SAC-CI on Gaussian03:
from fine spectroscopy to molecular biology

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Since the publication of the SAC-CI theory and its coding in 1978, many developments and applications have been done in our laboratory. The incorporation of the SAC-CI program into the Gaussian suite of programs has been a big project of our laboratory for these many years and finally we have completed it recently. The SAC-CI on Gaussian03 has been released in early spring of 2003. Here, we summarize the present features and the future plan.

The SAC-CI theory itself is exact and yet very simple: it describes compactly the physics of the excited electronic structure. For this reason, it has the following merits.

1. This theory covers very wide range of different electronic states in a same good accuracy (Fig. 1).
2. It describes not only the one-electron excited states from the ground state, but also the multi-electron excited states.
3. Energy-gradient is calculated for any states of Fig. 1 in both one- and multi-electron excited states: this is also true for geometry optimization.
4. Chemistry and physics are investigated with the same methodology from very fine accurate calculations of small molecules to less accurate but reliable calculations of large molecules.

Fig.1 shows the states that can be studied by the G03 version of the SAC-CI program: it covers from singlet to septet ground and excited states and we can compare directly the energies and the properties of different electronic states. This is an important merit for studying a variety of chemical phenomena. For spectroscopic studies, the theory must be able to describe accurately not only the main peak due to the one-electron excitation, but also the satellite peak due to the multi-electron excitation. In the SAC-CI program, the SD-R method is used for the former and the general-R method for the latter. We can reproduce even the very fine details of the excitation and ionization spectra with the general-R method, which we call 'fine theoretical spectroscopy', which can expand the frontiers of spectroscopy. For studying geometries, vibrations, and reactions, the force or the energy gradient acting on the constituent nuclei are very important information: in our present code we can calculate this quantity for any state shown in Fig.1. In the SAC-CI G03 program, we adopt perturbation selection procedure and therefore, by choosing accuracy, we can perform from very accurate calculations for small molecules to less-accurate calculations for large molecular systems in the same theoretical framework. For this merit, we could study the spectra and the electron transfer pathway of the reaction center of the photosynthetic bacteria.

For systems for which the SAC method must be replaced with the MR-SAC method, we already have MEG/EX-MEG program and combining it with the G03 program is an easy matter.

Finally, the so-called EOM-CC and CCLRT are theoretically equivalent with the SAC-CI, though the coding algorithm is different.