropped and active MOs cannot be obtained by the following relation, which stems from the orthonormality condition and causes the mixing between active and dropped MOs.²⁶

$$U_{vp}^{\chi} = -\frac{1}{2}S_{vp}^{\chi}$$

We may use the above relation for the CPHF coefficients between dropped occupied MOs, between active occupied MOs, between active virtual MOs, and between dropped virtual MOs while the CPHF coefficients between dropped and active MOs are handled by using a separate Z-vector equation. Such partitioning of the CPHF blocks, however, has little advantage and causes just an additional complexity in programming. Instead of using these relations, the canonical property of orbitals are used for the solution of the Z-vector equation not only for the occupied-virtual block, but also for the occupied-occupied and virtual-virtual parts. More explicitly, the above equation from the orthonormality is never used in the present drop-MO method.

There is the third problem if restricted open-shell Hartree-Fock (ROHF) orbitals are used. The standard ROHF orbitals satisfy the Brillouin condition for the Z-vector equation of the occupied-virtual part, but do not satisfy the canonical condition for the occupied-occupied or virtual-virtual part. In order to prevent the mixing of dropped and active occupied (or virtual) orbitals, as mentioned in the above second problem, the Z-vector equation for the occupied-occupied or the virtual-virtual blocks have to be solved by imposing the semicanonical condition on the α - and the β -spin occupied and virtual orbitals. In other words, the standard orbitals can not be used here. This semicanonical condition has been used to obtain the analytic gradients for the ROHF-CCSD(T) methods,²⁴ and we have utilized exactly the same technique here. Simply saying the technique, the procedure to solve the ROHF Z-vector equation has to be modified as the following. At first the orbital-response densities in terms of standard orbitals are transformed to those in terms of semicanonical orbitals by using the transformation matrices which rotate the standard orbitals into the semicanonical representation. After the contraction of the orbital-response densities with two-electron integrals and Fock matrix elements are performed in the semicanonical representation, the contracted intermediate matrices are transformed back into the standard orbitals. Then the updated orbital-response matrices are constructed again, and these steps are repeated until convergence is achieved. It has to be emphasized here that the drop-MO analytic gradient with ROHF orbitals is possible only with semicanonical ones.

The above considerations for the analytic gradient of an excite state have been implemented into the ACES II program,¹⁶ and the geometry optimization for an excited state is now possible with the equation-of-motion coupled-cluster singles and doubles level of theory. First order properties of the excited state also can be computed with a reduced MO

space without any further considerations. The second derivatives for harmonic frequencies are obtained by numerical differentiation of the first analytic gradients.

Results and Discussions

The first purpose of this section is to make a systematic study on the performance of the present extension and to get an expected magnitude and trends of the effects of the dropped MOs on bond lengths, angles, harmonic frequencies, IR intensities, and excitation energies of excited states. We want to reduce the computation times in the application of the EOM-CCSD gradient method by dropping core molecular orbitals with little ambiguity. To minimize such ambiguity, only the MOs corresponding to 1s atomic orbitals (AOs) of the first row atoms, 1s, 2s, and 2p AOs of the second row atoms, and 1s, 2s, 2p, 3s, and 3p AOs of the third row atoms will be dropped. The possibility of dropping MOs corresponding to 3d AOs of the third row atoms will also be discussed with the results for the GeSe molecule. The plausibility of the drop-MO method with drastically reduced MO space is the second point of this section, which will be delivered with the results for the first and the second excited states of HCN and HNC.

