

Abstract

Title: The coupled cluster method for the description of the high-spin excited states based on the neutral and ionized reference states

Author: Łukasz Lupa, M.Sc.

Supervisor: Prof. Monika Musiał

The new variants of the coupled cluster (CC) method have been developed aimed at the description of the high-spin excited states, mainly triplets and quintets. The novelty of the approach relies on the new CC equations derived for the high-spin components of the triplet ($S_z = 1$) and quintet ($S_z = 2$) states replacing the standard approaches relying on extracting the high-spin states solutions from the set of all solutions obtained for $S_z = 0$.

The methods introduced here are based on the EOM (Equation-of-Motion) approach which turns out to be an efficient tool in the studies of the excited states within the framework of the CC theory. In addition the focusing on the high-spin components leads to the simpler equations (in some cases substantially simpler) and to smaller number of amplitudes to be computed.

Three different variants of the EOM scheme are discussed. The first one is a modification of the standard EE (Excited States)-EOM approach in which the EOM operator is responsible for the single and double excitations from the reference state. In the high-spin approach the EOM operator works basically in the same way, with the exception that when operating on the closed-shell reference state it generates excited configurations corresponding to the $S_z = 1$ (triplets) and to the $S_z = 2$ (quintets).

In the second formulation, DEA-EOM, the EOM operator is responsible for the attachment of two electrons (Double Electron Attachment) to the reference. If the latter is, e.g. a doubly ionized structure then the DEA-EOM method yields the solutions pertinent to the neutral molecule. This approach is particularly useful in the calculations of the potential energy curves, e.g. for the dimers of the alkali-metals. In the latter case a closed-shell neutral molecule, e.g. Na_2 , dissociates into open-shell fragments which seriously complicates the calculations. The DEA approach makes it possible to adopt as a reference state the Na_2^{+2} system which dissociates into the closed-shell fragments ($Na_2^{+2} \rightarrow Na^+ + Na^+$) and after attachment of two electrons provides – in the whole range of the interatomic distances – the energy of the neutral molecule. In the current work the new equations were derived and programmed referring to the high-spin component of triplets and quintets.

The third variant of the EOM approach for which the new high-spin equations are derived here is a DIP (Double Ionization Potential)-EOM. In the latter scheme the EOM operator removes two electrons from the system. This approach can be exploited in the

situations when the reference state contains two excessive electrons and by applying DIP-EOM scheme the energy of the neutral state is recovered.

The main advantage of the double electron affinity and double ionization potential schemes is that both can be used successfully to evaluate other molecular properties than the direct DIP or DEA energies. E.g., these strategies are particularly convenient in the calculation of the excited state energies for some open-shell systems or in generation of the potential energy curves for the molecules whose double positive ions (DEA) or double electron attached systems (DIP) dissociate into closed-shell fragments.

The newly developed methods were applied to the studies of the potential energy curves for the selected diatomics (C_2 , Na_2 , B_2) and to its spectroscopic characteristics. The DEA schemes were also successfully applied in the calculations of the energies of the excited states of C and Si atoms. On the other hand the DIP-EOM approach has provided a correct dependence of the molecular energy on the dihedral HN-NH angle in the diazene molecule. The result which normally can be achieved only with the multireference schemes.