Double Electron Affinity for Potential Energy Curves of Closed Shell Molecules

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Abstract—**The newly proposed method [M. Musiał, *J. Chem. Phys.*, 136, 134111 (2012)] based on the multireference coupled cluster (CC) theory formulated in the (2,0) sector of the Fock space (FS) (essential in the double electron affinity (DEA) calculation) is applied to the alkali metal diatomics to generate smooth potential energy curves which correctly describe the dissociation process of the studied molecules. To avoid intruder state problems the method is realized within the framework of the intermediate Hamiltonian which provides efficient size-extensive computational scheme. The DEA strategy makes it possible to describe electronic states of the neutral molecule, e.g. potassium dimer K_2, by adopting as a reference its doubly ionized cation K_2^{+2}. The FS-CC(2,0) scheme offers an attractive *first principle* method without any model or effective potential parameters for the description of the bond breaking processes.**

Keywords: multireference coupled cluster theory in Fock space, potential energy curves, alkali metal dimers, dissociation of the single bond, double electron affinity

1 Introduction

The quantum chemical description of the dissociation of the standard single bond formed by a pair of electrons is not a trivial task. The difficulty originates from the fact that in the vicinity of the equilibrium the molecule is correctly represented by a closed shell configuration easily obtained with the restricted Hartree-Fock (RHF) scheme. However, when the closed shell molecule dissociates into open shell fragments the RHF leads to the incorrect dissociation results and in such case the proper computational variant is the UHF (unrestricted HF). The latter, though, has some inconvenient features like poorly determined spin or certain convergence problems, in particular when applied as the reference for the correlated treatment. The ideal and very welcome situation occurs when the closed shell system dissociates into closed shell fragments. In such case the RHF function makes a suitable reference for the whole range of interatomic distances. Such situations do not occur, however, for real chemical bonds, they can be encountered in the van der Waals type molecules engaging, e.g., noble gas atoms. We notice, however, that the conditions mentioned above may be met in the cases when we dissociate a double positive ion instead of the neutral molecule. Let us consider as an example the K_2 molecule which dissociates into the open shell atoms each with an unpaired electron.

$$K_2 \rightarrow K^{\cdot} + K^{\cdot} \tag{1}$$

However, the double positive ion of the K_2 dissociates as

$$K_2^{+2} \rightarrow K^+ + K^+ \tag{2}$$

and we obtain closed shell products, K^+, isoelectronic with the Argon atom. These observations help us to establish a new approach to the single bond dissociation process on condition that we have at our disposition the computational scheme capable to treat the states with attached two electrons (DEA). In other words: capable to describe the neutral molecule on the basis of the doubly ionized reference. If so we may apply it to calculate the potential energy curves (PECs) for any electronic states. In order to take advantage of the above observations we introduce the so called DEA approach to the single bond dissociation problem.

2 Synopsis of the theory

The DEA approach [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11] can be applied in the situation which is well exemplified by the above case of the K_2 molecule, i.e. when the molecule after removal of two electrons dissociates into closed shell fragments. The necessary condition for the successful application of the DEA strategy is an access to the high accuracy method which at the correlated level recovers the wave function for the neutral molecule. Such approaches have been recently developed [1, 2], one within the equation-of-motion (EOM) framework of the coupled cluster (CC) theory [1] and the other – formulated within the (2,0) sector of the Fock space (FS) concept of the multireference (MR) CC theory [2]. Thus the DEA strategy can be summarized in the following steps:

- remove two electrons from the AB molecule and do the RHF calculations for the AB^{+2} system

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- do the correlated calculations with the DEA type method, i.e. the method which is capable to accurately describe the electronic states resultant from the attachment of a pair of electrons to the reference

The DEA calculations usually are associated with the evaluation of the double electron affinity, however, in the cases where as a reference we assume the unit deprived of two electrons, the DEA provides the description of the neutral state. Thus, we may write it as:

- DEA in general: double electron attachment
  $AB \rightarrow AB^{-2}$
  $E_{DEA} = E_{AB} - E_{AB^{-2}}$
- in our case :
  reference function: AB^{+2}
  DEA calculations: AB

  $AB^{+2}\ \overrightarrow{DEA}\ AB$

Obviously, the DEA strategy can be applied also to other systems not only to the alkali metal diatomics. A general condition for the successful application of this methodology is the requirement that the closed shell unit dissociates into closed shell fragments. Hence the diatomics involving Boron group or certain transition-metal elements are also a good candidate to be treated with the DEA approach. As it has been stated above there are two principal computational schemes used so far as the correlated methods fulfilling the DEA conditions: the EOM-CC and MRCC. Both methods can be introduced in a compact way on the basis of a few definitions related to the CC theory. In both approaches we seek the solution of the Schrödinger equation;

$$H\Psi_k = E_k\Psi_k \tag{3}$$

where the E_k and Ψ_k are the energy and wave function for the k-state.