The bond lengths, harmonic frequencies, IR intensities, and adiabatic excitation energies are calculated for the ground state and excited states of several diatomic molecules. Because the present work is not to study any unknown electronic state but to investigate the drop-MO effects, only the excited states well characterized by experiments are studied here. In order to cover as wide as possible chemical bonds with as simple as possible diatomic molecules, a variety combinations among the second and third row main group elements are selected. The Table 1 is the results for molecules (BF, CO, CN, N₂) consisted of the first row atoms while the Table 2 is for molecules (AlCl, SiS, P₂) of the second row atoms. The results for molecules (BCl, AlF, CS, SiO, PN) composed of one first row atom and another second row atom are given in Table 3. On the other hand, Table 4 for GeSe is to show the results with different selection of frozen core MOs. The ground and excited doublet states of CN are calculated with the ROHF orbitals, while the singlet ground and excited states of all other molecules are calculated with the RHF orbitals. We consider the 6-31G* basis is the minimal size for the study of an excited state while the aug-cc-pVTZ basis is the proper choice for quantitative theoretical values. The Cartesian six *d*-functions are used for 6-31G* and 6-311G* basis sets²⁷ while spherical five *d*- and seven *f*-functions are used for aug-cc-pVTZ²⁸ and the TZV + *f*²⁹ basis sets. In order to emphasize the performance of the present method, the values obtained by using the drop-MO method and the differences (Δ) from the all-MO results are presented in the tables, and compared with experimental values.³⁰ The designations, drop-MO(n_c/n_v) and drop-MO(n_c), are used to represent that the n_c innermost occupied and the n_v outermost virtual molecular orbitals are dropped in the CCSD and the EOM-CCSD calculations. The n_c can be eas-

Table 1. The bond length (r in Å), harmonic frequency (ω in cm^{-1}), IR intensity (Int. in km/mol), and adiabatic excitation energy (T_e in eV) for the ground and the excited states of BF, CO, CN, and N_2 by using the drop-MO method. The difference of the drop-MO result from the all-MO method is designated by $\Delta = (\text{all-MO result}) - (\text{drop-MO result})$

		drop-MO	6-31G*		aug-cc-pVTZ		Exptl. ^a	
			(2/0)	Δ	(2/1)	Δ		
BF	$X^1\Sigma^+$	r	1.2831	-0.0024	1.2701	-0.0072	1.2626	
		ω	1392	+8	1401	+24	1402	
		Int.	158.7	-1.0	182.4	-2.4		
	$A^1\Pi$	r	1.3474	-0.0018	1.3108	-0.0073	1.3038	
		ω	1191	+9	1259	+22	1265	
		Int.	39.9	+0.2	119.8	+3.8		
	CO	$X^1\Sigma^+$	r	1.1421	-0.0009	1.1275	-0.0034	1.1283
			ω	2217	+6	2230	+13	2170
			Int.	64.1	-0.01	76.9	-0.3	
$A^1\Pi$		R	1.2536	-0.0016	1.2303	-0.0065	1.2353	
		ω	1552	+7	1544	+39	1518	
		Int.	4.9	-0.3	22.0	-0.1		
CN		$X^2\Sigma^+$	r	1.1811	-0.0011	1.1680	-0.0049	1.1718
			ω	2142	+5	2138	+28	2068
			Int.	17.0	+0.2	22.9	+0.8	
	$A^2\Pi$	r	1.2379	+0.0012	1.2270	-0.0057	1.2333	
		ω	1895	-5	1887	+25	1812	
		Int.	27.4	0.0	28.8	+0.1		
	$B^2\Pi$	r	1.1664	-0.0011	1.1511	-0.0047	1.1506	
		ω	2168	+7	2199	+33	2164	
		Int.	166.2	0.1	192.0	+0.8		
N_2	$X^1\Sigma^+$	r	1.1135	-0.0006	1.0965	-0.0036	1.0977	
		ω	2412	+4	2423	+25	2359	
		Int.	17.0	+0.2	22.9	+0.8		
	$A^1\Pi$	r	1.2219	-0.0009	1.2066	-0.0048	1.2203	
		ω	1852	+4	1838	+17	1694	
		T_e	8.751	+0.009	8.789	+0.051	8.590	

^aReference 30.

ily determined prior to calculations based on the shell structure of atoms in a molecule, while the n_v can be determined based on virtual orbital energies after the Hartree-Fock calculations. Only a few artificially high lying virtual orbitals are dropped at present, and the results in Table 1-4 are almost not changed by either including or dropping them.

