Calculation of Molecular Properties from Relativistic Electron Dynamics

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The calculation of molecular spectra and other properties from the solution of the time-dependent Schrödinger equation has gained popularity in recent years. However, the relativistic Dirac equation has to be considered if molecules of interest contain atoms of heavy elements or exhibit strong spin-orbit coupling. We present the advances in the development of relativistic four- and two-component electron dynamics.

The electron dynamics approach represents an alternative to the more standard response theory and utilizes a direct stepwise time propagation of the electronic state. Molecular properties can be obtained in the course of the simulation and their analysis enables the calculation of spectra in various regions including near resonant frequencies without the need to calculate the response kernel. To identify the nature of electronic transitions in the spectra we have developed the dipole-weighted transition matrix analysis [1]. Moreover, the application of orbital-selective perturbation eliminates non-physical excitations that arise particularly in the X-ray region [2]. Finally, to accelerate the simulations we have combined the electron dynamics with the modern two-component X2C Hamiltonian that offers almost a 10-times speed-up and reproduces fully relativistic results very well as demonstrated by the calculation of non-linear optical properties [3].

References

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