The coupled cluster ground state function is expressed via exponential Ansatz [12, 13, 14]

$$\Psi_0 = e^T\Phi_0 \tag{4}$$

where T is a cluster operator in the current project approximated by the sum of the operators responsible for the single (T_1) and double (T_2) excitations [15]

$$T = T_1 + T_2 \tag{5}$$

or, in the case of the CCSDT model, also by that responsible for triple excitations (T_3) [16]

$$T = T_1 + T_2 + T_3 \tag{6}$$

Both in the EOM-CC [14, 17, 18, 19, 20] and MRCC [21, 22] approaches the crucial role is played by the similarity transformed Hamiltonian known as $\bar{H}$ defined as

$$\bar{H} = e^{-T}He^{T} \tag{7}$$

After introducing the $\bar{H}$ operator the DEA-EOM-CC [1] can be briefly defined as a method relying on the diagonalization of the $\bar{H}$ operator within the subspace of the configurations Φ^{ab}. The set of the Φ^{ab} configurations is obtained by all possible distribution of the two attached electrons (DEA) among all virtual levels a,b. For the DEA-EOM-CCSDT model [1] this subspace is augmented by the set of Φ_i^{abc} configurations in which placement of two additional electrons on the levels a,b is accompanied by the excitation of the third electron from occupied level i into the virtual level c.

The connection between DEA-EOM-CC scheme and the Fock space MRCC approach formulated in the (2,0) sector [2] is immediately seen upon explanation that the (2,0) sector is formed by the configurations obtained by distributing the additional two electrons among valence virtual levels. The essence of the multireference approach is represented by the equation

$$H_{eff}\tilde{\Psi}_k = E_k\tilde{\Psi}_k \tag{8}$$

i.e. the exact eigenvalues E_k can be obtained by the diagonalization of the effective Hamiltonian operator ($H_{eff}(\equiv PH\Omega P$ where P is a projection operator and Ω is the valence universal wave operator, $\Omega = \{e^S\}P)$ within the model space formed by $\Phi^{\alpha\beta}$ configurations constructed in the same way as those in the case of the DEA-EOM-CCSD approach with the important exception that the former arise by distribution of the two additional electrons among valence levels which is a subset of all virtual one-particle levels.
Thus, we may summarize steps in the Fock space CC calculations:

1. get the ground state CC solution,
2. construct $\bar{H}$ elements using converged T amplitudes,
3. select active space → model space,
4. solve the FS equations to get the S amplitudes,
5. construct the H_{eff} operator,
6. diagonalize the H_{eff} operator within the model space to get the energy of the system,
7. if the energy did not converge go to step 4.

It should be mentioned that in the practical realization the intermediate Hamiltonian (IH) [23, 24, 25] variant of the FS-CCSD approach [2] is used (see our previous work