From the values in Tables 1 and 2, it can be seen that the effects of the drop-MOs are small and almost the same in magnitude for both the ground and the excited state. Especially when the 6-31G* basis sets are used, the difference between results by the drop-MO and the all-MO method are about 0.003 Å for bond lengths, 10 cm^{-1} for harmonic frequencies, and 0.5 km/mol for IR intensities. It also can be noted that, except the $A^2\Pi$ state of CN with the 6-31G* basis, bond lengths increase while harmonic frequencies decrease by dropping core orbitals which means a little more flat potential curve, but the differences are very small as we

Table 2. Results for AlCl, SiS, and P_2 . All symbols and entries have the same meaning as in Table 1

		drop-MO	6-31G*		Aug-cc-pVTZ		Exptl. ^a		
			(10/0)	Δ	(10/0)	Δ			
AlCl	$X^1\Sigma^+$	R	2.1402	-0.0022	2.1577	-0.0116	2.1301		
		ω	497	+1	475	+7	481		
		Int	133.1	+0.1	132.8	-0.6			
	$A^1\Pi$	R	2.1777	-0.0029	2.1519	-0.0129	2.067		
		ω	402	+2	449	+12	450		
		Int	6.7	+0.2	21.4	+1.7			
		T_e	4.972	0.000	4.762	-0.005	4.743		
		SiS	$X^1\Sigma^+$	R	1.9390	-0.0020	1.9408	-0.0074	1.9293
				ω	771	+2	765	+9	750
Int	37.0			+0.3	765	+9			
$D^1\Pi$	R	2.0761	-0.0035	2.0697	-0.0134	2.0591			
	ω	534	+3	533	+13	513			
	Int	45.9	-0.1	36.9	-1.1				
	T_e	4.511	0.002	4.366	0.019	4.343			
	P_2	$X^1\Sigma_g^+$	R	1.9088	-0.0022	1.8997	-0.0070	1.8934	
			ω	794	+3	806	+12	781	
Int			166.2	0.1	192.0	+0.8			
$A^1\Pi_g$	R	1.9919	-0.0027	1.9865	-0.0096	1.9887			
	ω	665	+2	663	+12	619			
	T_e	4.568	-0.002	4.351	+0.011	4.279			

^aReference 30.

emphasize here. The adiabatic excitation energies are reduced by the drop-MO effect in most cases and increased in some cases, but the magnitude are so small to make any argument here, *i.e.*, less than 0.002 eV. The drop-MO effects turn out to become a little larger when the aug-cc-pVTZ basis sets are used. This may be due to the fact that the aug-cc-pVTZ basis sets are optimized not for core part but for valence part. We expect that the difference can be reduced much if a tight basis function is added to the family of cc-pVXZ basis, or if the basis sets are re-optimized for core part. Such possibilities, however, are not explored in this work. In spite of that, the calculated results by using the drop-MO method in conjunction with the aug-cc-pVTZ basis are quite good in agreement with experimental values. The magnitude of the drop-MO effects in Table 2 for molecules with the second row atoms are roughly twice of those in Table 1 for molecules of the first row atoms. On the other hand, the magnitude in Table 3 for molecules with one first row atom and another second row atom turn out to be between those in Table 1 and Table 2. It is worth to notice that the computation times are reduced down to about a factor of 1/3, 1/27, and 1/10 for molecules in Table 1, Table 2, and Table 3, respectively, by using the drop-MO method.

One of the important things here is that the magnitude and trend of the drop-MO effects are almost the same for both the ground and the excited states, and the magnitudes are still small enough, regardless of the molecules and basis sets. Such features hold for all molecules through Table 1 to 3. Similar magnitude and trends are expected to hold for any molecules not explicitly studied here.

The results in Table 4 show another interesting point.

Table 3. Results for BCl, AlF, CS, SiO, and PN. All symbols and entries have the same meaning as in Table 1

