Application of High-Level Iterative Coupled-Cluster Methods to the Cytosine Molecule

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The need for inclusion higher-order correlation effects for adequate description of the excitation energies of the DNA bases became clear in the past few years. In particular, we demonstrated that the inclusion of triply excited configurations may play an important role in a proper description of the excitation energies of the cytosine molecule in realistic environment. In this paper we discuss the accuracies of excitation energies for the cystosine molecule in the gas phase and in the aqueous solution calculated with noniterative and iterative coupled-cluster methods that include the effect of triply excited configurations.

I. Introduction

Recently, several studies[1–9] clearly pointed out that in order to obtain reliable results for low-lying excited states of DNA bases a balanced inclusion of electron correlation effects is necessary.[10–12] These studies also made a clear distinction between the accuracies provided by wave function approaches such as complete active space second-order perturbation theory (CASPT2),[13] multireference configuration interaction method with singles and doubles (MRDCI),[14,15] several variants of equation of motion coupled cluster (EOMCC) approaches,[16,17] and the accuracies provided by time-dependent density functional theory (TDDFT). The cytosine molecule epitomizes the most essential problems that these theories stumble into. While the wave function approaches uniformly predict the sizable separation between first and second excited states of cytosine, TDDFT methods significantly distort this picture by producing nearly degenerate excitation energies for the $\pi\pi^*$ and $n_O\pi^*$ transitions.[18] Equally important in studies of DNA bases is the inclusion of the effect of the surrounding environment either in the aqueous solution or DNA backbone, which may result in a sizable blue shifts of excitation energies on the order of 0.5 eV.

The purpose of this paper is two-fold. First, we demonstrate that with proper utilization of massively parallel computing platforms it becomes possible to use expensive iterative CC/EOMCC methods such as the active-space EOMCCSDt (equation of motion coupled cluster approaches with singles, doubles, and active-space triples;[19–23] for original active space coupled-cluster (CC) ideas see refs 24−27) and EOMCCSDT-1[28] methods. Second, we employ the active-space EOMCCSDt to validate the accuracies of noniterative completely renormalized EOMCCSD approach with noniterative triples (CR-EOMCCSD(T)).[29,30]

The paper is organized as follows: in section II we provide brief description of main theoretical threads, whereas section III deals with the excitation energies calculated on the EOMCCSDt, EOMCCSDT-1, and CR-EOMCCSD(T) level of theory. The excitation energies are discussed in the context of gas-phase and aqueous solution using our QM/MM formalism[7,31] combined with the DFT (used for geometry optimization) and CC modules.

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II. Theory

This section only briefly addresses the basic tenets of the correlated methods accounting for the effect of triples either in iterative (EOMCCSDT-1, EOMCCSDt) or noniterative (CR-EOMCCSD(T)) fashion. For a more detailed description we refer the reader to original papers.[19–22,28–30]

The EOMCCSDT-1 approach is perhaps the simplest iterative approximation to the full EOMCCSDT method in which the CCSDT similarity transformed Hamiltonian in the normal product form $\bar{H}_N^{\mathrm{CCSDT}} = e^{-(T_1+T_2+T_3)}He^{T_1+T_2+T_3} - \langle\Phi|e^{-(T_1+T_2+T_3)}He^{T_1+T_2+T_3}|\Phi\rangle$ (T_1, T_2, T_3 are the cluster operators obtained in the CCSDT calculations), is diagonalized in the space of singly, doubly, and triply excited configurations

$$(Q_1+Q_2+Q_3)\bar{H}_N^{\mathrm{CCSDT}}R_\mu^{\mathrm{EOMCCSDT}}|\Phi\rangle = \omega_\mu^{\mathrm{EOMCCSDT}}(Q_1+Q_2+Q_3)R_\mu^{\mathrm{EOMCCSDT}}|\Phi\rangle \quad (1)$$

where Q_i is the projection operator on the space of all i-tuply excited configurations, $\omega_\mu^{\mathrm{EOMCCSDT}}$ designates the EOMCCSDT excitation energy for the μth state, and $R_\mu^{\mathrm{EOMCCSDT}}$ is the excitation operator

$$R_\mu^{\mathrm{EOMCCSDT}} = R_{\mu,0} + R_{\mu,1} + R_{\mu,2} + R_{\mu,3} \quad (2)$$

