Monte Carlo Configuration Generation for Molecules and Nanostructures

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Arbitrarily accurate solutions to the many-body Schrödinger equation are possible through a brute force expansion of the wave function in determinants or spin coupled sums of determinants ('configuration state functions'), the so called configuration interaction (CI) or superposition of configurations method. Due to the length required for a complete many-body expansion, the brute force approach becomes computationally intractable except for few-electron problems.

A Monte Carlo technique for sampling configurations and evaluating their contribution to the energy or their weight in the many-electron wave function is designed to find only the most import configurations in many-electron wave functions [1,2] and has been applied to a variety of molecular problems. Using this Monte Carlo configuration interaction (MCCI) method, singlet and triplet electronic excitation energies have been calculated for few electron molecules for systems with single and multi-reference 0th order wave functions. We find that vertical photoexcitation energies can be predicted to within a few tens of meV (to within an accuracy of < 1%) of full CI (FCI) limits using expansions consisting of only a few thousand configuration state functions as compared to the O(10¹⁰) to O(10¹²) configurations occurring in the corresponding FCI expansions [3].

Interactions between localized molecular bound states and a continuum of states such as occurring for molecules bonded to surfaces or between electrodes in nanoscale tunnel junctions can be modeled by using an (energy-dependent) self-energy, or approximately through use of a complex potential. We discuss the relation between the two approaches and give a prescription for using the self-energy to construct an energy-independent complex potential [4] that generalizes single-electron electrode self-energies for use with many-electron wave functions. This allows for a treatment of molecular correlations on a nanoscale sub-system while 'opening' the system to allow interaction with larger systems such as bulk bands coupling to localized defect states or molecules-surface interactions.

Recent results for the calculation molecular dissociation energies and electron correlations in atomic chains and quasi- one dimensional nanowires will be presented.

References

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