	Drop-MO	6-31G*		Aug-cc-pVTZ		Exptl. ^a	
		(6/0)	Δ	(6/0)	Δ		
BCl $X^1\Sigma^+$	R	1.7271	-0.0030	1.7278	-0.0141	1.7159	
	ω	862	+3	836	+27	839	
	Int	245.3	-0.9	254.1	+6.4		
	$A^1\Pi$	R	1.7335	-0.0034	1.717	-0.0142	1.6894
		ω	779	+7	823	+34	849
		Int	15.7	+0.4	14.0	+0.4	
T_e	4.980	-0.017	4.661	-0.028	4.556		
AlF $X^1\Sigma^+$	R	1.6679	+0.0008	1.6744	-0.0060	1.6544	
	ω	842	-1	787	+8	802	
	Int	88.5	+0.4	120.4	-0.6		
	$A^1\Pi$	R	1.6837	+0.0018	1.6679	-0.0064	1.6485
		ω	775	-1	792	+9	804
		Int	17.7	-0.1	65.4	+0.7	
T_e	5.767	-0.003	5.440	-0.001	5.449		
CS $X^1\Sigma^+$	R	1.5425	-0.0015	1.5375	-0.0063	1.5349	
	ω	1329	+5	1324	+12	1285	
	Int	71.7	0.0	81.8	-0.1		
	$A^1\Pi$	R	1.5939	-0.0023	1.5780	-0.0085	1.5739
		ω	1053	+6	1080	+19	1073
		Int	3.6	-0.3	0.2	+0.3	
T_e	5.211	-0.003	4.956	+0.001	4.823		
SiO $X^1\Sigma^+$	r	1.5236	-0.0001	1.5173	-0.0043	1.5097	
	ω	1267	+3	1270	+10	1242	
	Int	26.6	+0.1	54.9	+0.4		
	$A^1\Pi$	r	1.6414	-0.0013	1.6222	-0.0073	1.6206
		ω	894	+6	899	+4	853
		Int	59.8	+0.2	77.4	-1.3	
T_e	5.520	-0.003	5.359	+0.018	5.311		
PN $X^1\Sigma^+$	r	1.5015	-0.0008	1.4943	-0.0054	1.4909	
	ω	1363	+7	1384	+11	1337	
	Int	3.1	0.0	1.8	-0.1		
	$A^1\Pi$	r	1.5569	-0.0014	1.5461	-0.0065	1.5467
		ω	1163	+5	1177	+10	1103
		Int	38.8	+0.3	66.2	+1.9	
T_e	5.360	-0.002	5.068	+0.010	4.935		

^aReference 30.

Because third row atoms have 3d atomic orbitals, it is interesting to see the effects of dropping MOs corresponding to 3d AOs. In order to make direct comparisons among results with different MO space, all the calculated values are given in Table 4. The TZV + f basis is constructed by adding one set of *f*-functions to the TZV basis.²⁹ The exponents of the *f*-functions are 0.2670 and 0.4000 for Ge and Se, respectively. The MOs corresponding to 1s, 2s, and 2p AOs are dropped in the drop-MO(10) method, and additional MOs corresponding to 3s and 3p AO are also dropped in the drop-MO(18) method. The drop-MO(28) method is what even the MOs mainly consisted of 3d AOs are dropped.

The differences between the drop-MO(18) and the all-MO results are noticeably smaller for this molecule consisted of the third row atoms, which demonstrate the usefulness of the

Table 4. Results for the ground and the first excited states of GeSe by using the CCSD and the EOM-CCSD method

	$X^1\Sigma^+$			$A^1\Pi$			
	r	ω	Int	r	ω	Int	T_e
6-311G*							
All-MO	2.1547	412	17.5	2.3146	277	21.0	3.908
Drop-MO(10/2)	2.1550	412	17.5	2.3153	277	21.0	3.908
Drop-MO(18/12)	2.1511	413	17.3	2.3127	276	20.9	3.928
Δ_{18}^a	+0.0036	-1	+0.2	+0.0019	+1	+0.1	-0.020
Drop-MO(28/12)	2.1625	409	17.0	2.3283	272	21.4	3.903
Δ_{28}^b	-0.0078	+3	+0.5	-0.0137	+5	-0.4	+0.005
TZV + f							
All-MO	2.1338	416	13.6	2.2880	283	21.1	3.750
Drop-MO(10/0)	2.1341	416	13.6	2.2885	283	21.2	3.750
Drop-MO(18/0)	2.1333	416	13.5	2.2903	280	21.2	3.760
Δ_{18}^a	+0.0005	0	+0.1	-0.0023	+3	-0.1	-0.010
Drop-MO(28/0)	2.1490	409	13.0	2.3141	273	21.8	3.718
Δ_{28}^b	-0.0152	+7	+0.6	-0.0261	+10	-0.7	+0.032
Exptl. ^c	2.1346	409		269			3.824

^a Δ_{18} = (all-MO result) - (drop-MO(18) result). ^b Δ_{28} = (all-MO result) - (drop-MO(28) result). ^cReference 30.