In the above formula, the $R_{\mu,i}$ operator refers to i-tuply excited component of the EOMCCSDT excitation operator $R_\mu^{\mathrm{EOMCCSDT}}$. The EOMCDCSDT-1 approach is obtained by replacing the $\bar{H}_N^{\mathrm{CCSDT}}$ operator by its CCSD counterpart $\bar{H}_N^{\mathrm{CCSD}} = e^{-(T_1+T_2)}He^{T_1+T_2} - \langle\Phi|e^{-(T_1+T_2)}He^{T_1+T_2}|\Phi\rangle$ (now T_1 and T_2 cluster operators are taken from the CCSD calculations) and by reducing the triples equations to the form

$$Q_3(F_NR_{\mu,3} + V_NR_{\mu,2}|\Phi\rangle = \omega_\mu^{\mathrm{EOMCCSDT-1}}Q_3R_{\mu,3}|\Phi\rangle, \quad (3)$$

where F_N and V_N represent one- and two-body part of electronic Hamiltonian H in normal product form ($H_N = H - \langle\Phi|H|\Phi\rangle$). In contrast to N^8 scaling of the EOMCCSDT method (N refers here to the system size), the EOMCCSDT-1 is characterized by N^7 scaling.

As explained in ref 22, the main purpose of the active-space CCSDt/EOMCCSDt methods is to effectively mimic their full CCSDT/EOMCCSDT counterparts by the inclusion of the most essential parts of three-body T_3 and $R_{\mu,3}$ operators. The selection of the important triply excited part of the T and R_μ operators

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can be done on the basis of active orbitals or active space. The form of the cluster operator defining the CCSDt approach and the form of the excitation operator (for the μth state) defining the EOMCCSDt approach are given by the formulas

$$T^{\mathrm{CCSDt}} = T_1 + T_2 + t_3, \tag{4}$$

$$R_\mu^{\mathrm{EOMCCSDt}} = R_{\mu,0} + R_{\mu,1} + R_{\mu,2} + r_{\mu,3}, \tag{5}$$

where

$$t_3 = \sum_{i<j<K,A<b<c} t_{Abc}^{ijK} X_A^\dagger X_b^\dagger X_c^\dagger X_K X_j X_i, \tag{6}$$

$$r_{\mu,3} = \sum_{i<j<K,A<b<c} r_{\mu,Abc}^{ijK} X_A^\dagger X_b^\dagger X_c^\dagger X_K X_j X_i \tag{7}$$

As always, the $X_p^\dagger$ (X_p) are the creation (annihilation) operators associated with spin−orbitals $|p\rangle$. In defining the cluster amplitudes t_{Abc}^{ijK} entering eq 6, we employ a convention in which the generic occupied (unoccupied) spin−orbital indices (active as well as inactive) are labeled by the italic letters $i, j, k, \ldots$ ($a, b, c, \ldots$), whereas the upper-case symbols designate active spin−orbitals. The form of the t_3 and $r_{\mu,3}$ amplitudes invoked in eqs 6 and 7 refers to the so-called variant I of the CCSDt/EOMCCSDt approaches (or for brevity CCSDt(I) and EOMCCSDt(I) approaches).

In addition to variant I two other simplified variants (II and III or CCSDt(II)/EOMCCSDt(II) or CCSDt(III)/EOMCCSDt(III)) of variant I can be considered. Variant II uses t_3 and $r_{\mu,3}$ amplitudes that carry at least two pairs of active spinorbitals

$$t_3(\mathrm{II}) = \sum_{i<J<K,A<B<c} t_{ABc}^{iJK} X_A^\dagger X_B^\dagger X_c^\dagger X_K X_J X_i \tag{8}$$

$$r_{\mu,3}(\mathrm{II}) = \sum_{i<J<K,A<B<c} r_{\mu,ABc}^{iJK} X_A^\dagger X_B^\dagger X_c^\dagger X_K X_J X_i \tag{9}$$

whereas in the variant III all spin−orbital indices defining triples are active. For obvious reasons the variant III is characterized by the lowest memory/time requirements. Typical accuracies obtained in the EOMCCSDt I, II, and III calculations depends on the character of excited states. For singly excited states of small benchmark systems the I, II, III EOMCCSDt approaches give almost the same accuracies. In this situation the differences between EOMCCSDt(I) and EOMCCSDt(III) excitation energies should not exceed 0.1 eV (see ref 22). For doubly excited states, the effect of neglecting important configurations in the cluster/excitation operators is more visible. For example, for doubly excited states of the Be_3 system,[22] the differences in excitation energies obtained with variant I and III may become as large as 0.6 eV (at the same time version II gives results with error around 0.2 eV with respect to version I). So far, the CCSDt/EOMCCSDt approaches have been applied to small two−three atomic systems. In the next section we discuss the application of active-space methods to the cytosine molecule, which constitutes a realistic system of biological importance. In the next section we adopt the EOMCCSDt(X)(m,n) notation for the active-space EOMCCSDt calculations, where X refers to the variant used (X = I, II, III) and m and n refer to the numbers of the active occupied and active unoccupied orbitals.

