Adiabatic Potential–Energy Curves of the Cesium Dimer

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Introduction

The required level of accuracy in calculations of molecular system makes that the relatively small and subtle effects have to be taken into account. Two most important effects, which have to be included, are correlation and relativity. Practical calculations of heavy atomic systems are performed with the frozen closed-shell cores. Even more simple is replacing those cores by pseudo-potentials or model potentials. Usually, the relativistic effects are taken into account by perturbation manner.

Here, we present alternative adiabatic potential for Cs_2 as representations of alkali-metal dimers, which have been already intensively studied [1]. The configuration interaction method together with self-consistent-field procedure is used by means of the MOLPRO program [2].

Computational Methods

The potential–energy curves have been determined by *ab initio* calculations with configuration interaction for a large number of interatomic distances in the range of $3.0 \leq R \leq 70.0$ a.u. The self-consistent-field (SCF) calculations have been performed with the MOLPRO package. The configuration interaction (CI) has been performed according to the configuration interaction theory where wave functions are selected by Multireference Rayleigh–Schrödinger Perturbation method.

The basis of Gaussian functions used in the calculation has been determined from the basis set previously constructed for Cesium. For Cesium, an optimized $7s6p/[5s4p]$ basis set has been constructed from the basis sets from ECPs. A pseudopotential *Effective Core Potential*-ECP46MWB with *Core Polarization Potential*-CPP has been used to describe the core orbitals of the Cs atoms. The ECP46MWB basis has been completed by MIDI ($18s12p6d/[7s6p2d]$) and AHLRICHS-CFIT ($5s2p2d$) bases, because the ECP46MWB do not describe correctly d orbitals in Cesium atom. We can also choose different pseudopotential (ECP54SDF $4s4p/[2s2p]$), but we observe then very strong interaction between two atomic cores with 54 electrons each one. We are going to calculate adiabatic potential–energy curves of Cs_2 and Cs_2^+ systems with using ECP54SDF basis in the future.

Results

The figures present our preliminary theoretical results of adiabatic potential–energy curves of the Cesium dimer. Our curves are calculated for the first time by using the MOLPRO package. The ground states $^1\Sigma_g^+$ and $^3\Sigma_u^+$ of Cs_2 are shown in Fig.1. and Fig.4. The excited states 0_u^+, 1_g, 0_g^- and 1_u are shown in Fig.2., Fig.5. and Fig.6.

The ground state $^3\Sigma_u^+$ is very important for formation of cold Cs_2 molecules through photoassociation [3], so it should be very well describe. The second important state for the formation of cold molecules is excited state 0_g^- with its double–well structure.

We compare our results with Fioretti *et all* (1998) (Fig.4., Fig.5., Fig.6.). In all figures our curves are higher, because we do not take, up to now, Cesium cores interaction into consideration in our theoretical calculations. In the nearest future we would like to complete our results of adiabatic potential–energy curves of Cs_2 molecule by addition cores interaction and extension ECP46MWB and ECP54SDF bases sets and we are going to prepare similar curves of the Cs_2^+ system.

Conclusions

The adiabatic potential–energy curves of the Cs_2 and Cs_2^+ systems are important for the spectroscopy of cold atoms [3-5], identification of the observed satellite bands [6-8] and photoassociation processes [9, 10]. We hope that our theoretical calculations can increase knowledge about above modern field of molecular physics and chemistry.