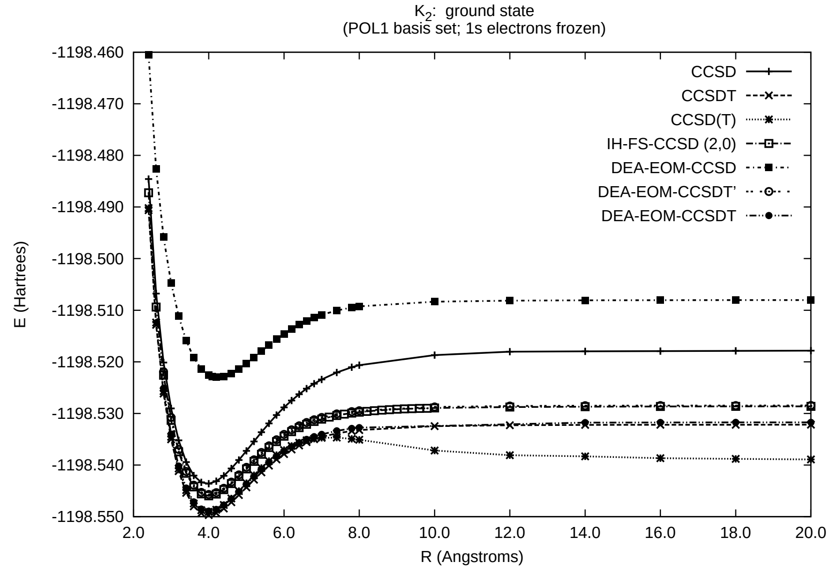

Figure 1: Potential energy curves for the ground state of the K_2 molecule with various CC methods in the POL1 basis set.

[2] for details). The latter allows to avoid a so called intruder state problem plaguing the standard FS-CC approach and limiting its use to small model spaces. In a summary of the DEA approaches we should mention one important feature of the FS approach, namely its rigorous size-extensivity. This means that the energy of the dimer computed at the infinite distance is identically equal to the sum of the energy of both atoms. This feature is particularly useful in the studies of the dissociation process.

3 Results and discussion

All calculations were done using the ACES II [26] program system supplemented with the IH-FS-CC (2,0) module [2]. The polarized basis set POL1 of Sadlej [27] was used. The core ($1s^2$) electrons were frozen and spherical harmonic polarization functions were used. The results are collected in Figures 1 and 2. In the case of the FS calculations the active space is defined by the single number m indicating the number of active particle levels; in the current calculations m is equal to 15. Throughout all double electron attachment calculations the orbitals we used were obtained by the RHF solution for the A^{+2} system in accordance with the overall computational strategy described in the introduction.

In Figure 1 we present the potential energy curves for the ground state of the K_2 molecule as a function of the internuclear distance. The standard CC (i.e., CCSD [15], CCSDT [16] and CCSD(T) [28]) curves are shown here for comparison purposes. We also quote the DEA-EOM-CC results at the CCSD and CCSDT level and the hybrid one (i.e., DEA-EOM-CCSDT′) (scaling n^6). In the latter method the ground state is solved at the CCSD level (scaling n^6) instead of CCSDT (scaling n^8) and in EOM part the R_2 ($2p$, p-particle) and R_3 ($3p1h$, h-hole) equations are taken as in the full CCSDT method (see our previous work for more details, Ref. [1]).

We see from Figure 1 that all curves representing DEA schemes stay parallel to the CCSDT curve, we consider the latter here as the reference one. However, the DEA-EOM-CCSD graph, although of correct shape, is moved upwards to higher energy. On the other hand, the FS curve as well as the EOM curves engaging R_2 and R_3 remain close to the reference CCSDT plot.

The advantage of the FS approach over the EOM can be shown when considering the size-extensivity issue. The EOM-CC possesses the so called size-intensivity property which says that upon dissociation of the molecule into fragments all the processes that occurs within one fragment (i.e., locally) retains the size-extensive character. This means that when doing independent calculations for the fragment we should obtain the same results as from the supermolecular calculation provided the interaction between fragments is negligible. When the studied process, e.g., charge transfer (CT) excitation or the double electron attachment involves two fragments the size-extensivity property is lost. The FS-CC approach shows correct separability and provides the size-extensive results (see Table 1). In the latter Table we see that the ground state energy of the K_2 molecule at the infinite separation is exactly equal to the doubled energy of the K atom (see the values of the first part of Table 1 under the heading K(4s)+K(4s) limit). On the other hand the excitation energy of the K_2 molecule computed at the dissociation limit corresponding to the K(4s)+K(4p) state is identical to the (4p) atomic excitation energy. The same refers to the relation of the K(4s)+K(5s) asymptote to the (5s) atomic energy.

