COUPLED-CLUSTER STUDY OF SPECTROSCOPIC CONSTANTS OF THE ALKALI METAL DIATOMICS: GROUND AND THE SINGLET EXCITED STATES OF Na_2, NaLi, NaK, and NaRb

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It is our honor to dedicate this paper to Professor Josef Paldus, a pioneer of many-body methods in theoretical chemistry. We would like to thank Prof. Paldus for inspiring us with many brilliant ideas which have affected our work including ideas directly implemented in the present paper.

A newly implemented two-determinant coupled-cluster method including single and double excitation operators (TD-CCSD) is applied to calculations of spectroscopic constants of alkali metal diatomics. The equilibrium bond length, harmonic vibrational frequency, anharmonicity, the dissociation energy and excitation energies are derived from the potential curves calculated for the ground state $X^1\Sigma_g^+$ and the two singlet mono-excited states, $A^1\Sigma_u^+$ and $B^1\Pi_u$ of Na_2 as well as for the ground $X^1\Sigma^+$ and the singlet excited $A^1\Sigma^+$ and $B^1\Pi$ states of the heteronuclear NaLi, NaK, and NaRb molecules. Spectroscopic constants and excitation energies agree reasonably well with experiment. Our results demonstrate that the relatively simple CCSD method for the excited states represented by two-reference determinants is a viable technique. The computer time needed for an excited singlet state is practically identical to the time which a standard single-determinant-based CCSD calculation takes.

Keywords: Multireference coupled-cluster calculations; Incomplete active space; Complete active space; Potential energy curves; Singlet excited states; Na_2, NaLi, NaK, and NaRb; *Ab initio* calculations; TD-CCSD.

During the last four decades the coupled-cluster (CC) theory[1] has developed into one of the most powerful methods in electronic structure theory. The theoretical background of the CC theory has been discussed in excellent re-

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views[2–6]. While calculations on closed-shell systems can now be performed routinely, description of open-shell systems are plagued by several complications. For high-spin systems, the appropriate generalization of the closed-shell methods can be used[7,8], but issues like spin-contamination or symmetry breaking need to be considered. Low-spin open-shell systems, however, such as open-shell singlet states, are more challenging since the zeroth-order description of these states requires more than one determinant and the standard CC approaches based on a single determinant reference cannot therefore be used. These systems can be treated using, e.g., the unitary group coupled-cluster approach (UGA CC) developed by Li and Paldus[9]. Although several other potential solutions to this problem have been suggested in the literature, we still do not have a standard, widely accepted method to treat open-shell singlet states.

In the present paper, one of the methods developed for this purpose, the so-called two-determinant CC (TD-CC) method[10–12] which is based on the Hilbert-space formulation[2,13] of the multireference CC problem is applied. The principal aim of this study is to accumulate information on the applicability of the method and particularly on its performance in the so-called incomplete active space (IAS) situation. For this purpose we calculate here the spectroscopic properties for the ground state and selected low-lying singlet excited states of some alkali metal diatomic molecules, Na_2, NaLi, NaK, and NaRb, as very suitable test cases for our method. In the last decades alkali diatomics have been a focus of intensive experimental studies and *ab initio* calculations of the adiabatic potential curves for both ground and excited electronic states. From the theoretical point of view, special attention has been paid to the determination of highly accurate ground state potentials and properties over a wide range of internuclear separations in order to be able to adequately model the photodissociation spectroscopy of cold and ultracold alkali atom containing molecules and other laser cooling experiments. The ground state properties, the $X^1\Sigma_g^+$ state for Na_2 and the $X^1\Sigma^+$ states for heteronuclear molecules, are thus well known both experimentally and theoretically. A comprehensive summary of earlier work on the Na_2 ground state is given in ref.[14] and corresponding references to more recent studies can be found for Na_2 [15], for NaK [16] and for NaRb [17]. Less information, experimental and theoretical, however, is available for the excited states, particularly for the excited singlet states which are of main interest here, the $A^1\Sigma_u^+$ and $B^1\Pi_u$ states of Na_2 and the $A^1\Sigma^+$ and $B^1\Pi$ states of the NaLi, NaK, and NaRb molecules. Particularly interesting in this context are the $A^1\Sigma^+$ states of NaLi, NaK, and NaRb. Calculations of this state for the heteronuclear molecules appears to be more difficult compared with the corresponding $A^1\Sigma_u^+$ state of Na_2. Due to the reduced symmetry the σ orbitals, which are the equivalents of the σ_g and σ_u orbitals in Na_2, belong to the same symmetry in NaMe, which makes the construction of the complete active space more difficult. Potential energy curves have previously been computed in the framework of pseudopotential or model potential methods for, e.g., 58 electronic states of NaK by Magnier and Millie[18]. A combined experimental and theoretical investigation of NaRb has been presented by Tamanis et al.[19] These authors used relativistic pseudopotentials diagonalizing the state-selective effective Hamiltonian for the valence two-electron subsystem and the second-order many-body multipartitioning perturbation theory for calculations of excited states of NaRb. A highly correlated technique related to the present work, namely the Fock space open-shell CC method, was applied by Kaldor and Ilyabaev[20] to excited states of Na_2 and K_2. Chattopadhyay et al. have applied the state-specific multireference CC method in a study[21] of potential energy curves of Na_2 and some other molecules. Other related theoretical work has been published by Malrieu, Adamowicz et al.[22,23]

Rather than aiming in the present calculations to reach the benchmark accuracy for the spectroscopic constants, the paper demonstrates the ability of our new TD-CC approach for the complete and incomplete active space to describe the main characteristics of the excited singlet states with reasonable accuracy. The satisfactory agreement of the theoretical results obtained using this approach with experiment justifies further developments of the method.

OVERVIEW OF THE THEORY

In this paper singlet states of two different kinds have been investigated. Ground states of the studied molecules, Na_2, NaLi, NaK, and NaRb, are typically dominated by a single closed-shell determinant, at least around the equilibrium geometry. These systems can be treated by standard single-determinant-based CC (or other) techniques, which are well established[2–6].

Excited $A^1\Sigma$ and $B^1\Pi$ are schematically created by excitation of one electron from the doubly occupied σ HOMO orbital (denoted by m) to one of the low-lying unoccupied orbitals n. For the systems studied in this paper, this orbital is either the σ LUMO or the lowest orbital with the π symmetry. For the singlet coupling of the two open-shell electrons, two low-spin ($S_z = 0$) excited determinants must be considered:

$$|\Phi_p\rangle = |\ldots, m_\alpha, n_\beta\rangle \qquad |\Phi_q\rangle = |\ldots, m_\beta, n_\alpha\rangle \,. \tag{1}$$

However, neither of these two determinants can be used as a proper zeroth-order wave function. A proper singlet combination which is an eigenfunction of the S^2 operator can be formed as follows:

$$|\Phi_{\mathrm{ref}}\rangle = \frac{1}{\sqrt{2}}(|\Phi_p\rangle - |\Phi_q\rangle)\ . \tag{2}$$

This configuration state function (CSF) is the dominant component of the wave functions of the studied excited states. Molecules where a single CSF of this kind is dominating still belong to the single-reference systems in the sense that the ratio of $|\Phi_p\rangle$ and $|\Phi_q\rangle$ is fixed. Standard CC theory, however, is essentially based on a single determinant representation of the reference function and is thus not directly applicable in this case. Therefore, CC methods developed for the multireference situation need to be exploited here.

