Accurately solving the electronic Schrödinger equation of small atoms and molecules using explicitly correlated (r_{12}-)MR-ACPF

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THE recently proposed r_{12}-MR-CI method — which includes terms that are linear in the interelectronic distances (r_{12}) in the ansatz for the wavefunction [1] — in combination with MR-ACPF [2] allows for systematically solving the electronic Schrödinger equation of small atoms and molecules to accuracies which cannot be obtained with present day (traditional) CI methods and computers without extrapolating to the basis set limit.

For the purpose of validation, the method has been applied to the computation of (with accuracies given in parenthesis): a) the potential energy curve of N_2 ($\Delta D_e = -0.2$ kcal/mol, $\Delta R_e < +10^{-4}$ Å, $\Delta\omega_e = +2$ cm^{-1}) [3]; b) the ground-state energies of He and Li (-0.05), Be (-0.013), B ($+0.12$), C and N (-0.1), O ($+0.3$), and F and Ne ($+0.6$ mE_h) and their respective positive ions [4]; and c) the electron affinities of Li ($+0.3$), B ($+2.3$), C (-0.6), O (-15), and F (-16 meV) [5]. All results are corrected for relativistic effects.

Very recently, the new method has been applied to the ground-state dimers of helium [6] and beryllium [7] which are both difficult to treat theoretically as well as experimentally. In both cases I reached accuracies that challenge the latest experiments.

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