THE FOCK-SPACE COUPLED-CLUSTER METHOD IN THE CALCULATION OF EXCITED STATE PROPERTIES

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Dedicated to Professor Josef Paldus on the occasion of his 70th birthday.

Our recently developed intermediate Hamiltonian Fock-space coupled-cluster (FS-CC) method with singles and doubles is applied to calculation of equilibrium geometries, harmonic frequencies and adiabatic excitation energies for some excited states of N_2 and CO. Due to the intermediate Hamiltonian formulation, which provides a robust computational scheme for solving the FS-CC equations, and the efficient factorization strategy, relatively large basis sets and reference spaces are employed permitting a comparison of calculated properties with experimental data.

Keywords: *Ab initio* calculations; Multireference coupled-cluster methods; Properties of excited states; Intermediate Hamiltonian FS-CCSD; Quantum chemistry.

The coupled-cluster (CC)[1–3] method, which for many years has been primarily considered as an efficient tool for description of the energetics and properties of the ground state, is now gaining importance also in the studies devoted to excited states. This path of development of the CC theory is due, on one hand, to successful combining of the ground state CC wave function with the equation-of-motion (EOM) treatment of excited states, and, on the other, to the significant progress made in the multireference (MR) formulations of the CC theory.

The EOM-CC approach[4], which is to a large extent equivalent to the coupled cluster linear response (LRCC) theory[5], offers a pretty straightforward computational scheme which is a CI-like approach applied to a similarity-transformed Hamiltonian. The transformation is defined by the ground state single-reference coupled cluster wave operator. The EOM-CC excitation energies, in spite of being size-intensive[6], are contaminated with dis-

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connected contributions and this is an inherent shortcoming of the method[7,8]. Size-intensity is a concept introduced to characterize methods for calculation of transition energies. It can be considered as analogous to separability conditions in energy calculations. Both proper separability of the energy and size-intensivity of excitation energies, are only necessary but not sufficient conditions for size-extensivity. Size-extensivity is a more general property. It is convenient to relate size-extensivity to connectivity of the energy or excitation energy expressions if possible. Separability conditions and size-intensivity are associated with considering specific features of a method while applied to systems consisting of noninteracting subsystems. Such considerations provide us with useful information about the method but are not able to give its full characteristic.

As alternatives to the EOM-CC approach to excited states, the multireference formulations of the coupled cluster method[9,10] can be considered. Distinguishing two types of electron correlation, the MR-CC methods assume a different treatment of each of them. Each type of electron correlation is associated with one of two subspaces in which the functional space is partitioned. The reference space, containing all strongly interacting zeroth-order functions, corresponds to static correlation effects while its orthogonal complement is related to dynamic correlation. Eigenvalues of the so-called effective Hamiltonian, whose action is restricted to the reference space, constitute a subset of eigenvalues of the Hamiltonian. The effective Hamiltonian contains the so-called wave operator which provides information about dynamic correlation. The MR-CC approaches introduce cluster expansions for the wave operator whose efficiency has been proved in single-reference cases. The standard MR-CC formulations lead to a two-step procedure of finding solutions of the Schrödinger equations. In the first step cluster amplitudes must be determined. The second step is the construction of the effective Hamiltonian and its diagonalization. It follows that to preserve full size-extensivity of such an approach not only the cluster amplitudes and the effective Hamiltonian should be represented by connected quantities but also diagonalization of the effective Hamiltonian should not generate disconnected contributions to the energies in the second step.

Although the first multireference CC approaches were proposed very soon after introduction of the coupled cluster theory[11–14] to the quantum chemistry[1], it took a long time to obtain MRCC formulations suitable for the black-box-type implementations. The original MR-CC approaches are formally complicated and numerically expensive since the calculation must be performed for several states at a time. Moreover, the calculations are often plagued with the so-called intruder state problem as well as with the problem of multiple solutions. Within one of the two basic MR-CC formulations, the Fock-space (or valence-universal) CC method[9,11–13], most of these problems can be efficaciously overcome by the intermediate Hamiltonian (IH)[15,16] reformulation of the method[17]. In addition to several formal simplifications, the IH version of the Fock-space (FS) CC method provides a very efficient single-root algorithm for solving the CC equations[17–19], which is very resistant to intruders[20]. The standard formulation of the Fock-space CC approach, involving iterative procedures for solving equations for cluster amplitudes, turned out to be very sensitive to intruder states, which frequently results in poor convergence or divergence[21]. Contrary to that, the IH approach is a very elegant and computationally attractive scheme which replaces the standard two-step procedure of obtaining cluster amplitudes, and constructing and diagonalizing the effective Hamiltonian with a simple one-step procedure of solving the eigenvalue problem for the intermediate Hamiltonian[17].