We have developed a new CCSD code applicable for such cases, i.e. for the two-determinant reference. The method is based on the multireference CC formalism, suggested by Jeziorski and Monkhorst[13]. Their formulation, which represents the background for the state-universal or the Hilbert space (HS) MR-CC method, uses the technique of effective Hamiltonians (H^{eff}). Working equations and the computer code have been presented by Kucharski and Bartlett[24], while the application of this method for the open-shell singlet case has been suggested by Balkova and Bartlett[10]. Full implementation of this so called two-determinant CC (TD-CC) method has been reported by Szalay and Bartlett[11].

Here we present only some basic ideas of the effective Hamiltonian formalism. For more details, the reader is referred to instructive overviews, see, e.g., ref.[2] or ref.[3] We choose a group of reference determinants $|\Phi_j\rangle$, $j = 1, M$, which span the model space M_0. Now we are looking for such an operator, H^{eff}, the spectrum of which on M_0

$$H^{\mathrm{eff}}|\tilde{\Phi}_j\rangle = E_j|\tilde{\Phi}_j\rangle \tag{3}$$

is identical to a required part of the spectrum of exact Hamiltonian. Eigenvectors $|\tilde{\Phi}_j\rangle$ are linear combinations of $|\Phi_j\rangle$, $j = 1, M$. Eigenvalues E_j correspond to a group of exact eigenfunctions Ψ_{j},

$$H|\Psi_j\rangle = E_j|\Psi_j\rangle\ . \tag{4}$$

Function $|\Psi_j\rangle$ can be obtained from $|\tilde{\Phi}_j\rangle$ by introducing a wave operator U[25]. The inverse process can be realized using the operator P projecting onto the model space M_0:

$$U|\tilde{\Phi}_j\rangle = |\Psi_j\rangle \qquad |\tilde{\Phi}_j\rangle = P|\Psi_j\rangle\,. \tag{5}$$

U is required to act only on M_0, so that $U = UP$. It is also convenient to introduce intermediate normalization, which guarantees that all interactions within the model space are completely included within the diagonalization of the H^{eff} matrix

$$PU = P \quad \text{or} \quad \langle\Phi_i|\tilde{\Psi}_j\rangle = \delta_{ij} \tag{6}$$

where $|\tilde{\Psi}_j\rangle = U|\Phi_j\rangle$. Using the above relations, one can find that the effective Hamiltonian can be expressed as

$$H^{\text{eff}} = PHU = PHUP\,. \tag{7}$$

To determine the wave operator U, it is useful to introduce the Bloch equation:

$$HU = UHU \qquad HU = UH^{\text{eff}}\,. \tag{8}$$

Jeziorski and Monkhorst[13] introduced the wave operator in the following form:

$$U = \sum_j e^{T^j}|\Phi_j\rangle\langle\Phi_j|\,. \tag{9}$$

Inserting this form of the wave operator into the Bloch equation they obtained equations which can be used to solve for the amplitudes T^p:

$$\langle\Phi_{ij..}^{ab..}(p)|e^{-T^p}He^{T^p}\Phi_p\rangle = \sum_{q\neq p} H_{qp}^{\text{eff}}\langle\Phi_{ij..}^{ab..}(p)|e^{-T^p}e^{T^q}\Phi_q\rangle \tag{10}$$

with

$$H_{qp}^{\mathrm{eff}} = \langle \Phi_q | \mathrm{e}^{-T^p} H \mathrm{e}^{T^p} \Phi_p \rangle \, . \tag{11}$$

At this point it is necessary do discuss the properties of the determinants which span the model space. The orbitals forming the determinants can be classified as *inactive* orbitals k, i.e. those that are doubly occupied in all determinants $|\Phi_j\rangle$, $j = 1, M$, and *active* orbitals l, which are occupied (either doubly or singly) by remaining $N - 2k$ active electrons only in some of the determinants. If the model space is spanned by all determinants that can be constructed by all possible distributions of active electrons among active orbitals considering the desired space and spin symmetry, we have a complete active space (CAS). If we take only some of them, we consider an incomplete active space (IAS).

In the MR-CC formalism for the CAS case, those excitation operators that are labeled exclusively by indices from active orbitals are excluded from the cluster operators T^p since all determinants that can be obtained via such excitations from an arbitrary $|\Phi_j\rangle \in M_0$ are already included in M_0. Thus, intermediate normalization is fulfilled automatically and the HS formalism is quite straightforward. The proof of connectedness for this case has been already given in the original work by Jeziorski and Monkhorst[13]. Later Kucharski and Bartlett[24] reported a complete formulation of the corresponding HS MR-CCSD method based on diagrammatic technique. The model space M_0 considered in this work included determinants up to sextuple excitations[24]. To deal with IAS is much more complicated. The main problem is that some excitation operators labeled purely by active indices must be included in the cluster operator T^p since they create determinants which belong to CAS, but are not included in the model space. In what follows we denote these operators as ${}^{\mathrm{act}}T_j$. Obviously,

$$\langle \Phi_i | T^j \Phi_j \rangle = \delta_{ij} \qquad i, j \in M_0 \tag{12}$$

is still valid, but (unlike CI) in complete exponential expansion

$$\langle \Phi_i | \mathrm{e}^{T^j} \Phi_j \rangle \neq \delta_{ij} \qquad i, j \in M_0 \tag{13}$$

because some of the products may generate other determinants from model space

$$^{\mathrm{act1}}T^{j}\ {}^{\mathrm{act2}}T^{j}|\Phi_j\rangle = c|\Phi_i\rangle\ . \tag{14}$$

Thus, without introducing additional conditions, the intermediate normalization may be broken and the whole concept may become problematic. Meissner et al.[26] have shown that for special types of IAS, namely when any excitation operator is uniquely classified as a external or internal operator (i.e. producing determinants $\in M_0$ or $\in M_0^{\perp}$ with respect to all determinants in the reference space), size extensivity can be saved by introducing alternative normalization conditions. Although the two-determinant IAS belongs to this type and the concept could be used, this technology seems to be too complex to be coded effectively. For the sake of completeness, we note that the method has been extended to a general type of IAS [27]. A significant invention in solving HS MR-CC for an incomplete active reference space comes finally from the laboratory of Paldus and coworkers[28,29]. They exploit the concept of the so-called *C-conditions*, i.e. introducing CI-like coefficients C^i, which make it possible to rewrite $\tilde{\Psi}_i$ formally in the linear form

$$|\tilde{\Psi}_i\rangle = U|\Phi_i\rangle = \mathrm{e}^{T^i}|\Phi_i\rangle = |\Phi_i\rangle + \tilde{C}^i|\Phi_i\rangle\ . \tag{15}$$

Obviously,

$$\tilde{C}_1^i = T_1^i \tag{16}$$

$$\tilde{C}_2^i = T_2^i + \frac{1}{2}T_1^i \cdot T_1^i \tag{17}$$

etc., where the subscript in T_n^i indicates the level of the excitation operator. This idea goes back to equations (*68*)–(*73*) of ref.[13] Within this framework the solution of the problem can be formulated in a very clear and elegant way: instead of requiring $(t_n^i)_\mu = 0$ (the small letter denotes the value of amplitude corresponding to a particular excitation μ of a given type) when $(T_n^i)_\mu|\Phi_i\rangle = (t_n^i)_\mu|\Phi_j\rangle$ generates another determinant from reference space

$|\Phi_j\rangle$, we will require $(\tilde{c}_n^{\,i})_\mu = 0$. Thus, the values of external excitation amplitudes will be determined using Bloch equation (*10*), and internal amplitudes via *C-conditions*, given by Eqs (*16*) and (*17*). Evidently, the amplitude of any monoexcitation producing a reference function arising from another reference function must vanish automatically. However, starting from internal biexcitations, their amplitudes may be of nonzero magnitude (in contrast to CAS-like solutions) to eliminate the undesired contributions produced by products of lower rank excitations operators ${}^{\mathrm{act}}T^{\,i}_{<n}$ (like a case, presented in Eq. (*14*)). Now it becomes obvious that *C-conditions* represent a simple and powerful tool to preserve intermediate normalization and thus main features of the original HS MR-CC concept. In particular, for two electrons, the *C-conditions*-based solution automatically leads to FCI.

