Accuracy of the fixed-node and pseudopotential approximations in diffusion Monte Carlo[1] RICHARD G. HENNIG, JULIEN TOULOUSE, CYRUS J. UMRIGAR, Cornell University — Diffusion Monte Carlo is one of the most accurate methods for molecules and solids. Its accuracy is controlled by the fixed-node and pseudopotential approximations. For atoms and small molecular systems, efficient energy optimization methods enable the optimization of all parameters of many-body wave functions and systematically eliminate the fixed error. This enables our pseudopotential tests. Calculations for Si and C atoms and dimers demonstrate the importance of optimized multi-determinant trial-wave functions for chemical accuracy. The fixed-node error of the two seemingly similar dimers, Si_2 and C_2, differs dramatically with values of 0.1 eV and 1 eV, respectively. Calculations of the ionization energies and electron affinities of Si and C as well as binding energies and bond lengths for the Si_2 and C_2 for relativistic LDA, PBE and HF pseudopotentials of the Troullier-Martins, Vanderbilt and Gaussian form assess their accuracy and efficiency. The results are compared to experimental and quantum chemistry data. Reduced non-locality by larger cutoff distances and the Vanderbilt construction improve the efficiency. PBE and HF pseudopotentials result in accurate energies and HF pseudopotential are the most accurate for the dimer geometries.

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