present drop-MO methods. The unexpected small differences seem to come from the counter poisoning of the drop-MO effects of inner shells in these cases. In other words, the bond lengths are slightly increased from the all-MO to the drop-MO(10), and then decreased by the drop-MO(18), except the $^1\Pi$ state with the TZV + f basis in which bond length increases monotonically by the drop-MO effects but the result shows still very small difference, -0.0023 Å. As the result, all the values in Table 4 by the drop-MO(18) method are almost the same as those by the all-MO method, *i.e.*, the differences (Δ_{18}) are fairly small. The computation time to solve the CCSD and the EOM-CCSD equations of the drop-MO(18) and the drop-MO(28) methods requires less than 10% and 0.5%, respectively, of the all-MO method. Though the results by the drop-MO(28) method are also reasonably good enough and the differences (Δ_{28}) are relatively small in these cases, the differences could be larger in other cases, especially for bond angles and bending vibrations.

Table 5 and 6 are showing a somewhat different aspect of the present method. The geometries and vibrational properties of the first and the second excited singlet states of HCN and HNC are calculated by the EOM-CCSD with different MO spaces. The pure spherical *d*- and *f*-functions are used in the DZP and TZ2P basis sets. The details of the DZP and TZ2P basis sets are given elsewhere.³¹ When only two innermost MOs are dropped, the magnitudes of the drop-MO effects are almost the same as shown in Table 1. It should be noted that the drop-MO effects on bond angles and bending frequencies are also very small. The main point here is that the results obtained by the drop-MO(2/24) with the DZP basis and the drop-MO(2/48) with the TZ2P basis. Such drastically small MO space means that only six lowest virtual molecular orbitals are included in the reduced MO spaces. More than 60% computation time has already been

Table 5. The stationary point bond lengths (r in Å), angle (\angle in degrees), harmonic frequencies (ω in cm^{-1}), IR intensities (Int in km/mol), dipole moments (μ in Debye), and vertical excitation energies (v_e in eV) of the lowest two excited singlet states, $\tilde{A}^1 A''$ and $\tilde{B}^1 A'$, of HCN

Basis Method	DZP			TZ2P		
	Drop-MO		Drop-MO	Drop-MO		Drop-MO
	$\Delta(2/2)^a$	(2/2)	(2/48)	$\Delta(2/2)^a$	(2/2)	(2/48)
HCN $\tilde{A}^1 A''$						
r_{CN}	-0.0012	1.3036	1.2864	-0.0020	1.2892	1.2808
r_{CH}	-0.0015	1.1380	1.1691	-0.0010	1.1205	1.1157
\angle_{HCN}	+0.1	121.5	126.5	+0.1	121.8	124.5
ω_1	+3	920	969	+5	940	983
ω_2	+5	1558	1711	+6	1557	1706
ω_3	+9	2020	2215	0	2686	2558
Int ₁	-0.5	134.4	115.0	-0.9	142.0	150.1
Int ₂	0	22.7	71.1	+0.1	15.9	46.8
Int ₃	-1	101.8	204.9	-0.5	46.3	63.6
μ	0.008	1.822	2.093	+0.14	1.851	2.133
v_e	0.01	5.37	5.80	+0.02	5.39	5.79
HCN $\tilde{B}^1 A'$						
r_{CN}	-0.0017	1.3035	1.2966	-0.0039	1.2793	1.2973
r_{CH}	-0.002	1.1743	1.1950	-0.0027	1.1511	1.1870
\angle_{HCN}	+0.3	98.2	107.0	+1.1	103.5	100.5
ω_1	-13	617	381	-25	449	691
ω_2	+6	1360	1303	+15	1397	1224
ω_3	+9	2252	1921	+11	2356	1713
Int ₁	-0.4	2.6	20.7	+6.7	16.2	42.6
Int ₂	+0.4	11.5	83.6	+3.6	15.4	42.7
Int ₃	-1.7	113.1	124.1	-1.2	43.6	130.1
μ	+0.002	1.070	1.058	-0.004	1.126	1.049
v_e	+0.03	5.13	5.51	+0.06	5.45	5.50

^a $\Delta(2/2)$ = (all-MO result)-(drop-MO(2/2) result).