Let us shortly recall some important steps needed for the numerical implementation of TD-CC and *C-conditions*. Balková and Bartlett[10] presented the equations and implementation of the code, in which the renormalization term (i.e. terms on the right hand-side of Eq. (*10*)) is limited to contributions, which are linear or at most quadratic in t. Their program allows to treat both CAS and IAS model spaces. This code was used in several calculations, including the study of first few excited states of LiH [12], which is isoelectronic with our molecules in the valence space.

Szalay and Bartlett[11] implemented a code where the renormalization term was treated completely, i.e. it contains also cubic and quartic terms. These terms are usually not large in comparison with (mainly) linear contributions, but they may play an important role in the orbital relaxation. The choice of reference orbitals for the TD-CC method is more important than in standard single-determinant-based cases. In some cases we are using orbitals, which are not optimized specifically for a selected TD CSF (e.g., we use ground-state closed-shell orbitals; more details will be discussed later). Thus, the presence of complete orbital relaxation, which is realized via exp (T_1) is particularly important. The code[11] is limited to CAS model spaces.

C-conditions for incomplete MS (or a general MS) were successfully implemented into the Brillouin–Wigner (BW) MR CC method by Pittner, Li and Paldus[29]. Although the BW CC approach seems to be rather different from the RS one, Pittner[30] showed that these two methods can be treated within the same framework introducing an arbitrary denominator shift in BW CC. This allows to obtain RS MRCC results using the MR BWCC code. Actually this helped us in testing of our code. The BW treatment of MR CC is suitable especially in the presence of intruder states, but the method is not exactly size-consistent. However, innovations introduced recently[30,31] make it possible to reduce the magnitude of the size inconsistency significantly.

COMPUTATIONAL DETAILS

The computer program used in this work was written by one of us (P. N.). It is implemented in the MOLCAS 5.2 computer program[32]. The program uses essentially the same methodology as the previous one[11] and is its extension also for incomplete model space using the *C-conditions* concept. Specifically for our TD-CC approach, it is sufficient to create a set of excitation amplitudes only for one of the determinants since amplitudes for the second determinant are one to one related via complete spin-flip relations[10]. Thus, in contrast to general MR implementations, the numerical requirements are comparable with a standard single-determinant-based CCSD method, because the evaluation of the renormalization term needs marginal computational effort. Our program allows to use arbitrary molecular orbitals to form both determinants. This feature is similar to the QRHF method of Rittby and Bartlett[8]. The details will be presented elsewhere[33].

We used both nonrelativistic Pol [34] and relativistically contracted NpPol basis sets[35]. Since rubidium is already a relatively heavy element, all calculations were performed considering scalar relativistic effects within the no-pair Douglas–Kroll–Hess quasirelativistic approximation[36]. The main portion of results were obtained using more extended basis sets of the NpHyPol type[37]. These bases were created from corresponding NpPol basis sets decontracting the basis set function with the lowest exponents of the d subset into two individual primitive functions and introducing the f subset with the same exponents. However, these bases were not available for our elements until recently. Actually, only nonrelativistic HyPol basis sets for Li and Na were available[37]. Thus, we have produced all needed NpHyPol basis sets in an analogous way. Both NpPol and NpHyPol basis sets are designated for the treatment of electric properties. The usefulness of NpPol basis sets in calculations of intermetallic diatomics and their bonding properties was demonstrated in previous papers, see, e.g.[38,39]. These basis sets contain sufficiently diffuse basis functions and are thus suitable for describing relatively weak bonds. The disadvantage is that the basis set superposition error (BSSE)[40] is relatively large.

In all correlated calculations inner shell orbitals were frozen. More specifically, orbitals corresponding to 1s electrons of the Na element and the 1s2s2p and the 1s2s2p3s3p3d electrons of the K and Rb elements, respectively, were left uncorrelated.

The selection of the reference orbitals applicable to subsequent CC calculations is unique for the closed-shell and the high-spin open-shell systems. For the ground state of Na_2 ($X^1\Sigma_g^+$) and NaMe molecules ($X^1\Sigma$), with Me =

Li, K, or Rb, it is possible to create a single-determinant reference which was actually used as a reference for all CCSD and CCSD(T) calculations.

The selection of reference orbitals for more general open-shell systems, particularly the excited singlet states, needs special attention. The most natural selection would be using the orbitals that represent the state under consideration, what in our case means orbitals, corresponding to the references of the type defined by Eq. (*2*). If *m* and *n* orbitals (from Eq. (*1*)) belong to different irreducible representations, reference function (*2*) represents CAS. This is the case of $A^1\Sigma_u$ and $B^1\Pi_u$ states of Na_2. Considering the computational D_{2h} symmetry, the inactive/active orbitals in particular irreducible representations were (31103110/10001000) for the $A^1\Sigma_u$ state and (31103110/11000000) for the $B^1\Pi_u$ states, respectively, with two active electrons. This reference will be denoted as “A” for the $A^1\Sigma_u$ state and as “B” for the $B^1\Pi_u$ state. The above mentioned situation is also the case for the $B^1\Pi$ states of heteronuclear NaMe molecules, with corresponding active space of the (1100) type within the C_{2v} symmetry (this reference will be also denoted as “B”).

For the $A^1\Sigma$ state of heteronuclear molecules, the absence of the center of symmetry merges our *m* and *n* orbitals (σ_g and σ_u in a homonuclear molecule) into the same irreducible representation. Consequently, our CSF, given by Eq. (*2*), represents IAS. In general it should be possible to produce orbitals, corresponding to this reference (which would be the most natural choice of orbitals for subsequent TD-CC calculations). However, our implementation is based on the RASSCF code from MOLCAS as an orbital generator, which in the present version does not allow to treat this type of the reference separately. Two additional (mostly undesired[10]) doubly occupied configurations m^2 and n^2, which supplement the model space to the (2000) CAS (with two active electrons) are, unintentionally, included as well. Such CAS reference would be adequate around the minima. At large distances, however, the weight of undesired configurations increases, which leads to deterioration of the long-range part of the potential energy curves. For this reason we did not use the CAS reference yet.

Attempting to trace the effect of the choice of different reference orbitals, we have calculated potential energy curves for both excited singlet states of Na_2 and the $B^1\Pi$ excited state of NaLi, NaK, and NaRb using the ground state reference orbitals (denoted as “X” reference orbitals) and the triplet $a^3\Sigma$ state reference orbitals (denoted as “a” reference orbitals) along with their genuine reference orbitals created from the two-determinant complete space.