The coupled cluster-based approaches are being more and more frequently used in calculations of molecular properties for excited states. That mainly concerns the EOM-CC and SimilarityTransformed EOM (STEOM) methods[22]. Both approaches usually use analytical gradients[23,24]. The EOM-CC method has been employed by Sattelmeyer et al.[25] to compute the equilibrium geometry and harmonic frequencies for low-lying excited states of several diatomics. The standard CC scheme with singles and doubles (CCSD) plus some approximate variants including triples (CC3 [26] and CCSDT-1 [27]) was used. Results for larger molecular systems obtained with EOM [28] and STEOM [29] have been also reported. Larsen et al.[30] compared the equilibrium geometry and harmonic frequencies obtained with different versions of LRCC with the full CI results for N_2 molecule. The approximations considered ranged from CIS, CC2, CCSD up to CC3 [26,31]. The full EOM-CCSDT treatment of equilibrium geometry and adiabatic excitation energies have been reported in ref.[32] for three lowest excited states of CO and N_2 with several basis sets including quadruple-zeta. Pal and coworkers employed analytical gradients[33] for the FS-CCSD approach to compute dipole moments for both singlet and triplet excited states for H_2O [34] and the radicals like OH, OOH and COOH [35].

The aim of the current work is to investigate the performance of the Fock-space CCSD method in the calculation of the equilibrium geometry (R_e) and harmonic frequencies (ω) of low-lying excited states of N_2 and CO molecules. Evaluation of the equilibrium geometry automatically provides adiabatic excitation energies. The Fock-space CCSD values will be confronted with the EOM-CCSD quantities and related to the experimental data.

METHOD

A common feature of all possible versions of the Fock-space CC approach is the use of single Fermi vacuum to define cluster operators. In the FS-CCSD method used in this calculation, the Hartree–Fock (HF) determinant is selected to be a Fermi vacuum. Due to this selection the method is designed to provide excitation energies from the ground state which should be relatively well described by the single-reference CCSD method[36].

Multireference CC formulations are obtained by replacing the single-reference determinant with a multidimensional reference space. The reference space determinants enter the MR-CC expansion directly while the orthogonal space contributions are generated by the second-quantized cluster excitation operators, or their products, acting on the reference space[9,10]. There are two problems associated with the use of single Fermi vacuum. The first one is the redundancy of the cluster operators meaning that the same excitation can be generated by more than one cluster operator, thus the number of cluster amplitudes that must be determined exceeds the number of equations that can be obtained by considering the CC equations with the fixed number of particles (or quasiparticles in our version of the FS-CC method). This problem has been solved by introducing valence-universal strategy of solving the equations, which introduces a sequence of sets of additional equations generated by problems with a lower number of quasi-particles[9]. That gives the method a Fock-space character. The other problem is associated with the fact that, contrary to the single-reference case, excitation operators defined with respect to a single vacuum, in general, do not commute. The reason is that, in addition to quasi-particle creation operators, they can have quasiparticle annihilation operators. This problem has been solved by introducing the normal-ordered form of the exponential expansion which prevents contractions between cluster operators[12,13].