In an affordable noniterative CR-EOMCCSD(T) approach the correction $\delta_\mu^{\mathrm{CR\text{-}EOMCCSD(T)}}$ that accounts for the effect of triples takes the form

$$\delta_\mu^{\mathrm{CR-EOMCCSD(T)}} = \frac{\langle \Psi_\mu(3)|M_{\mu,3}(2)|\Phi\rangle}{\langle \Psi_\mu(3)|\Psi_\mu^{\mathrm{EOMCCSD}}\rangle} \tag{10}$$

where $M_{\mu,3}(2)$ represents triply excited moments of the EOMCCSD equations. In our calculations this correction is explicitly added to the corresponding EOMCCSD excitation energy. In contrast to the iterative approaches, the CR-EOMCCSD(T) correction is constructed on-the-fly, and there is no need to store triply excited amplitudes.

TABLE 1: Vertical Excitation Energies (in eV) of the Cytosine Molecule in the Gas Phase and Aqueous Solution (All CC Calculations Were Performed with the cc-pVDZ Basis Set; All Core Orbitals Were Kept Frozen)

	$\pi\pi^*$transition		$n_O\pi^*$transition
method	gas-phase	solution	solution
TDDFT		4.89	5.14
MRDCI[a]	4.96		
CASPT2[a]	4.39		
EOMCCSD	4.89	5.17	5.74
CR-EOMCCSD(T)	4.63	4.91	5.53
EOMCCSDt(II)(6,3)		5.17	5.78
EOMCCSDt(I)(5,3)		5.05	
EOMCCSDT-1	4.90	5.22	

[a] From ref 10.

III. Results

The system considered in this work consisted of a cytosine base (treated quantum mechanically) embedded into an 80 Å cubic box of classical SPC/E[32] waters. Prior to excited-state calculations the entire system was relaxed using the QM/MM optimization procedure.[31] In these calculations the quantum mechanical treatment was based on density functional description with B3LYP[33] exchange correlation functional and cc-pVDZ basis set.[34]

In all excited-state calculations we utilized the cc-pVDZ basis set.[34] Moreover, all core electrons were kept frozen. Consequently, 42 electrons were correlated using 129 orbitals. The most expensive active-space EOMCCSDt(I)(5,3) approach employed the active space consisting of the five highest occupied and three lowest unoccupied orbitals, which is in general agreement with the model spaces used in previous MRDCI calculations.[8,9] We also performed EOMCCSDt(II) calculations for a slightly bigger active space (6,3). Our calculations based on the EOMCCSDt(I) and EOMCCSDT-1 approaches were performed in parallel (128 CPU) on the HP/Linux Itanium-2 cluster. The average time per CCSDT-1 iteration oscillated around 300 s. Given the good scalability of current implementations of the EOMCCSDt and EOMCCSDT-1 formalisms in the NWChem suite of codes,[36] the calculation for larger basis sets and larger systems can be envisioned.

It has been documented[7] that the effect of environment (DNA backbone) uniformly shifts all EOMCC excitations energies for a given state. For example the $\pi\pi^*$ excitation energy is blue-shifted by 0.24 and 0.25 eV for EOMCCSD and CR-EOMCCSD(T) approaches, respectively.[7] In Table 1 we collected our results obtained with the TDDFT approach (based on B3LYP functional), the iterative methods defined by the manifold of singly and doubly excited excitations (this includes the EOMCCSD, the noniterative CR-EOMCCSD(T) approach (variant IA [29]), and two variants of iterative active-space EOMCCSDt approaches, the EOMCCSDt(II)(6,3) and EOMCCSDt(I)(5,3), and with the EOMCCSDT-1 method, for the gas phase and for the aqueous solution. We performed the EOMCCSDt(I)(5,3) and EOMCCSDT-1 calculations only for the $\pi\pi^*$ transition. In all calculations we used the same optimized geometry described in the previous paragraph. The results (see Table 1) obtained for this geometry in the presence of water molecules will be referred to as the "solution" results.

The "gas-phase" results will be referred to when all water molecules are removed.