The active space for CASSCF/CASPT2 calculations was (21102110) and (4220) for Na_2 and NaMe molecules, respectively. It comprises the highest doubly occupied σ orbital and additional three σ orbitals created from the valence *n*s and np_z orbitals of the metal element. Remaining orbitals in the active space are created from np_x and np_y orbitals. Such active space allows proper dissociation to the products over the whole potential energy curve. Two electrons were active in CASSCF, which means that essentially no dynamic electron correlation is included at this level of sophistication. An essential part of the dynamic electron correlation was considered in the CASPT2 step. Results for the A state were obtained as the 2nd root for totally symmetric irreducible representation in all cases except for Na_2, where X and A states have different symmetry.

All potential energy curves and all spectroscopic constants were calculated considering BSSE.

Dissociation Products and the BSSE Correction

Dissociation products of the Na_2 $X^1\Sigma_g^+$ state are two Na atoms in the ^2S state. Analogously, dissociation products for the $X^1\Sigma$ states of heteronuclear molecules NaMe (with Me = Li, K or Rb) are the Na ^2S and the Me ^2S states, respectively. Dissociation products for the $A^1\Sigma_u$ and $B^1\Pi_u$ states of Na_2 and the $A^1\Sigma$ and $B^1\Pi$ states of NaMe are Na ^2S and Me ^2P states. Other dissociation channels, which would represent products like Na ^2P and Me ^2S, were not studied in detail in this work.

We note that our methods are not true multireference methods and are, in general, not aimed at calculation of the potential energy curves over the whole energy surface. Concerning calculation of the dissociation energy, one can, of course, calculate the energy around the minimum of the potential energy curve for our molecules in the state of interest and to use the standard CCSD or the CCSD(T) method with the restricted open-shell Hartree–Fock reference[41–44] for calculating the dissociation products, i.e. energies of a Me element in the corresponding doublet state.

We need to address a specific problem concerning BSSE in relation to the dissociation products. Namely, we should realize that the Me ^2P dissociation product can be represented by a singly occupied orbital with electron occupying either np_z or np_x (np_y) orbital, i.e. the orbital oriented in the direction of the principal axis of the NaMe molecule or perpendicularly. Both are energetically degenerate in standard atomic calculations. However, this is not the case when calculating BSSE correction due to the presence of the ghost basis set in one of the axes (say *z*). Thus, in evaluation of BSSE we need to use results with np_z (let us assign it as ^2P_z) as the singly occupied orbital in the dissociation process of the A state, while the np_x or np_y orbital (^2P_x) is needed for the dissociation of B state. Unfortunately, our CC code does not enable us to calculate the ^2P_z case, because it belongs to the same symmetry as ^2S, while there are no problems with ^2P_x. However, our numerical tests show, that the distance (R) dependence of BSSE is almost identical for the ^2S and ^2P_x states (at least from the point of view of the magnitude of errors in final bonding energies). Since these two states are physically much more different than are ^2P_x and ^2P_z states, we can estimate that the R dependence of ^2P_z will be also very similar. Thus, we use ^2P_x energies for both cases.

RESULTS AND DISCUSSION

A comparison with experiment is a necessary requirement for assessment of correctness of newly developed concepts for calculating molecular properties. In this respect the potential energy function determined over wide ranges of internuclear distances plays an essential role. The potential energy curve of diatomics is a fundamental molecular characteristic accumulating much information about basic properties such as the equilibrium internuclear distance, stability of the molecule, and its dissociation products. In addition, each stable molecular electronic state possesses a system of vibrational and rotational energy levels on its own and transitions between these states are responsible for the rovibronic spectra of the molecule. These spectra are largely determined by the shapes and mutual arrangement of the potential energy curves of the combining electronic states.

We start the discussion here with summarizing the results calculated for the dissociation and excitation energies of Na_2, NaLi, NaK, and NaRb. Along with these molecular quantities we also present the relevant lowest alkali atomic excitation energies for which accurate experimental data are available. A comparison of the theoretical and experimental atomic excitation energies provides a direct check of the performance of NpPol and NpHyPol basis sets. These properties are calculated using both the open-shell ROHF CCSD and CCSD(T) methods[41–46] and they are listed here together with the corresponding results obtained from CASSCF and CASPT2 calculations. After evaluating these basic energetics a discussion of the results obtained for the equilibrium bond distances, R_e, the harmonic vibrational frequencies, ω_e, and anharmonicities, $\omega_e x_e$, follows. In this discussion the spectroscopic constants of the Na_2 molecule in its ground and lowest excited singlet states are considered separately from those of the heteronuclear NaLi, NaK, and NaRb molecules which are characterized by an incomplete active space.

Dissociation and Excitation Energies of Na_2, NaLi, NaK, and NaRb

Dissociation energies of Na_2, NaLi, NaK, and NaRb derived from the CCSD and CCSD(T) potential energy calculations are compared in Table I with the corresponding CASSCF and CASPT2 results and with experiment if available. The ground state dissociation energies at the CCSD(T) and CASPT2 levels agree with experimental data usually within 0.01–0.04 eV. The same uncertainty margin actually applies to experimental data collected from different sources. A larger difference between theory and experiment is found for the D_e of NaRb, up to 0.04–0.08 eV, depending on the experimental value used for comparison whereas the CCSD(T) and CASPT2 results in this case are in excellent agreement with each other. The contribution from triple excitations in the CCSD(T) results to the ground state dissociation energies is quite small for NaLi with 0.018 eV, increasing to 0.045 eV for NaRb. Inclusion of triples improves the agreement between theoretical CC data and experiment. On the other hand, by taking the uncertainty of experimental dissociation energies into account, this improvement is of the same order of magnitude. Experimental dissociation energies for the singlet excited A and B states are only available for Na_2 and NaK and for the B state of NaRb. The agreement between our theoretical CCSD and CASPT2 dissociation energies and the experimental values for these states was found to be comparable with that for the ground states. For NaLi, apart from the ground state, experimental results are not available for comparison. Previous theoretical D_e values[60], however, obtained on the configuration interaction (CI) level of theory are in relatively good agreement with the present results.

In the upper part of Table II results for the excitation energies $^2S - {}^2P$ of Li, Na, K, and Rb are summarized. A reasonably accurate representation of these quantities on the different theory levels is essential since the atomic ^2S and ^2P states are the dissociation products on the potential energy curves. In general, CCSD(T) and CASPT2 values agree with J-weighted average experimental values very well. Surprisingly, the largest difference between theoretical and experimental excitation energy occurs for Li (60 cm^{-1}). Electron correlation contributions are found to be important, they increase from Li (–57 cm^{-1}) to Rb (1825 cm^{-1}) according to the CCSD(T) results. The contribution of triples is small, changing only rather little for different al-

