Monte Carlo Configuration Interaction for Molecules and Nanostructures

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Wave function methods such as configuration interaction and coupled cluster theory provide systematic treatments of electron correlations in nanoscale systems and provide accurate prediction for photoexcitation spectra in finite quantum systems. 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. Recently 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, or complete many-body basis sets) limits using expansions consisting of only a few thousand configuration state functions as compared to the $O(10^{10})$ to $O(10^{12})$ configurations occurring in the corresponding FCI expansions [3]. The method thus represents the state-of-that art for predicting electronic excitations in few-electron systems with accuracy comparable to the equation-of-motion coupled cluster method with the inclusion of full triple excitations.

Interactions between localized molecular bound states and a continuum of states such as occurring for molecules bonded 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 electrodes, coupling to bulk bands for localized defect states, or for molecules-surface interactions.

The use of MCCI to the study of the charged nitrogen-vacancy (NV^-) center in diamond [5] is presented; interest in the center is motivated by its potential use as a qubit. Within these calculations 116 electrons are correlated using 130 orbitals/260 spin orbitals. Use of the MCCI method allows for a study of the symmetry and spin of the electronic excitations needed to understand the mechanism for spin relaxation and hence lifetimes of the excited states. Our study suggested that the assumed ordering is unlikely to be correct and this theoretical prediction is consistent with recent experimental studies [6].

We will also report on recent results for porting the method to the IBM Blue Gene and discuss scaling of the algorithm in massively parallel environments. Recently several new methods that adaptively construct and refine a many-electron wave function have been reported using quantum Monte Carlo in a determinant space, coupled cluster theory, CI methods and the density matrix renormalization group theory. An overview of the common elements of these recent approaches is highlighted.

References

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[5] P. Delaney, J.C. Greer and J.A. Larsson, Nano Letters **10** (2010) 610
[6] N.B. Manson, L. Rogers, M.W. Doherty, and L.C.L. Hollenberg, arXiv:1011.2840

Figures

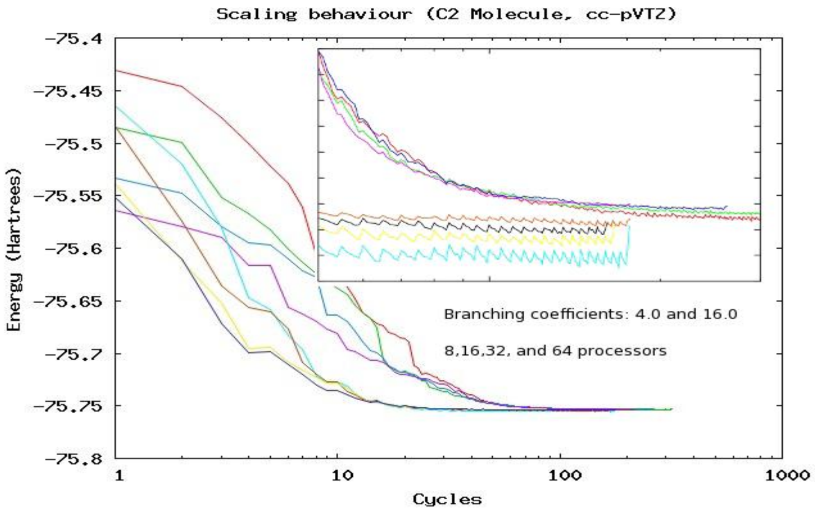

Figure 1: Convergence behavior for the MCCI algorithm for the C_2 *molecule in a correlation consistent polarized valence quadruple-ζ (cc-pVQZ) basis set. The inset reveals that with different sampling conditions, the final total electronic energy agree within a few milli-electron Volt or approximately 1 part in* 10^4 *In the correlation energy.*

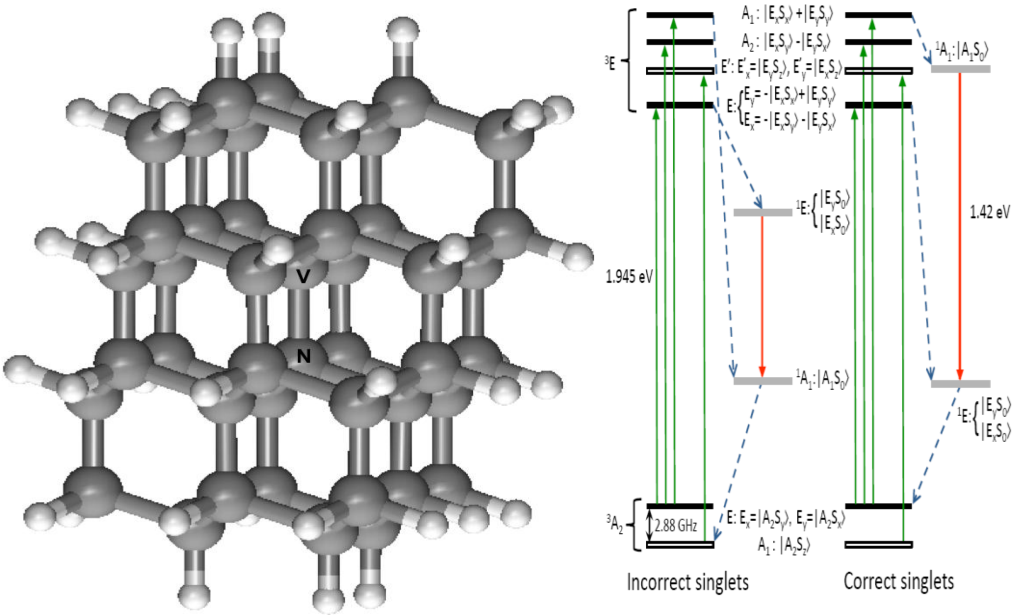

Figure 2: Cluster model of the NV- center in diamond. MCCI spectra suggests that the ordering assumed for the singlet A_1 *and degenerate E state should be reversed, with the singlet* A_1 *state lying higher in energy.*