The states we want to describe are low-lying excited states dominated by single excitations with respect to the HF determinant. Thus, selecting active occupied and active unoccupied orbital levels, the reference space is spanned by determinants obtained from the HF one by single excitations from active occupied to active unoccupied spin orbitals (by creating one active hole and one active particle in the HF determinant). The reference space is denoted by $M^{(1,1)}$ and corresponds to the problem with two quasi-particles. Contributions from its orthogonal complement are generated by cluster operators. The cluster operators that have to be considered at the (1,1) level can contain at most two active quasi-particle annihilation operators, which is the number of quasi-particles in the reference determinants. The FS-CCSD approximation assumes the inclusion of one- and two-particle components in the cluster operator *S*; so for each type of cluster operators we have

$$T = T_1 + T_2 \,, \quad T \equiv S^{(0,0)} \tag{1}$$

$$S^{(1,0)} = S_1^{(1,0)} + S_2^{(1,0)} \,, \qquad S^{(0,1)} = S_1^{(0,1)} + S_2^{(0,1)} \tag{2}$$

$$S^{(1,1)} = S_2^{(1,1)} \tag{3}$$

where the superscript (*i*, *j*) is used to denote the number of active particle (*i*) and hole (*j*) annihilation operators in the cluster operators. The subscript denotes the particle-rank of the operator. It must be mentioned that the $S^{(1,1)}$ operator does not have to contain deexcitation operators (excitations leading from the reference space to the HF determinant)[7]. The standard FS-CCSD equations for the cluster amplitudes at the (1,1) level can be written in the form[17]

$$P_{\mathrm{I}}^{(1,1)}(1 - X^{(1,1)})\overline{H}(1 + X^{(1,1)})P^{(1,1)} = 0 \tag{4}$$

with

$$\overline{H} = \mathrm{e}^{-T} H \mathrm{e}^{T} \tag{5}$$

$$X^{(1,1)} = N[\mathrm{e}^{S} - 1]P^{(1,1)} = N[S^{(1,0)} + S^{(0,1)} + S^{(1,0)}S^{(0,1)} + S^{(1,1)}]P^{(1,1)} \tag{6}$$

where $P^{(1,1)}$ and $P_{\mathrm{I}}^{(1,1)}$ are projections on $M^{(1,1)}$ and a subspace of the orthogonal space that is generated by $S^{(1,1)}$ while acting on $M^{(1,1)}$, respectively. *N*[...] stands for the normal-ordered form of the operator. According to valence-universal strategy the *T*, $S^{(1,0)}$ and $S^{(0,1)}$ cluster amplitudes are provided by the lower-valence-level calculations, i.e., by the standard single-reference CCSD calculation for the ground state (zero-quasi-particle (0,0) sector), and then by the electron-affinity (EA) and ionization-potential (IP) (one-quasi-particle (1,0) and (0,1) sectors) FS-CCSD calculations, respectively. The energies for selected excited states, or excitation energies if the so-called normal order form $\overline{H}_N = \overline{H} - \langle \Phi | \overline{H} | \Phi \rangle$ is used instead of $\overline{H}$, are obtained by diagonalization of the effective Hamiltonian

$$H_{\text{eff}}^{(1,1)} = P^{(1,1)} \overline{H} (1 + X^{(1,1)}) P^{(1,1)} \tag{7}$$

which is nothing else but the $P^{(1,1)}$–$P^{(1,1)}$ block of the transformed Hamiltonian appearing in Eq. (*4*). Thus the effective Hamiltonian formulation of the FS-CCSD method consists of two steps. The first one is to solve Eq. (*4*) iteratively for $S^{(1,1)}$. This, in many cases, can pose serious problems and many such examples are known from the literature[21]. The second step comprises the construction of the effective Hamiltonian and its diagonalization. A simultaneous determination of all cluster amplitudes is required and the calculation is performed for several states at a time.

The use of the intermediate Hamiltonian technique in the case of the FS-CC approaches is especially advantageous. This is because of valence-universal strategy of solving the FS-CC equations, which leads to a linear expansion in X in terms of the unknown cluster amplitudes at each valence level beyond the zero-one. The intermediate Hamiltonian formalism introduces diagonalization as an alternative to less effective iterative ways of solving the equations. In the case of the FS-CC methods that provides a very simple and dependable computational scheme. To obtain the intermediate Hamiltonian formulation, the $X^{(1,1)}$ operator is divided into two parts[17]

$$X^{(1,1)} = Y^{(1,1)} + Z^{(1,1)} \tag{8}$$

$$Z^{(1,1)} = P_{\text{I}}^{(1,1)} X^{(1,1)} . \tag{9}$$

It should be noted here that all unknown cluster amplitudes at the (1,1) level are contained in the $Z^{(1,1)}$ operator. The $Y^{(1,1)}$ and $Z^{(1,1)}$ operators can be used to split the transformation in Eq. (*4*) into a sequence of two similarity transformations since

