Time-Dependent Two-Component Spinor: Excited State Spin-Orbit Coupling and Coherent Spin Dynamics

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Relativistic effects are of great importance for the description the electronic properties of systems containing heavy atoms and magnetic materials. Central to these phenomena is the treatment of electron spin. Allowing electron spin to vary in response to magnetic fields or spin interactions (e.g. spin-orbit coupling) necessitates the use of multi-component electron wave functions. Here we explore the two component spinor basis (within the Douglas-Kroll Hess transformation) for the study of excited states of molecular systems.

The two-component method based on the Douglas-Kroll-Hess transformation will be employed within the context of linear response time-dependent methods, and we present results showing the effect of relativistic corrections in the description of excited states of test systems. Special care will be taken to include picture-change effects into the calculation of transition properties coupling the ground and excited states. A characteristic property of relativistic corrections is the explicit presence of spin-orbit coupling effects, which should be included in both the Hamiltonian and the property operators, allowing the coupling of states of different spins, whose transitions are spin-forbidden within non-relativistic theory.

Additionally, we have investigated the effect of utilizing a two-component spinor basis on both electronic and nuclear dynamics. This should, in principle, allow for a description of spin dynamics, as the two component basis gives electron spin the ability to vary over time. Though the initial results are promising, there remain several unanswered questions, such as how to properly incorporate strong magnetic fields (which can introduce severe gauge origin dependencies) and how to place the real time dynamics on the proper relativistic footing (which is the proper foundation for all magnetic phenomena). The answers to these questions will strongly dictate the utility of ab initio molecular dynamics for spintronic and magnetic systems.

Here we report our investigations toward ab initio electron and molecular dynamics that includes the proper treatment of spin interactions. In particular, we explore the challenges of introducing spin-orbit coupling to the electronic dynamics as well as the challenges associated with introducing strong magnetic fields.