Comments On "QUANTUM MONTE CARLO CALCULATIONS ON Be AND LiH"

R. J. Harrison and N. C. Handy, Chem. Phys. Lett., 113, 257 (1985)

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The subject paper describes a thorough investigation of the quantum Monte Carlo (QMC) method in the diffusion Monte Carlo (DMC) variant of the approach. The DMC method had been introduced by J. B. Anderson into chemical physics in the seventies [1] and our work in the early eighties presented a new algorithm with results that exemplified the potential of the approach [2]. The Handy and Harrison (HH) paper appeared at a relatively early stage in the development of DMC for atoms and molecules

The writer became aware of Handy's interest in QMC when he visited Berkeley in July 1984 and described the research using DMC that he and Harrison had carried out on Be. The present publication is broader in content then the Berkeley talk and reports the results of calculations on He, Be^{2+}, Be, and LiH The authors invoked the short-time approximation that characterizes DMC and used Hylleraas's two- and six-term correlated wave functions for He as DMC trial functions for He and Be^{2+} and concluded that the error of the short time approximation was less than the fixed-node error. The fixed node approximation involves the imposition of the nodes of an approximate known trial function on the unknown exact wave function. This is done in order to obtain a positive definite product distribution - an essential element of the DMC formalism. The quality of the resulting distribution is reflected in the quality of the computed observables. The quantities studied in the present paper were the energy and, for the molecules considered, the dipole moment.

Major findings of the HH study were that multiconfiguration self consistent field (MCSCF) trial functions would be needed for systems in which there is substantial configuration mixing, and the suggestion of improved forms of correlation function. The trial functions used for DMC are typically expressed as a product of an independent particle function and a correlation function that is dependent explicitly upon interparticle distance. The HH suggestion of using the function of Handy and Boys developed in the transcorrelated method [3] as a DMC correlation function was subsequently pursued by Schmidt and Moskowitz [4]. The Handy-Boys function is presently the most commonly used form for the correlation function in DMC calculations.

References

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