

# Potential energy curves for alkali metal diatomics with the multireference coupled cluster method

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In the current work we study the potential energy curves (PECs) for the low lying electronic states of lithium dimer, sodium dimer and LiNa diatomic. In all cases we were able to compute the smooth PECs for the whole range of interatomic distances from equilibrium to the dissociation limit. Computed spectroscopic parameters reproduce the experiment with a very good accuracy. The applied multireference coupled cluster (CC) scheme in Fock space (FS) formalism for the (2,0) sector [1] (essential in the double electron affinity (DEA) calculation) has a useful feature that the description of the electronic states of the neutral molecule is obtained for the doubly ionized reference. This is a very convenient situation since the alkali metal diatomics after removal of two electrons dissociate into closed shell fragments. Generally, the standard methods have the problem with the adequate treatment of the dissociation process of the closed shell molecule because of the fact that the reference function based on the restricted Hartree-Fock calculations cannot correctly describe the system at large interatomic distances. The DEA strategy avoids the use of the unrestricted Hartree-Fock reference. The latter has well-known disadvantages connected with the broken space (spin) symmetry problems as well as with difficulties in reaching converged solutions around the critical geometries. The other advantage of the current FS-CCSD (2,0) approach is its rigorous size-extensivity allowing to reproduce the atomic excitation energies at the infinite interatomic distance. This feature is of particular importance in the high accuracy calculation of the potential energy curves. The DEA approach realized via intermediate Hamiltonian scheme offers a robust *first principle* method which for adequate basis sets provides excellent results without any additional fixed parameters for studied molecules.

[1] M. Musiał, *J. Chem. Phys.*, **136**, 134111 (2012).