It is interesting to notice that the CR-EOMCCSD(T) corrections lower the corresponding EOMCCSD energies by around 0.26 eV for both the gas phase and the solution. For the gas phase the CR-EOMCCSD(T) $\pi\pi^*$ excitation energy is located between MRDCI (with Davidson correction [37]) excitation energy (4.96 eV) obtained for basis set of DZP quality and CASPT2 excitation energy (4.39 eV) obtained for slightly different basis set (see ref 10). The EOMCCSD and EOMCCSDT-1 results, in this particular case, are of MRDCI quality. As we can see, for the $\pi\pi^*$ transition the blue shifts obtained with the EOMCCSD and CR-EOMCCSD(T) approaches are exactly the same, 0.28 eV. The EOMCCSDT-1 excitation energy for the gas phase is of the EOMCCSD quality while for the aqueous solution is slightly above the EOMCCSD one. In effect, the EOMCCSDT-1 excitation energy is blue-shifted by 0.33 eV. One should be aware of the fact that the differences (0.03−0.04 eV) between EOMCCSD and CR-EOMCCSD(T) blue shifts reported in ref 7 and in present studies are the result of temperature averaging carried out in ref 7. All results shown in Table 1 were obtained in single-point calculations for the optimized geometry. One can see that the active-space approach EOMCCSDt(II)(6,3) gives the excitation energies for the $\pi\pi^*$ and $n_O\pi^*$ states of the same quality as the EOMCCSD approach. In fact, in both cases the EOMCCSDt(II)(6,3) excitation energies are located slightly above the EOMCCSD ones. As seen from Table 1 the bulk of correlation effects due to triples requires a more complete treatment of the manifold of triply excited configurations. The calculations for the $\pi\pi^*$ excitation energy clearly show that EOMCCSDt(I)(5,3) lowers the EOMCCSD excitation energy by 0.12 eV. The CR-EOMCCSD(T) method produces the excitation energies for $\pi\pi^*$ and $n_O\pi^*$ transitions that are significantly below the EOMCCSD ones (by 0.26 and 0.21 eV, respectively). Even though the CR-EOMCCSD(T) $\pi\pi^*$ excitation energy is 0.13 eV below the EOMCCSDt(I)(5,3) result, in the light of benchmark full EOMCCSDT studies discussed in ref 35, we believe that the CR-EOMCCSD(T) approach in the case of cytosine does not significantly underestimate the full EOMCCSDT result. We should also notice that the EOMCCSDT-1 excitation energy for the $\pi\pi^*$ state is slightly above the EOMCCSD one. A more complete inclusion of the excited-state correlation effects on the EOMCCSDT-3 level will lead to a better estimates of the EOMCCSDT excitation energies. It is also instructive to discuss the TDDFT (B3LYP) results in the light of the EOMCC results. We observe, in analogy to the EOMCC calculations for cytosine in a realistic environment,[7] that despite a good quality of TDDFT excitation energy for $\pi\pi^*$ transition, the excitation energy of $n_O\pi^*$ transition (5.136 eV) seems to be too low. This observation is of quite general nature and holds irrespective of surrounding environment.

In contrast to other DNA bases the absorption bands of cytosine disclose a strong solvent dependence. Additionally, the absorption bands strongly overlaps, which makes difficult to resolve the absorption spectrum in 5.0−6.0 eV region.[38–41] This causes that the proper inclusion of the surrounding environment in theoretical simulation may play a pivotal role in a unique assignment of the low-lying excited states to specific bands. Our CR-EOMCCSD(T) results for the $\pi\pi^*$ and $n_O\pi^*$ transitions in solution, 4.91 and 5.53 eV, respectively, agree reasonably well with experimentally inferred values of 4.6−4.7 and 5.2−5.8 eV. Also for the $\pi\pi^*$ transition the corresponding red shift (0.28 eV) is in agreement with its 0.3 eV estimate discussed in ref 10.

It is also important to understand how our results can be related to real gas-phase results. For this purpose we optimized the geometry of cytosine in gas-phase using B3LYP level of theory with the aug-cc-pVTZ basis set[34] and performed EOMCC calculations for the $\pi\pi^*$ transition. The vertical excitation energies obtained with the EOMCCSD and CR-EOMCCSD(T) approaches in the cc-pVDZ basis set are equal to 5.10 and 4.84 eV, respectively. Assuming that the environment uniformly shifts the $\pi\pi^*$ excitation energy by 0.28 eV, its CR-EOMCCSD(T) estimate in solution (obtained for true gas-phase geometry, discussed in this paragraph) would be around 5.12 eV, which is significantly above the experimental result and the CR-EOMCCSD(T) estimate (4.91 eV) obtained for the cytosine in solution (see Table 1). In our opinion this is a clear demonstration of the role played by geometry effects.

In conclusion, our calculations are the first excited-state CC calculations employing a high level of correlation for system of biological importance with the inclusion of a realistic environment. It is justified to anticipate that using ever growing power of computers these calculations will be routinely performed on massively parallel computer architectures in the foreseeable future. The usage of highly correlated CC approaches with iterative triples (currently the massively parallel implementations of the EOMCCSDT-*n* formalisms are under intensive development in our group) in conjunction with the QM/MM methodology, will also give us a powerful tool to analyze the excited-state potential energy surfaces with highly adequate characterization of many vital features such as the location of conical intersections in various environments. At the same time the EOMCCSDt formalism provided us with further evidence confirming the usefulness of much cheaper noniterative approaches such as the CR-EOMCCSD(T) method. Our tests showed that for singly excited-state such as $\pi\pi^*$ the difference between CR-EOMCCSD(T) and EOMCCSDt(I)(5,3) excitation energies is as small as 0.13 eV.

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