References

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Potential Energy Curves

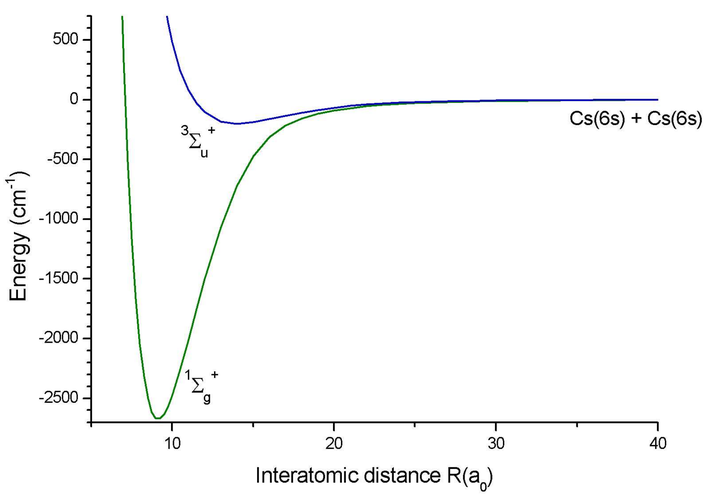

Fig.1. Adiabatic potential–energy curves for ground states $^1\Sigma_g^+$ and $^3\Sigma_u^+$ for ECP46MWB with CPP. Both states dissociating to $Cs(6^2S_{1/2}) + Cs(6^2S_{1/2})$

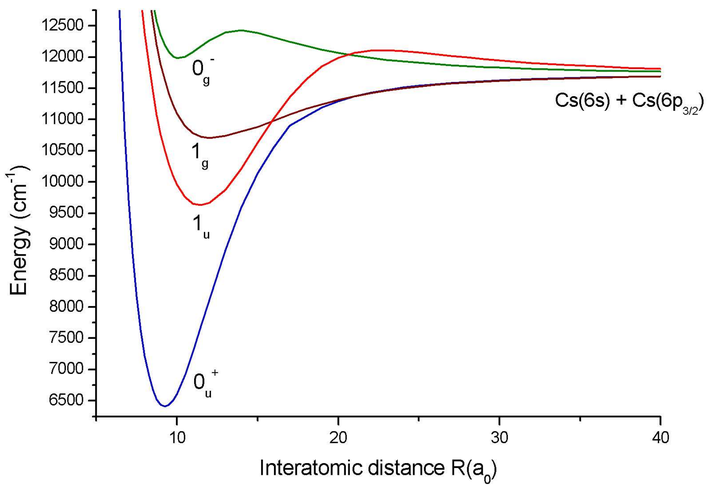

Fig.2. Adiabatic potential–energy curves for 0_u^+, 0_g^-, 1_u and 1_g for ECP46MWB with CPP. All of above states dissociating to $Cs(6^2S_{1/2}) + Cs(6^2P_{3/2})$

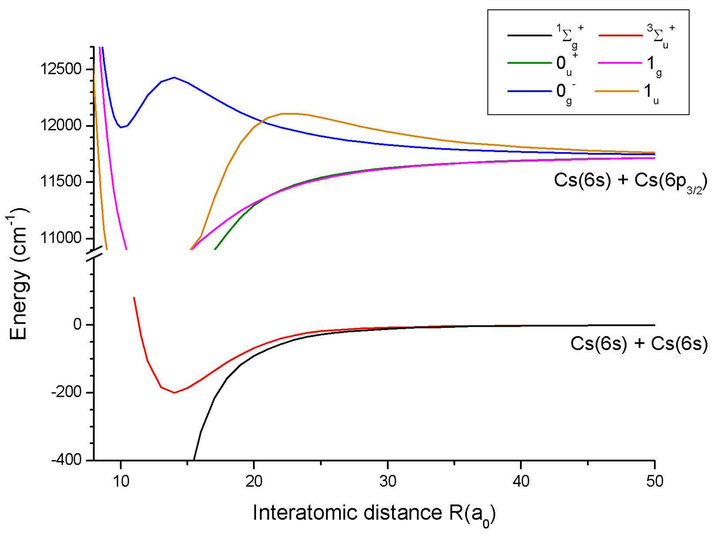

Fig.3. General figure of adiabatic potential–energy curves for Cs_2 in our work. Comparison Fig.1. and Fig.2.

