Wave Function Theories towards Materials Developments: Heavy Elements and Singlet Fission

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Our research group is interested in connecting high-level electron correlation theories and materials developments. I will first discuss an algorithm for evaluating Fock matrices with the Breit interaction in 4-component relativistic electronic structure theories. An efficient algorithm is presented for computing 2-electron integrals over the so-called gauge-dependent term in the Breit interaction, which is cheaper than the electronic repulsion integrals (per Cartesian component). The same algorithm can be used for the direct spin-spin coupling term in the quasi-relativistic Breit–Pauli Hamiltonian. The integral codes have been interfaced to a Dirac–Fock builder using density fitting, which will be the basis of multi-reference electron correlation theories to simulate magnetic molecules containing heavy elements. Together with our experimentalist collaborators, we aim to rationally design new magnetic materials.

Second, I will present a new active-space theory for singlet fission (SF). SF is a process, in which organic chromophores produce long-lived multiple exciton states that are singlet-coupled triplets. SF would be useful for next generation solar cells that overcome the so-called Shockley–Queisser limit. The final state of SF is, however, a two-electron excited state, which makes it difficult for conventional theories to accurately describe this process. We have recently developed an active-space method with factorized active spaces using molecular geometries. We extract information from monomer calculations, so that the size of a dimer configuration vector is only $2N_{\mathrm{conf}}$ (not N_{conf}^2) with N_{conf} being that of the monomer calculations. The prospect of going beyond the standard dimer picture will be discussed.

Finally I will present recent developments in our program package, BAGEL, which has been developed by our group to implement parallelized, efficient, portable electronic structure programs with the object-oriented design. All the methods discussed in this talk have been implemented in the BAGEL package.