$$1 + X^{(1,1)} = (1 + Y^{(1,1)})(1 + Z^{(1,1)}) . \tag{10}$$

Defining $P_0{}^{(1,1)} = P^{(1,1)} + P_{\text{I}}{}^{(1,1)}$ it is easy to see that the operators

$$P_0^{(1,1)} (1 - X^{(1,1)}) \overline{H} (1 + X^{(1,1)}) P_0^{(1,1)} \tag{11}$$

$$P_0^{(1,1)} (1 - Y^{(1,1)}) \overline{H} (1 + Y^{(1,1)}) P_0^{(1,1)} \tag{12}$$

have the same eigenvalues since they are related through a similarity transformation. Because of Eq. (*4*), all eigenvalues of the effective Hamiltonian (*7*) are among eigenvalues of the transformed Hamiltonian (*11*)[16]; thus they are among eigenvalues of the operator (*12*). It follows that all eigenvalues of the FS-CCSD effective Hamiltonian can be obtained as eigenvalues of the operator

$$H_{\mathrm{I}}^{(1,1)} = P_0^{(1,1)} \overline{H}(1 + Y^{(1,1)}) P_0^{(1,1)} \qquad (13)$$

which is called the intermediate Hamiltonian[17]. Let us point out several advantages of the intermediate Hamiltonian formulation[17]. First, the energies can be obtained without necessity of determining the cluster amplitudes since the intermediate Hamiltonian does not depend on $Z^{(1,1)}$. If necessary, the cluster amplitudes can be calculated from a set of its eigenvectors. This order is opposite to what is required in the effective Hamiltonian formulation where determination of the energies follows the determination of cluster amplitudes. As a consequence, the intermediate Hamiltonian formulation leads to decoupling of the eigenvalue problems corresponding to different states and separate calculations for individual states are possible by employing single-root diagonalization procedures. Second, the intermediate Hamiltonian version introduces many formal simplifications that can be seen while analyzing Eq. (*13*)[17]. Finally, the method offers an efficient way of solving the equations, which is resistant to intruder states. It is worth mentioning that in all cases when the traditionally formulated method fails to reach convergence, the intermediate Hamiltonian formulation provides, without any problem, not only the principal solution but also alternative solutions of the standard approach.

The (0,0) level calculation is just an ordinary application of the single-reference CCSD method to the ground state. At the (1,0) and (0,1) level the intermediate Hamiltonian formulation reduces the FS-CCSD method to the EA-EOM-CCSD and IP-EOM-CCSD ones. The only difference is that the $S^{(1,0)}$ and $S^{(0,1)}$ cluster amplitudes must be determined from the sets of the EA- and IP-EOM-CCSD eigenvectors. These cluster amplitudes are required at the (1,1) level.

RESULTS AND DISCUSSION

The intermediate Hamiltonian reformulation of the FS-CCSD method provides a convenient framework for a numerical implementation of the method. The method has been implemented at the state-of-art level using factorization and efficient numerical procedures. That enables calculations using relatively large basis sets and reference spaces. Since there are no convergence problems; basically arbitrary sets of active unoccupied and occupied orbitals levels, determining our reference space, can be used. To denote different reference spaces we use the standard notation (i, j) with i and j being the numbers of lowest unoccupied and highest occupied orbitals in the HF determinant treated as active.

Our paper is devoted to excited-state properties like equilibrium geometry, harmonic frequency as well as vertical and adiabatic excitation energies. The results are reported for two diatomic molecules: N_2 and CO. The IH-FS-CCSD results are, for comparison, supplemented with the EOMCCSD ones. Two different basis sets are used: polarized basis set POL1 by Sadlej[37] and large augmented correlation-consistent quadruple-zeta (aug-cc-pVQZ) basis set by Dunning[38]. Also two different reference spaces are used in the FS-CCSD calculations. In all calculations the core electrons are frozen and the d functions are spherical. The results are collected in Tables I–III and confronted with the experimental data. Although the ground state equilibrium geometry and harmonic frequency of the N_2 and CO molecules have been calculated at various levels of the CC theory several times (e.g. ref.[39]), we show the CCSD results in Table I just for completeness of the presentation. Table II shows results obtained for two excited states of N_2 ($^1\Sigma_u^-$, $^1\Delta_u$) and in Table III results for excited states of CO ($^1\Pi$, $^1\Sigma^-$) are presented.