reduced just by dropping only the two core MOs. In addition to that, by leaving only six virtual MOs, the computation times for solving the CCSD and the EOM-CCSD equations became about one hundredth and one thousandth for the case with DZP and TZ2P basis, respectively! We are not saying that the total computation time is actually reduced so much because the computation times for other steps such as integral calculations, Hartree-Fock calculations, and integral transformation are now becoming dominant time-consuming steps. But it is clear that the calculations for excited state are becoming extremely faster with such drastically reduced MO space. Of course the results with such small MO space are not good enough for a quantitative purpose. The results, however, are not so bad and are qualitatively reasonable for geometries and harmonic frequencies. Needless to say such small MO space can be used only for valence excited states. Considering the fact that most photochemical phenomena are related to valence excited state, the present results suggest that the EOM-CCSD method, with such small MO space, can be a new alternative method for a qualitative study of photochemical processes. This viewpoint has already been suggested in the previous communication for

Table 6. Results for HNC. All entries and symbols have the same meaning as in Table 5

Basis Method	DZP			TZ2P		
	Drop-MO		Drop-MO	Drop-MO		Drop-MO
	$\Delta(2/2)$	(2/2)	(2/48)	$\Delta(2/2)$	(2/2)	(2/48)
HNC $\tilde{A}^1 A''$						
r_{NN}	-0.0016	1.1446	1.4330	-0.0027	1.3981	1.4200
r_{CH}	-0.0009	1.0450	1.0421	-0.0007	1.0342	1.0073
\angle_{HNC}	+0.1	109.2	108.5	+0.1	109.5	108.7
ω_1	+2	1105	1053	+1	1120	1159
ω_2	+3	1211	1153	+4	1214	1173
ω_3	+5	3202	3111	+3	3234	3541
Int ₁	-0.1	103.3	241.0	-0.8	131.6	149.1
Int ₂	+0.6	38.3	32.8	+1.7	17.5	2.8
Int ₃	-0.2	20.1	37.5	0	2.2	59.7
μ	+0.007	2.151	2.154	+0.012	2.202	2.113
v_e	+0.02	4.37	4.08	+0.03	4.52	4.41
HNC $\tilde{B}^1 A'$						
r_{CN}	-0.0021	1.3329	1.3571	-0.0035	1.3123	1.3452
r_{NH}	-0.0009	1.0551	1.0535	-0.0005	1.0421	1.0165
\angle_{HNC}	0	108.0	108.9	+0.2	108.4	112.1
ω_1	+2	1119	1030	-1	1142	986
ω_2	+4	1241	1217	+7	1250	1253
ω_3	+4	2981	2859	-2	3056	3311
Int ₁	-0.9	28.4	105.0	-3.2	30.2	129.5
Int ₂	+2	13.9	100.6	+5.2	30.8	33.1
Int ₃	+0.2	72.8	135.9	+0.7	15.0	133.6
μ	-0.003	1.535	1.694	-0.053	1.515	1.713
v_e	+0.02	5.38	5.30	+0.02	5.56	5.77

the first excited state of formaldehyde,¹⁷ in which the comparison with the results by CIS are also given. The present method with such small MO space, however, may be not robust enough for simple mind applications. More studies for the reliability of the method and the possibility to improve the results of using such small MO space by re-optimizing the virtual MO space, somehow, are opened at this point.

Conclusions

The analytic gradient method for an excited state with the equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) theory is extended to use a reduced molecular orbital (MO) space, by which a substantial amount of computation time can be reduced without deteriorating calculated results. The systematic study for the magnitudes and trends of the drop-MO effects on geometries, vibrational properties, and adiabatic excitation energies are conducted. When the MOs corresponding to chemically inert atomic core orbitals are dropped to make the reduced MO space, the differences between the results with the drop-MO and the all-MO space are very small and almost the same for both the ground and excited electronic states. Also shown is that the drop-MO method with drastically reduced MO space, which means

much faster calculations, has the possibility of providing qualitatively reasonable information for valence excited states involved in many photochemical phenomena.

The present results are quite encouraging that the high reliability of the EOM-CCSD method can be applied for wider range of molecules. The magnitude and trends of the dropped MOs on geometry and vibration frequencies, presented in this work, can be an useful reference for actual applications on larger molecules.

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