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Comparison

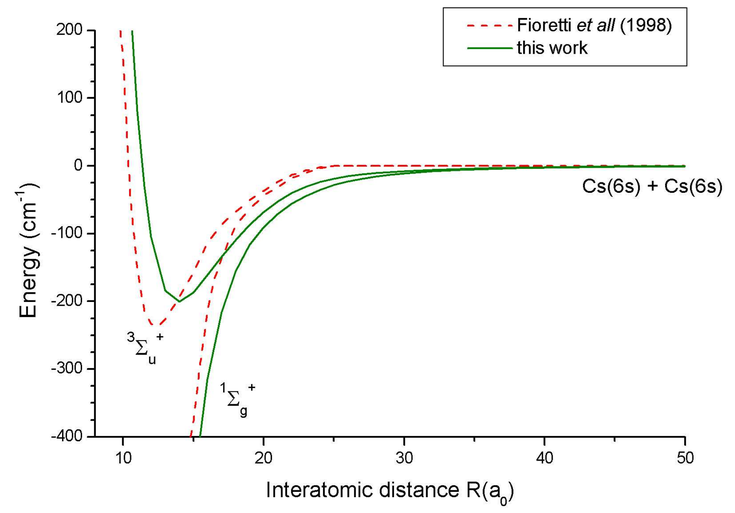

Fig.4. Adiabatic potential–energy curves for ground state level for ECP46MWB with CPP (green solid lines) and comparison with results obtained by Fioretti *et all* (1998) (red dash lines).

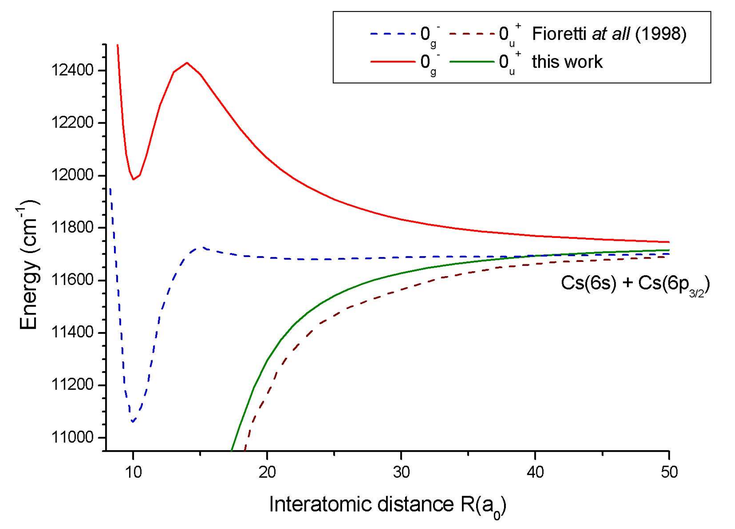

Fig.5. Adiabatic potential–energy curves for excited states 0_g^- and 0_u^+ for ECP46MWB with CPP (red and green solid lines) and comparison with the same states obtained by Fioretti *et all* (1998) (blue and brown dash lines).

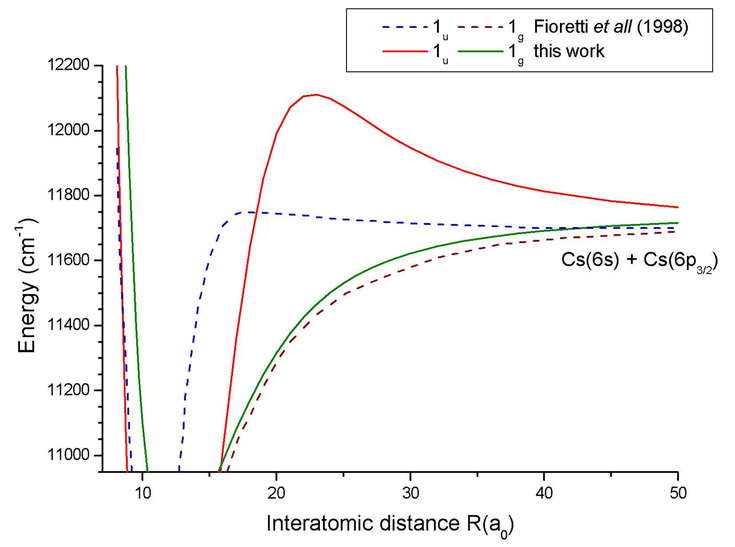

Fig.6. Adiabatic potential–energy curves for excited states 1_g and 1_u for ECP46MWB with CPP (red and green solid lines) and comparison with the same states obtained by Fioretti *et all* (1998) (blue and brown dash lines).