TABLE I
Total energies (in a.u.), equilibrium geometry (in Å) and harmonic frequencies (in cm^{-1}) for the ground state of N_2 and CO molecules at the CCSD level

	POL1	aug-cc-pVQZ	Exp.[a]
		N_2	
E	–109.290482	–109.386848	
R_e	1.1163	1.0932	1.0977
ω_e	2368	2434	2359
		CO	
E	–113.074127	–113.171640	
R_e	1.1419	1.1246	1.1283
ω_e	2187	2231	2170

[a] From ref.[40]

One of important factors influencing the FS-CCSD results is the selection of active orbital levels. In the standard FS-CC approaches, the use of large reference space is disadvantageous because that increases the number of cluster amplitudes and the size of the set of CC equations. Moreover, the iterative procedure of solving the equations is very sensitive to intruder states, which can result in convergence problems. The latter can occur in both one-quasi-particle sectors, (1,0) and (0,1), and at the two-quasi-particle level. The IH formulation shows that energies obtained at one quasi-particle level are independent of the reference space choice. Only the cluster operators which must be calculated from the EA- and IP-EOM-CCSD eigenvectors do depend on the active-orbital-level selection. The (1,1) equations are solved by the direct diagonalization of the intermediate Hamiltonian matrix whose size also does not depend on the reference space. Only the number of columns that require additional dressing intro-

TABLE II
Equilibrium geometries (in Å), harmonic frequencies (in cm^{-1}), vertical (VEE) and adiabatic (AEE) excitation energies (in eV) for N_2 with the IH-FS and EOM methods at the CCSD level

	POL1			aug-cc-pVQZ			
	IH-FS		EOM	IH-FS		EOM	Exp.[a]
	(6,4)	(13,4)		(6,4)	(13,4)		
				$^1\Sigma_u^-$			
R_e	1.2783	1.2686	1.2688	1.2749	1.2519	1.2505	1.2755
ω_e	1723	1710	1707	1813	1726	1724	1530
VEE[b]	10.054	9.660	9.885	11.059	10.034	10.131	9.92
AEE	8.607	8.440	8.665	8.906	8.664	8.793	8.450
				$^1\Delta_u$			
R_e	1.2723	1.2625	1.2637	1.2691	1.2454	1.2452	1.268
ω_e	1745	1732	1724	1844	1752	1744	1559
VEE[b]	10.531	10.139	10.316	11.533	10.517	10.568	10.27
AEE	9.173	9.000	9.167	9.490	9.238	9.306	8.939

[a] Adiabatic experimental EEs, geometry and harmonic frequencies are from ref.[40]; vertical experimental EEs from ref.[30] [b] VEEs are computed at the geometry given in Table I

duced by $\overline{H}Y^{(1,1)}$ is growing. Thus, the computational effort in the IH formulation is not significantly affected by the increasing number of active orbitals and one of the aspects of our study that we can easily investigate is the effect of the reference space size on the computed quantities.

For the N_2 molecule two reference spaces, (6,4) and (13,4), are selected. Concentrating on the equilibrium bond length it can be seen that the enlargement of the reference space from 24 to 52 reference functions introduces non-negligible effects. The equilibrium bond length is shortened for both considered states by approximately 0.01 Å in the case of the POL1 basis set and by more than 0.02 Å when the augmented cc-pVQZ basis set is used. As seen from Table II, the (6,4) R_e results are closer to the experimental bond length value than the (13,4) ones. However, the (13,4) R_e are very close to those of EOM-CCSD which suggests that this is not an incident. At first sight the large active space R_e values may look disappointing when compared with the smaller active space results. This deterioration of R_e rela-

TABLE III
Equilibrium geometries (in Å), harmonic frequencies (in cm^{-1}), vertical (VEE) and adiabatic (AEE) excitation energies (in eV) for CO with the IH-FS and EOM methods at the CCSD level