TABLE I
Dissociation energies D_e (eV) of Na_2, NaLi, NaK, and NaRb

State	Ref.[a]	CCSD	CCSD(T)	CASSCF[b]	CASPT2[b]	Experiment
Na_2						
$X^1\Sigma_g^+$	X	0.687	0.718	0.702	0.726	0.73[c], 0.746[d]
$A^1\Sigma_u^+$	A	1.026	–	0.986	1.015	1.030[d]
	X	1.009	–			
	a	0.993	–			
$B^1\Pi_u$	B	0.300	–	0.168	0.287	0.331[d]
	X	0.313	–			
NaLi						
$X^1\Sigma^+$	X	0.832	0.850	0.843	0.853	0.876[e], (0.82)[f]
$A^1\Sigma^+$	X	0.942	–	0.989	0.949	(0.95)[f]
	a	0.935	–			
$B^1\Pi$	B	0.206	–	0.127	0.194	(0.12)[f]
NaK						
$X^1\Sigma^+$	X	0.568	0.608	0.624	0.6140	0.621[c], 0.653[g], 0.654[h], 0.644[i]
$A^1\Sigma^+$	X	0.743	–	0.692	0.743	0.759[i]
	a	0.717	–			
$B^1\Pi$	B	0.133	–	0.080	0.124	0.164[j]
NaRb						
$X^1\Sigma^+$	X	0.535	0.579	0.605	0.575	0.66[k], 0.624[l]
$A^1\Sigma^+$	X	0.730	–	0.671	0.734	–
	a	0.744	–			
$B^1\Pi$	B	0.127	–	0.075	0.119	0.164[m]

[a] X, A, B and a mean that reference orbitals for CC calculations are taken from the $X^1\Sigma_g^+$ or $X^1\Sigma^+$, the $A^1\Sigma_u^+$ or $A^1\Sigma^+$, the $B^1\Pi_u$ or $B^1\Pi$, or from the triplet $a^3\Sigma_u^+$ or $a^3\Sigma^+$ single CSF (one or two determinant reference) SCF calculations for the homo- or heteronuclear species, respectively. [b] For CASSCF/CASPT2, only results using the (21102110) and the (4220) active space partitionings for the homo- or heteronuclear species, respectively, with 2 active electrons are presented (see text). [c] Experimental values from ref.[54] [d] From ref.[55] [e] From ref.[59] [f] Theoretical values in parentheses from ref.[60] [g] From ref.[62] [h] From ref.[16] [i] From ref.[63] [j] From ref.[52] [k] From ref.[65] [l] From ref.[17] [m] From ref.[53]

TABLE II
Excitation energies T_e (cm^{-1}) of atoms Li, Na, K, and Rb and molecules Na_2, NaLi, NaK, and NaRb

Process/Reference[a]	CCSD	CCSD(T)[b]	CASSCF	CASPT2	Experiment[c,d]
Li $^2S - {}^2P$	14844	14844	14901	14869	14904
Na $^2S - {}^2P$	16942	16975	15987	16877	16956, 16973
K $^2S - {}^2P$	13020	13058	11438	13014	12985, 13043
Rb $^2S - {}^2P$	12598	12654	10827	12683	12579, 12817
Na_2/Reference					
$X^1\Sigma_g^+ - A^1\Sigma_u^+$/A	14211	14494	13696	14550	14680
/X	14346	14629			
/a	14472	14755			
$X^1\Sigma_g^+ - B^1\Pi_u$/B	20068	20351	20294	20147	20319
NaLi/Reference					
$X^1\Sigma^+ - A^1\Sigma^+$/X	13957	14101	13726	14095	14214
/a	14008	14152			
$X^1\Sigma^+ - B^1\Pi$/B	19887	20031	20676	20183	20244
NaK/Reference					
$X^1\Sigma^+ - A^1\Sigma^+$/X	11610	11970	10888	11973	12137
/a	11818	12178			
$X^1\Sigma^+ - B^1\Pi$/B	16525	16855	15824	16966	16993
NaRb/Reference					
$X^1\Sigma^+ - A^1\Sigma^+$/X	11023	11439	10293	11399	11702
/a	10910	11324			
$X^1\Sigma^+ - B^1\Pi$/B	15883	16299	15102	16360	16528

[a] For reference orbitals for the excited state calculations, see footnote [a] in Table I. [b] The effect of triples for molecular excited states is estimated (see text). [c] Atomic experimental data from NIST (ref.[54]) for states $^2P_{1/2}$ and $^2P_{3/2}$, respectively. Weighted average of $J = 1/2$ and $J = 3/2$ experimental values is 16962, 13004, and 12658 cm^{-1} for Na, K, and Rb, respectively. [d] Molecular experimental data for excitations to the A and B states are taken from: refs[47,48] for Na_2; refs[49,50] for NaLi; refs[51,52] for NaK; refs[19,53] for NaRb.

kali atoms (33–56 cm^{-1}). But it is difficult to generalize this for the diatomic excitation processes discussed in the following. We are presently unable to include the triple excitation operator for excited singlet states in our new two-determinant CC method. The relatively small effect of triples obtained here for the atomic excitation energies may be considered to support the expectation that triples should also not be too critical for molecular species as well.

For the diatomic X–A and X–B excitation processes, excitation energies obtained here on the CC level as well as the CASPT2 results generally tend to be too small compared with available experimental values. Estimated contributions from triples applied to the CCSD results slightly improve the agreement. For both excitation processes, discrepancies between theoretical, either CC level or CASPT2, and experimental excitation energies are approximately in the range of 100–300 cm^{-1}, i.e. between 1 and 2%, with the trend to increase from NaLi to NaRb. The only exception is X–B in Na_2 with CCSD(T) and CASPT2 being slightly larger whereas CCSD is still too small by about 250 cm^{-1}. A major source of the remaining differences between the theoretical results and their experimental analogues has to be attributed to deficiencies of the not explicitly optimized basis sets used in the present calculations. In addition, it has to be kept in mind that the estimated CCSD(T) results are only approximate. They are obtained using CCSD(T) values for the ground state D_e's and the atomic excitation energies together with the CCSD values for the D_e's of the respective excited states. Apart from the existing numerical discrepancies, the calculations on different theory levels are able to reproduce the correct trends among the various excitation energies. This proves that the new concept used in the CCSD calculations is capable of describing the situation in the singlet excited electronic states of the diatomics correctly. Concerning the CCSD calculations for the X–A excitation in the heteronuclear diatomics, the results are influenced by the selection of the reference and corresponding orbital space for the $A^1\Sigma^+$ states. Excitation energies can differ by up to 208 cm^{-1} (NaK) when using orbitals either from the ground state (X) or from the triplet a-state. The effect on the X–A excitation energy determination using the new CCSD approach is thus not negligible and no preference can be safely derived from our calculations. On the other hand, the present CCSD results for the X–B excitation differ from experiment by a similar margin although for the $B^1\Pi$ states of the heteronuclear diatomics a complete active space can be created and the selection of the reference is thus unique.

Potential Energy Curves and Spectroscopic Constants of Na_2

Potential curves calculated for the $X^1\Sigma_g^+$ ground electronic state of Na_2 and the two low-lying singlet excited states, $A^1\Sigma_u$ and $B^1\Pi_u$, are displayed in Fig. 1 for internuclear distances *R* reaching up to 10 Å. The potential energy curves for all three states are plotted relative to the energy which corresponds to the dissociation limit of the $X^1\Sigma_g^+$ ground state.

The ground state potentials in the figure are obtained from calculations at three different theory levels. Of these the CASPT2 calculations utilizing an (21102110) active space partitioning are able to describe the dissociation into two Na (^2S) atoms properly. The potential calculations on the coupled-cluster level are affected by quasidegeneracy at large distances which is a well known problem in calculations of the dissociation potentials of closed-shell molecules represented by a single determinant reference. These curves are therefore truncated at $R = 7$ Å where the CCSD amplitudes become large. Comparison of the CCSD(T) and CCSD curves clearly shows the contribution from triples to the ground state potential.