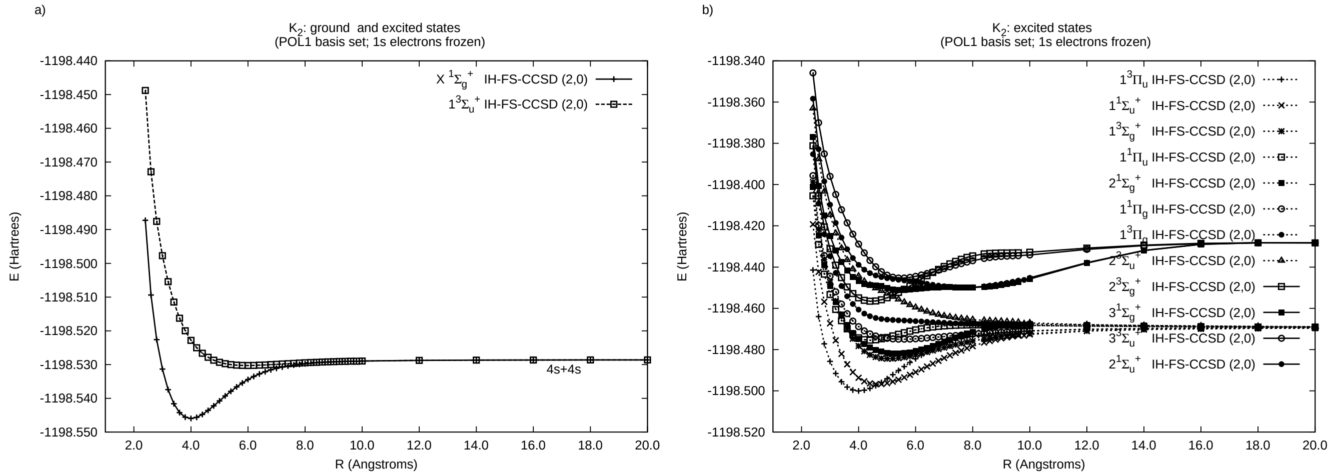

Figure 2: Potential energy curves for the ground and excited states of the K$_2$ molecule with the IH-FS-CCSD (2,0) method in POL1 basis set for a) K(4s)+K(4s) dissociation limit b) K(4s)+K(4p) and K(4s)+K(5s) dissociation limits.

Table 1: The asymptotics for the K$_2$ molecule compared to the atomic energies in the POL1 basis set.

System	Method
$K(4s) + K(4s)$ dissociation limit	
	IH-FS-CCSD (1,0)≡EA-EOM-CCSD
K	-599.264302 a.u.
	IH-FS-CCSD (2,0)
K$_2$	-1198.528604 a.u.
$K(4s) + K(4p)$ dissociation limit	
	IH-FS-CCSD (1,0)≡EA-EOM-CCSD
K	1.614274 eV
	IH-FS-CCSD (2,0)
K$_2$	1.614274 eV
Exp.$^{a)}$	1.617 eV
$K(4s) + K(5s)$ dissociation limit	
	IH-FS-CCSD (1,0)≡EA-EOM-CCSD
K	2.556006 eV
	IH-FS-CCSD (2,0)
K$_2$	2.556006 eV
Exp.$^{a)}$	2.607 eV

$^{a)}$ Ref. [29]

In Figure 2 we collect the PECs representing fourteen lowest lying electronic states of the K$_2$ molecule. The PECs are naturally assembled into three groups dissociating into three asymptotic limits. To the K(4s)+K(4s) limit two curves merge: the X$^1\Sigma_g^+$ ground state and the lowest triplet ($1^3\Sigma_u^+$) excited state (see Figure 2 part a)). At first sight the latter curve is of a nonbonding character, however, its closer inspection points out to a shallow well around R=5.4Å. The next group of curves coinciding with the K(4s)+K(4p) dissociation limit contains eight curves $1^3\Pi_u, 1^1\Sigma_u^+, 1^3\Sigma_g^+, 1^1\Pi_u, 2^1\Sigma_g^+, 1^1\Pi_g, 1^3\Pi_g, 2^3\Sigma_u^+$ (see Figure 2 part b)). The eight states correspond to twelve wave functions with four Π states being degenerate. The last four PECs: $2^3\Sigma_g^+, 3^1\Sigma_g^+, 3^3\Sigma_u^+, 2^1\Sigma_u^+$ (see Figure 2 part b)) approach the third dissociation limit (K(4s)+K(5s)). Out of the eight excited states of the Σ shown in Figure 2 only $2^3\Sigma_u^+$ state is repulsive in the whole range of interatomic distances.