	POL1			aug-cc-pVQZ			
	IH-FS		EOM	IH-FS		EOM	Exp.[a]
	(6,4)	(15,4)		(6,4)	(15,4)		
				$^1\Pi$			
R_e	1.2673	1.2547	1.2464	1.2409	1.2328	1.2254	1.2353
ω_e	1477	1483	1518	1565	1553	1581	1518
VEE[b]	8.727	8.460	8.641	8.779	8.536	8.656	8.51
AEE	8.135	7.989	8.227	8.180	8.071	8.244	8.068
				$^1\Sigma^-$			
R_e	1.4032	1.3933	1.3852	1.3750	1.3683	1.3617	1.3911
ω_e	1154	1147	1192	1207	1216	1240	1092
VEE[b]	10.054	9.738	9.919	10.345	10.074	10.171	9.88
AEE	7.896	7.848	8.076	8.193	8.151	8.313	8.069

[a] Adiabatic experimental EEs, geometry and harmonic frequencies are from ref.[40]; vertical experimental EEs from ref.[41] [b] VEEs are computed at the geometry given in Table I

tive to the experiment is particularly visible for the larger basis set. However, one should be aware that at the singles and doubles level, the equilibrium bond length is frequently too small and only more advanced treatment of electron correlation cures the problem. For example, the EOM-CC results reported in ref.[32] show that the effect of connected triple excitations can increase the bond length by about 0.02 Å. A similar effect may be expected in the FS-CC calculations, i.e., the inclusion of three-body clusters may give larger equilibrium distances.

An analogous situation is observed in the R_e calculation for the CO molecule. Larger reference space leads to shorter bonds with the effect about 0.01 Å for the small basis set and 0.008–0.007 Å for the large one. Again the inclusion of the three-body clusters may be seen as a remedy for too small equilibrium distances. Nevertheless, the (15,4) FS-CCSD equilibrium bond lengths are, in general, closer to the experimental ones than those of EOM-CCSD, which may indicate that the inclusion of higher-excitation effects is less important in the FS-CC calculation than in the EOM-CC one.

For harmonic frequencies the enlargement of the reference space has usually a moderate effect of several wavenumbers for the small basis set but it can have unexpectedly large effect of several tens of wavenumbers for the large one. The ground-state calculations show that, in majority of cases, an increase in the bond length is associated with decreasing value of the harmonic frequency and vice versa. The N_2 results reported in Table II show the opposite tendency, i.e., lower harmonic frequencies and smaller curvature at equilibrium are associated with shorter bonds. For the CO molecule this pattern of behavior is not preserved and, in fact, we have two different cases. The $^1\Sigma^-$ state case is similar to those observed for N_2 while the $^1\Pi$ state represents this more expected behavior. On the other hand, there are no irregularities in the relation between equilibrium bond length and harmonic frequency as far as the basis set size effect is concerned. Larger basis sets make the bond shorter and this increases the harmonic frequency.

In Tables II and III we also quote vertical and adiabatic excitation energies obtained for the discussed excited states of N_2 and CO. The IH-FS-CCSD method has been already applied to study vertical excitation energies of N_2 and CO [19]; the results, however, have been obtained at the experimental geometry. Here, we rely on theoretical values only reporting vertical EEs corresponding to the calculated ground state equilibrium geometry shown in Table I. Again we have found that the enlargement of the active space lowers excited state energies leading to smaller VEE values by about 0.4 eV for the POL1 basis set and by more than 1 eV for the aug-cc-pVQZ basis set.

For the CO molecule this effect is not so significant giving between 0.24 and 0.30 eV for all considered cases.