For the two low-lying singlet excited states of Na_2, both the CASPT2 potential curves in Fig. 1 converge to the dissociation limit corresponding to the products Na(^2S) + Na(^2P). The energy gap between the dissociation products of the $X^1\Sigma_g^+$ ground state and the dissociation products of both ex-

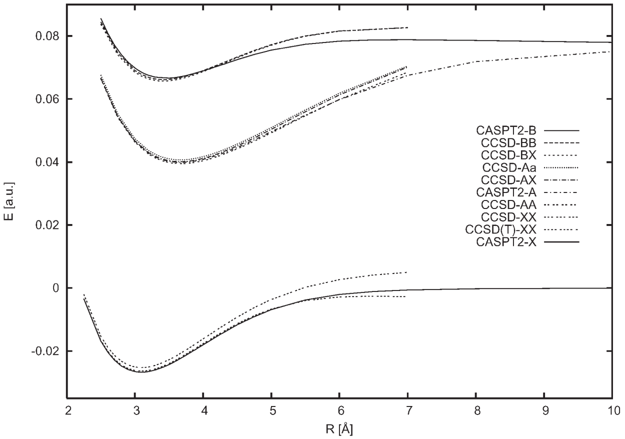

FIG. 1

Na_2 potential energy curves for the $X^1\Sigma_g^+$ ground state and $A^1\Sigma_u^+$ and $B^1\Pi_u$ excited states. Symbols for the reference functions in CC calculations are defined in the footnote of Table I (for example, the symbol CCSD-BX means the curve for the $B^1\Pi_u$ state utilizing the X reference orbitals) cited states corresponds thus to the ^{2}S – ^{2}P excitation energy of Na. The quasidegeneracy problem for larger R values encountered for the ground state occurs also for the excited states. The background behind the problem here is that for the representation of the open-shell $A^1\Sigma_u^+$ and $B^1\Pi_u$ states a two-determinant reference is used in the present CCSD approach rather than a true multideterminant reference. The proper description of the whole dissociation potential would require at least a (11001100) active orbital partitioning scheme, which makes s and p_x orbitals available for both atomic dissociation products (s(a) ± s(b) and p_x(a) ± p_x(b)). However, the formulation of the CCSD approach used here to describe the singlet excited states, is based on (10001000) and (11000000) partitioning schemes for the A and B excited states, respectively. TD-CCSD with these references is capable of representing the dynamical correlation in the minimum region very well. At a distance of about 4.5 Å, however, the CCSD amplitudes increase heavily and become unacceptable. Deterioration of the potential curve by quasidegeneracy problems in this outer part can affect the reliability of the anharmonicities derived from these calculations. Finally we note that the CASPT2 curve of the B state shows a shallow maximum at about 6.9 Å with an energy of 360 cm^{-1} above the dissociation level. This is caused by an avoided crossing of this state with the next higher state of the same symmetry. These results agree perfectly with experimental observations of an energy hump in the potential of this state with H_B = 379.3 cm^{-1} at R = 6.8 Å [56] or H_B = 377.7 cm^{-1} at R = 7.1 Å [57].

Basic spectroscopic constants R_e, ω_e, and $\omega_e x_e$ derived from potential calculations on the different theory levels are summarized in Table III for the three electronic states of Na_2 in comparison with experiment. The equilibrium bond distances are generally obtained too large, which is due to an overcompensation of the BSSE effect using the Boys–Bernardi correction procedure and it shows that the atomic basis sets used in the present calculations are not complete. Better agreement with experiment is obtained for the harmonic vibrational frequencies on all three correlated theory levels. In particular the new CCSD approach is doing rather well for the ground and the two excited states with maximum deviations of about 1% and less. The curvature of the potentials in the minimum region is thus described rather accurately by this approach, which underlines the above statement about the reliability of the two-determinant reference in this region.

Figure 2 directs attention to the influence of different reference orbitals on the shapes and the qualities of the calculated potentials in the case of the $A^1\Sigma_u^+$ state of Na_2. A more detailed numerical information determining the quality of the references is provided in Tables I–III. The shapes of the potential energy curves around the minimum are rather similar for the different references exploiting orbitals from the $A^1\Sigma_u^+$ state or from $X^1\Sigma_g^+$ or the $a^3\Sigma_u^+$ states. This finding is to some extent reflected by the fact that the results for the basic spectroscopic constants listed in Table III do not differ very much for different references. Larger is the influence of the reference orbitals on the determination of the excitation energy of X–A in Table II and on the dissociation energy in Table I especially when comparing the

TABLE III
Equilibrium bond distance R_e (Å), harmonic vibrational frequency ω_e and anharmonicity $\omega_e x_e$ (cm^{-1}) of the Na_2 molecule in its ground state and the lowest excited singlet states

State	Ref.[a]	CCSD	CCSD(T)	CASSCF	CASPT2	Experiment
R_e						
$X^1\Sigma_g^+$	X	3.095	3.095	3.186	3.095	3.079[b], 3.080[c]
$A^1\Sigma_u^+$	A	3.677	–	3.757	3.672	3.638[b], 3.635[c]
	X	3.662	–	–	–	
	a	3.666	–	–	–	
$B^1\Pi_u$	B	3.424	–	3.606	3.460	3.423[b], 3.413[c]
	X	3.414	–	–	–	
ω_e						
$X^1\Sigma_g^+$	X	158.2	156.6	150.7	157.2	159.1[b], 159.2[c]
$A^1\Sigma_u^+$	A	115.0	–	111.9	115.1	117.3[b,c]
	X	116.6	–	–	–	
	a	117.0	–	–	–	
$B^1\Pi_u$	B	125.5	–	112.3	120.4	124.1[b], 124.4[c]
	X	126.5	–	–	–	
$\omega_e x_e$						
$X^1\Sigma_g^+$	X	0.64	0.69	0.71	0.72	0.725[b]
$A^1\Sigma_u^+$	A	0.36	–	0.33	0.37	0.358[b]
	X	0.36	–	–	–	
	a	0.36	–	–	–	
$B^1\Pi_u$	B	0.68	–	0.86	0.82	0.700[b]
	X	0.67	–	–	–	

[a] See footnote [a] in Table I. [b] Experimental data from NIST (ref.[54]). [c] Other experimental values from ref.[55]

genuine A-reference with the one taken from the triplet a-state. This observation may serve as a guidance for calculations of A state potentials and possible choices of appropriate references for the heteronuclear diatomics discussed below. The figure also demonstrates the effect of the BSSE correction on the A state potential curve. Without BSSE correction, the dissociation energy would be D_e = 1.135 eV. Finally, also included in Fig. 2 is the CCSD curve obtained from calculations with the smaller NpPol basis set. The curve has a slightly different shape and its minimum is shifted to a larger R distance. The spectroscopic constants for the $A^1\Sigma_u^+$ state of Na_2 obtained from this potential are: D_e = 0.997 eV; R_e = 3.728 Å; ω_e = 110.6 cm^{-1}.

Potential Energy Curves and Spectroscopic Constants of NaLi, NaK, and NaRb

There is a basic difference in applying the TD-CCSD approach in potential calculations for the heteronuclear diatomics compared with the homonuclear Na_2 due to the fact that the heteronuclear species have a lower symmetry. The first consequence is that for heteronuclear molecules we were not able to construct a complete active space representation the excited singlet $A^1\Sigma^+$ state. On the other hand, reduced symmetry in heteronuclear species is favorable for a proper representing of the long-range part of the potential energy curves for the singlet excited states, aside from purely technical problems in creating proper IAS reference for the $A^1\Sigma^+$ state when using MOLCAS.