All the curves plotted in Figure 2 were obtained with the IH-FS-CCSD (2,0). The important observation is that the curves collected in this figure for each group dissociate into a common limit (see Table 1) and the shapes of curves are consistent with these from the literature [30, 31, 32]. Note that the atomic value is obtained within the IH-FS-CCSD (1,0) scheme (≡EA-EOM-CCSD). The observed identity of the atomic excitation energies with that of the dimer at the dissociation limit indicates the rigorous size-consistency of the IH-FS-CC (2,0) scheme.

4 Conclusions and Future Work

In the series of papers [1, 2, 3, 4, 5, 6, 7, 8, 9] we introduced new approaches to study potential energy curves corresponding to the dissociation of the selected single bonds. Highly accurate results reported so far were obtained with the ih-FS-CCSD (2,0) approach. The DEA approach realized via IH-FS-CC scheme offers a robust

first principle size-extensive method which for adequate basis sets provides excellent results without any additional fixed parameters for studied molecules.
The most important part of the future work is connected with an inclusion of the relativistic effects in order to increase range of systems for interesting and nontrivial applications.

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References

[1] Musiał, M., Kucharski, S. A., Bartlett, R. J., "Multireference Double Electron Attached Coupled Cluster Method with full Inclusion of the Connected Triple Excitations: MR-DA-CCSDT", *J. Chem. Theory Comput.*, **7**, 3088 (2011).

[2] Musiał, M., "Multireference Fock space coupled cluster method in the effective and intermediate Hamiltonian formulation for the (2,0) sector", *J. Chem. Phys.*, **136**, 134111 (2012).

[3] Musiał, M., Kucharski, S. A., "First Priciple Calculations of the Potential Energy Curves for Electronic States of the Lithium Dimer", *J. Chem. Theory Comput.*, **10**, 1200 (2014).

[4] Musiał, M., Kowalska-Szojda, K., Lyakh, D. I., Bartlett, R. J., "Potential energy curves via double electron-attachment calculations: Dissociation of alkali metal dimers", *J. Chem. Phys.*, **138**, 194103 (2013).

[5] Mieszczanin, P., Musiał, M., Kucharski, S. A., "Potential energy curves via double electron affinity calculations: example of NaLi molecule", *Mol. Phys.*, **112**, 726 (2014).

[6] Tomza, M., Goerz, M. H., Musiał, M., Moszynski, R., Koch, Ch. P., "Optimized production of ultracold ground state molecules: Stabilization employing potentials with ion pair character and strong spin-orbit coupling", *Phys. Rev. A*, **86**, 043424 (2012).

[7] Tomza, M., Skomorowski, W., Musiał, M., Gonzáles-Férez, r., Koch, Ch. P., Moszynski, R., "Interatomic potentials electronic properties and spectroscopy of the ground and excited states of the Rb_2 molecule: ab initio calculations and effect on a non-resonant field", *Mol. Phys.*, **111**, 1781 (2013).

[8] Musiał, M., Kucharski, S. A., Kałuża, P., Motyl, A., "Potential energy curves for electronic states of the NaLi molecule via multireference coupled cluster calculations", *J. Chem. Phys.* , submitted.

[9] Musiał, M., Lupa, Ł., Kucharski, S. A., "Equation-of-motion coupled cluster method for high spin double electron attachment calculations", *J. Chem. Phys.*, **140**, 114107 (2014).

[10] Olszówka, M., Musiał, M., "Coupled Cluster calculations in the (0,2) and (2,0) sectors of the Fock space for the lowest electronic states of the O_2 molecule", *Mol. Phys.*, **112**, 609 (2014).

[11] Shen, J., Piecuch, P., "Doubly electron-attached and doubly ionized equation-of-motion coupled-cluster methods with 4-particle-2-hole and 4-hole-2-particle excitations and their active space extensions", *J. Chem. Phys.*, **138**, 194102 (2013).

[12] Coester, F., Kümmel, H., "Short-range correlations in nuclear wave functions", *Nucl. Phys.*, **17**, 477 (1960).

[13] *Čižek*, J., "On the correlation problem in atomic and molecular systems. Calculation of Wavefunction Components in Ursell-Type expansion using quantum field theoretical methods", *J. Chem. Phys.*, **45**, 4256 (1966).

[14] Bartlett, R. J., Musiał, M., "Coupled-cluster theory in quantum chemistry", *Rev. Mod. Phys.*, **79**, 291 (2007) and references therein.