The adiabatic EEs (AEEs) seem less sensitive to the model space size. The largest differences observed for the N_2 molecule are about 0.25 eV in the aug-cc-pVQZ calculation. For CO these differences are much smaller, 0.11 and 0.04 eV for $^1\Pi$ and $^1\Sigma^-$, respectively. In all cases smaller values of AEEs correspond to larger reference spaces. Since the computed excitation energies are larger than the experimental ones, which is especially visible for the aug-ce-pVQZ basis set, hence, the extension of the model space works toward better agreement with the experiment. Enlargement of the reference space means that additional electron correlation effects are being included in the calculation. In spite of the fact that the dimension of $H_{\mathrm{I}}^{(1,1)}$ is constant, the number of columns modified by the additional term $HY^{(1,1)}$ in Eq. (*13*) is growing. Thus, as long as the cluster conditions are satisfied we can expect that larger reference space should lead to the improvement of the results. Although the FS-CCSD results can be considered quite satisfactory, another step which should give their further improvement is the inclusion of three-body term in the cluster operator. The aug-cc-pVQZ FS-CCSD vertical EEs differ from the experiment by 0.11 and 0.25 eV for $^1\Sigma_u^-$ and $^1\Delta_u$, respectively, while the corresponding adiabatic EEs come out a little bit worse being 0.21 and 0.30 eV off the experiment. For the CO molecule the situation is slightly better. The deviations of the vertical EEs are equal to 0.03 and 0.19 eV for the two considered states and the adiabatic EE errors are even reduced to 0.00 and 0.09 eV. What is interesting here is that the EOM-CC EEs are significantly more off the experiment. The average errors in the aug-cc-pVQZ N_2 calculation of VEEs are 0.18 eV for FS-CCSD ((13,4) reference space) and 0.26 eV for EOM-CCSD while for AEEs the corresponding errors are 0.26 and 0.35 eV. The errors in the aug-cc-pVQZ CO calculation of VEEs are 0.09 eV ((15,4) FS-CCSD) and 0.22 eV (EOM-CCSD) while the AEE calculation gives 0.04 eV for FS-CCSD and 0.21 eV for EOM-CCSD.

The results obtained in our preliminary calculations for N_2 and CO using the IH-FS-CCSD method show that the intermediate Hamiltonian version can be effectively employed to describe properties of excited states. Due to the reformulation the computational scheme is simple and resistant to intruder states. The results show that relatively large reference spaces may be required to reach a desired accuracy but the method does not show problems with reaching the convergence is such cases. In spite of the fact that some of the FS-CCSD results reported here may not be seen as highly accurate, they seem, in general, definitely more accurate than those given by the EOM-CCSD method when compared with experiment. Two sources of the errors with respect to experiment which can be considered are the basis set and the lack of higher-excitation effects in the expansion. While comparing the POL1 and aug-cc-pVQZ results, it looks like the smaller basis set, in many cases, gives better results than the large one. The POL1 basis set leads to definitely less accurate total energies. The results reported in Table I show a big difference between the ground state energies obtained within both basis sets. This indicates that the POL1 excited state energies must be equally inaccurate to give reasonable energy differences. It looks like the POL1 basis introduces a balanced description of the ground state and some excited states, which leads to quite effective cancellation of the errors. The aug-cc-pVQZ basis set is obtained from that constructed for accurate ground state calculations. In spite of including functions improving description of excited states it seems that it still retains the preferential treatment of the ground state. That can lead to the unbalanced description and to too large energy differences. So it seems that the standard aug-cc-pVQZ basis set needs further improvement to allow more accurate treatment of excited states. Since we cannot fully rely on the cancellation of errors in energy difference calculations, which is not systematic, we should try to describe all states under consideration as accurate as possible. A similar conclusion can be reached regarding the second aspect of the calculation, i.e., the importance of higher-level excitation in the expansion. The problem should be followed and discussed while analyzing the results, and, finally, the higher-level excitation effects should be included in the calculation if necessary.

CONCLUSION

In this paper the FS-CCSD method has been applied to calculate some molecular properties of excited states. The main goal of the paper is to show that the intermediate Hamiltonian formulation provides a very simple computational scheme which can be effectively coded and used in calculations requiring relatively large basis sets and reference spaces. In this preliminary study we performed calculations of equilibrium geometries, harmonic frequencies, vertical and adiabatic excitation energies for several excited states of N_2 and CO. We observe that in order to obtain a reasonable estimate of the properties of excited states, relatively large reference spaces should be used. Two different basis sets have been employed in the calculations and the effect of the basis set on the results has been discussed. Possible importance of higher-level excitations in the FS-CC and EOM-CC expansion has been also analyzed. The results obtained in this work seem to indicate that at the CCSD level the FS-CC method gives better agreement with experiment than EOM-CC.

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