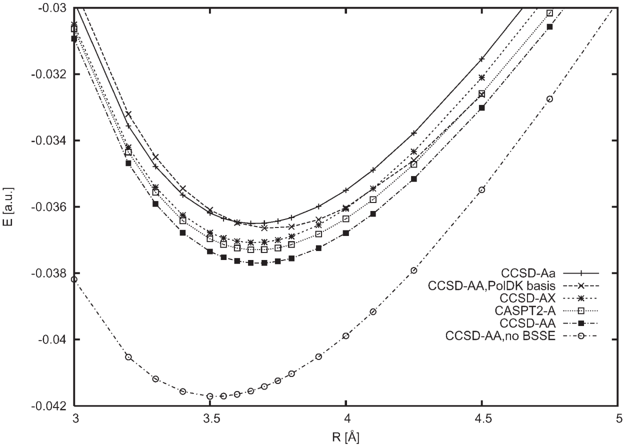

FIG. 2
Na_2 $A^1\Sigma_u^+$ excited state potential energy curves

The electronic structure of the $A^1\Sigma^+$ singlet excited state in the heteronuclear cases is characterized by two unpaired electrons localized in two σ orbitals of the same symmetry representation whereas in the A state of Na_2 the two electrons are distributed among the two singly occupied σ_g and the σ_u orbitals belonging to different symmetry species. The orbital partitioning ([core]/2000) used in the heteronuclear TD-CCSD potential calculations for the A state represents an incomplete active space (IAS) which requires a more complicated theoretical handling.

Figure 3 (in analogy to Fig. 1) compares for NaK the potential energy curves for the $X^1\Sigma^+$ ground state and the singlet excited $A^1\Sigma^+$ and $B^1\Pi$ states calculated at the coupled-cluster level with the corresponding CASPT2 curves. Like for the Na_2 ground state the effect of triples is shown in the CCSD(T) potential. The potentials for NaK are representative for all the other heteronuclear species considered here, the general features of the NaLi and NaRb curves are similar. Due to quasidegeneracy problems, the CC potential curves for the ground and the first excited A state are truncated. For the $B^1\Pi$ state the potential curve determined on the coupled-cluster level progresses close to the CASPT2 curve and behaves correctly up to the dissociation limit. The reference for the CCSD calculation arising from the (1100) active space is thus adequate for the heteronuclear dissociation potential calculations. This, however, does not guarantee smoothness in general. Like in Na_2, also for the $B^1\Pi$ state of NaLi an avoided crossing with the next higher state of the same symmetry seems to occur where the higher state

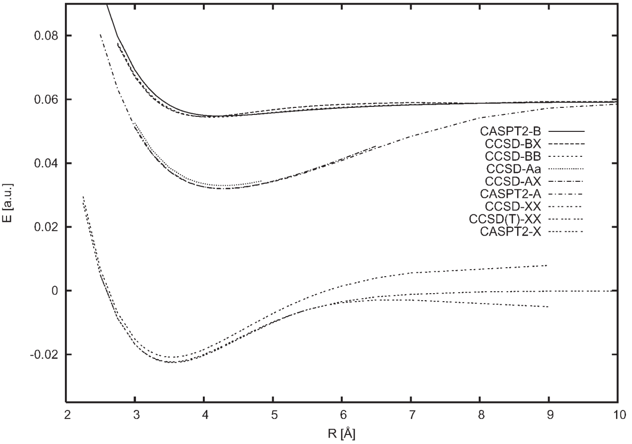

FIG. 3
NaK potential energy curves for the $X^1\Sigma$ ground state and $A^1\Sigma$ and $B^1\Pi$ excited states

after the avoided crossing dissociates to Na(^{2}P) + Li(^{2}S). Other than in Na_2, however, the crossing region is around R = 4.1 Å[60]. In the present potential calculations, in particular the curve obtained on the CASSCF level shows a shoulder in this region indicating a state interaction taking place (Fig. 4). Figure 3 also demonstrates the influence of different selections of reference orbitals on the potential curves of the $A^1\Sigma^+$ state of NaK. Whereas in Na_2 (Fig. 1) the curves obtained from CCSD calculations using the genuine $^1\Sigma_u^+$ reference orbitals show a proper behavior for large R values, in NaK (like in the other heteronuclear species) there is no genuine reference orbital basis available and the usage of the X or a-state references leads to the breakdown of the correct A state description at larger distances. Due to the deterioration of the potential energy curves relatively close to the minimum, the calculated $\omega_e x_e$ were not stable enough and are thus not included in the table.

In Fig. 4, a comparison of CASSCF, CASPT2 and CCSD potential energy curves for the $B^1\Pi_u$ state of Na_2 with the corresponding curves for the $B^1\Pi$ state of NaLi is given. The figure clearly shows that for the B state of Na_2 the CASPT2 and the related CASSCF curves show shallow energy maxima in the distance region 6.0 ≤ R ≤ 7.0 Å in good agreement with the experimental finding mentioned above. In contrast to the B state of NaLi, the CASSCF curve has a shoulder at about R = 4.1 Å whereas CASPT2 (and actually also CCSD) run smoothly through this region even if the curves seem to be misformed.

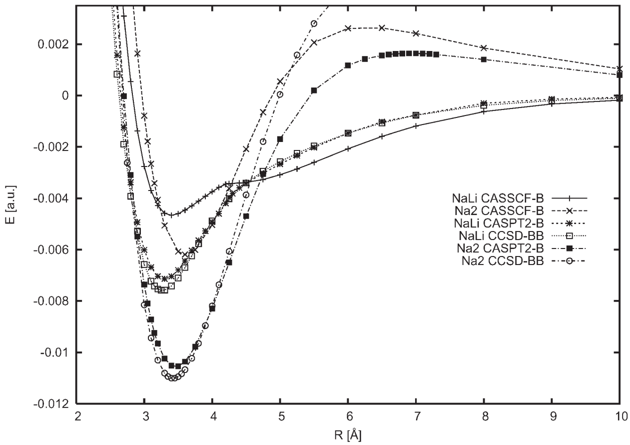

FIG. 4
Na_2 and NaLi potential energy curves for the $B^1\Pi$ singlet excited state. Comparison of CASSCF, CASPT2 and CCSD curves

More quantitative characterizations of the performance of the CCSD approach in describing the heteronuclear properties can be found in the tables. Looking at the energetics, dissociation and excitation energies in Tables I and II, it is seen that the CCSD results are generally low compared with experiment whereas CCSD(T) for the ground states and CASPT2 are mostly in better agreement. It was mentioned before that in the case of dissociation energies the missing triples are mostly responsible for the discrepancy. Results for basic spectroscopic properties collected in Tables IV–VI show that they follow the same trends like those for Na_2. Equilibrium bond distances tend to be too long compared with the values derived from experiment which was already previously attributed to basis set deficiencies (overcom-

TABLE IV
Equilibrium bond distance R_e (Å), harmonic vibrational frequency ω_e and anharmonicity $\omega_e x_e$ (cm^{-1}) of NaLi in its ground state and the lowest excited singlet states