[15] Purvis, G. D., Bartlett, R. J., "A full coupled-cluster singles and doubles model: The inclusion of disconnected triples", *J. Chem. Phys.*, **76**, 1910 (1982).

[16] Noga J., Bartlett, R. J., "The full CCSDT model for molecular electronic structure", *J. Chem. Phys.*, **86**, 7041 (1987).

[17] Stanton, J. F., Bartlett, R. J., "The equation of motion coupled-cluster method. A systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited state properties", *J. Chem. Phys.*, **98**, 7029 (1993).

[18] Krylov, A. I., "Equation-of-motion coupled-cluster methods for open-shell and electronically excited spiecies. The hitchiker's guide to Fock space", *Annu Rev. Phys. Chem.*, **59**, 433 (2008).

[19] Musiał, M., "The excited, ionized and electron attached states within the EOM-CC approach with full inclusion of connected triple excitations", *Mol. Phys.*, **108**, 2921 (2010).

[20] Piecuch, P., Kowalski, K., Pimienta, I. S. O., Fan, P.-D., Lodriguito, M., McGuire, M. J., Kucharski, S. A., Kuś, T., Musiał, M., "Method of moments of coupled-cluster equations: a new formalism for designing accurate electronic structure methods for ground and excited states", *Theor. Chem. Acc.*, **112**, 348 (2004).

[21] Mukherjee, D., Pal, S., "Use of cluster expansion methods in the open-shell correlation problem", *Adv. Quantum Chem.*, **20**, 292 (1989) and references therein.

[22] Lyakh, D., Musiał, M., Lotrich, V., Bartlett, R. J., "Multireference Nature of Chemistry: The Coupled Cluster View", *Chem. Rev.*, **112**, 182 (2012) and references therein.

[23] Meissner, L., "Fock space coupled-cluster method in the intermediate Hamiltonian formulation: Model with singles and doubles", *J. Chem. Phys.*, **108**, 9227 (1998).

[24] Musiał, M., Bartlett, R. J., Intermediate Hamiltonian Fock-space multireference coupled-cluster method with full triples for calculation of excitation energies", *J. Chem. Phys.*, **129**, 044101 (2008).

[25] Musiał, M., Bartlett, R. J., "Multireference Fock-space coupled-cluster and Equation-of-Motion coupled cluster theories: the detailed interconnections", *J. Chem. Phys.*, **129**, 134105 (2008).

[26] ACES II program is a product of the Quantum Theory Project, University of Florida Authors: J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. J. Lauderdale, S. A. Kucharski, S. R. Gwaltney, S. Beck, A. Balková, M. Musial, D. E. Bernholdt, K.-K. Baeck, H. Sekino, P. Rozyczko, C. Huber, R. J. Bartlett, Integral packages included are VMOL (J. Almlöf, P. Taylor); VPROPS (P. R. Taylor); A modified version of ABACUS integral derivative package (T. U. Helgaker, H. J. Aa. Jensen, J. Olsen, P. Jørgensen, P. R. Taylor).

[27] Sadlej, A. J., "Medium-size polarized basis sets for high-level correlated calculations of molecular electronic properties", *Collect. Czech. Chem. Commun.*, **53**, 1995 (1988).

[28] Raghavachari, K., Trucks, G. W., Pople, J. A., Head-Gordon, M., "A fifth-order perturbation comparison of electron correlation theories", *Chem. Phys. Lett.*, **157**, 479 (1989).

[29] Falke, S., Tiemann, E., Lisdat, C., Schantz, H., Grosche, G., "Transition frequencies of the D lines of ^{39}K, ^{40}K, and ^{41}K measured with a femtosecond laser frequency comb.", *Phys. Rev. A*, **74**, 032503 (2006).

[30] Ilyabaev, E., Kaldor, U., "Ground and excited states of K_2 and K_2^+ by the open-shell coupled cluster method", *J. Chem. Phys.*, **98**, 7126 (1993).

[31] Magnier, S., Millie, Ph., "Potential curves for the ground and numerous highly excited electronic states of K_2 and NaK", *Phys. Rev. A*, **54**, 204 (1996).

[32] Magnier, S., Aubert-Frecon, M., Allouche, A. R., "Theoretical determination of highly excited states of K_2 correlated adiabatically above $K(4p)$+$K(4p)$", *J. Chem. Phys.*, **121**, 1771 (2004).