State	Ref.[a]	CCSD	CCSD(T)	CASSCF	CASPT2	Experiment
R_e						
$X^1\Sigma^+$	X	2.911	2.909	2.949	2.909	2.81[b], 2.885[c], (2.868)[d]
$A^1\Sigma^+$	X	3.401	–	–	3.406	(3.349)[d], (3.381)[e]
	a	3.398	–	–	–	
$B^1\Pi$	B	3.266	–	–	3.296	3.20[b], (3.228)[d]
ω_e						
$X^1\Sigma^+$	X	253	252	247	253	256.8[b], 257.0[c], (250)[f]
$A^1\Sigma^+$	X	185.6	–	–	184.4	(190)[f]
	a	186.3	–	–	–	
$B^1\Pi$	B	175	–	–	165.4	(130)[f]
$\omega_e x_e$						
$X^1\Sigma^+$	X	1.56	1.62	1.61	1.53	1.612[b], (1.5)[g]
$A^1\Sigma^+$	X	0.84	–	–	0.84	(1.1)[g]
	a	0.85	–	–	–	
$B^1\Pi$[h]	B	–	–	–	–	(~1)[g]

[a] See footnote [a] in Table I. [b] Ref.[58] [c] Ref.[59] [d] Theoretical values in parentheses from ref.[60] [e] Theoretical value in parentheses from ref.[61] [f] Theoretical values in parentheses from ref.[60] [g] Theoretical values in parentheses from ref.[60] [h] Values were not stable enough.

pensation in the Boys–Bernardi BSSE correction procedure). Harmonic frequencies, on the other hand, are mostly in rather good agreement with reference results.

CONCLUSIONS

We present in this contribution some applications of our newly implemented CCSD method based on a two-determinant reference (TD-CCSD) which is appropriate to describe open-shell excited singlet states. Both, a complete or incomplete active space can be used in our approach. Another practical advantage of our method is that the computer time needed for calculating excited singlets with the two-determinant reference is essentially the same as that for a corresponding single reference calculation.

TABLE V
Equilibrium bond distance R_e (Å), harmonic vibrational frequency ω_e and anharmonicity $\omega_e x_e$ (cm^{-1}) of NaK in its ground state and the lowest excited singlet states

State	Ref.[a]	CCSD	CCSD(T)	CASSCF	CASPT2	Experiment
R_e						
$X^1\Sigma^+$	X	3.539	3.538	3.669	3.552	3.589[b], 3.498[c], 3.49[d]
$A^1\Sigma^+$	X	4.273	–	4.445	4.274	4.17[d]
	a	4.282	–	–	–	
$B^1\Pi$	B	4.121	–	4.594	4.237	4.04[d], 4.0134[e]
ω_e						
$X^1\Sigma^+$	X	122.4	120.4	115.3	120.4	124.1[b,d], 124[f]
$A^1\Sigma^+$	X	78.7	–	72.4	82	79.8[b], 81.3[d]
	a	78.5	–	–	–	
$B^1\Pi$	B	66.0	–	44.4	62.7	72.6[b], 71.463[e]
$\omega_e x_e$						
$X^1\Sigma^+$	X	0.43	0.47	0.44	0.46	0.511[b]
$A^1\Sigma^+$	X	0.25	–	0.22	0.27	0.087[b]
	a	0.26	–	–	–	
$B^1\Pi$	B	1.06	–	0.50	–[g]	1.475[b], 1.151[e]

[a] See footnote [a] in Table I. [b] Experimental data from NIST (ref.[54]). In this reference $^1\Pi$ state is called C-state. [c] Ref.[62] [d] Ref.[63] [e] Ref.[52], see also ref.[18] [f] Ref.[64] [g] Value was not stable enough.

In order to test the performance of the TD-CCSD approach we use the method of calculation of spectroscopic properties for the model diatomic molecules Na_2 in the $X^1\Sigma_g^+$ ground state and the two singlet mono-excited states, $A^1\Sigma_u^+$ and $B^1\Pi_u$. Analogous calculations are made for the $X^1\Sigma^+$, $A^1\Sigma^+$ and $B^1\Pi$ states of the NaLi, NaK, and NaRb heteronuclear molecules. The influence of different selections of orbitals for the construction of the the model space serving as reference for TD-CCSD is carefully analysed. For the $A^1\Sigma^+$ state of the heteronuclear species the reference can be created from orbitals obtained for the ground state or from the corresponding one-determinant solution for the analogous triplet state. Dissociation energies differ in this case typically by less than 0.02 eV and excitation energies from the ground $X^1\Sigma^+$ to the $A^1\Sigma^+$ state by about 50 cm^{-1} (NaLi) up to 200 cm^{-1} (NaK) depending on the selected reference. Theoretical CCSD dissociation

TABLE VI
Equilibrium bond distance R_e (Å), harmonic vibrational frequency ω_e and anharmonicity $\omega_e x_e$ (cm^{-1}) of NaRb in its ground state and the lowest excited singlet states

State	Ref.[a]	CCSD	CCSD(T)	CASSCF	CASPT2	Experiment
R_e						
$X^1\Sigma^+$	X	3.693	3.691		3.700	3.56[c], 3.644[d]
$A^1\Sigma^+$	X	4.502	–		4.514	(4.406)[e]
	a	4.493	–		–	–
$B^1\Pi$	B	4.293	–		4.406	4.177[f]
ω_e						
$X^1\Sigma^+$	X	105.4	103.4		101	106.6[b], 107[c]
$A^1\Sigma^+$	X	64.8	–		63.7	(66.0)[g]
	a	66.5	–		–	–
$B^1\Pi$	B	56.4	–		54	61.2[f]
$\omega_e x_e$						
$X^1\Sigma^+$	X	0.33	0.36		0.2	0.455[b]
$A^1\Sigma^+$	X	0.15	–		0.14	–
	a	0.05	–		–	–
$B^1\Pi$	B	0.83	–		–[h]	–

[a] See footnote [a] in Table I. [b] Experimental data from NIST (ref.[54]). [c] Ref.[65] [d] Ref.[17] [e] Theoretical value in parentheses from ref.[19] [f] Ref.[53] [g] Theoretical value in parentheses from ref.[19] [h] Value was not stable enough.

energies for excited singlet states deviate from available experimental values by amounts ranging from 0.006 eV for the $A^1\Sigma^+$ state of Na_2 up to 0.04 eV for the $B^1\Pi$ state of NaRb. For excitation energies the agreement between theory and experimental data is typically within 30 cm^{-1} (for the $X^1\Sigma^+ - B^1\Pi$ excitation in NaLi) up to 230 cm^{-1} for the same excitation process in NaRb. Theoretical CCSD bond distances R_e (Å) for excited singlet states deviate from available experimental values by 0.001 up to 0.1 Å ($X^1\Sigma^+$ and $B^1\Pi$ states of NaLi and the $B^1\Pi$ state of NaRb). Experimental results, however, are not especially accurate. Harmonic vibrational frequencies ω_e deviate from experimental values typically by less than 2–3 cm^{-1}. It is difficult to assess the accuracy of the anharmonicity. Apart from the fact that our potential energy curves are deteriorated in some cases by quasi-degeneracy problems at larger distances, another source of inaccuracies is the fitting procedure adjusting the free parameters of an appropriate potential expression to the calculated energy points. On the other hand, experimental reference data are also obviously affected by inaccuracies arising from the process of converting the direct measurements into physical constants.

In general, the reasonably good agreement of the theoretical results obtained here using the TD-CCSD approach with the experimental reference data appears to be promising even if the possibility of some error compensation cannot be excluded on this performance level. More accurate results would probably need triples to be included in the description although our calculations seem to indicate that triples are less important for excited states compared with the ground state.

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