Artificially intelligent zombie states - a possible new electronic structure method

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Electronic structure theory is integral to nearly all chemical simulation and requires either directly or indirectly solving the many-electron Shrödinger equation. However, simulations with a greater number of virtual orbitals and more accurately resolved energies means a greater computational expense. A single restricted Hartree-Fock slater determinant will give a reasonably accurate ground state energy[1] in a very short amount of time. Alternatively, finding the full configurationa interaction (FCI) ground state energy of a molecule, accounting for all possible electron configurations, is computationally expensive for small molecules and impossible for larger ones. Density Functional Theory (DFT) is possibly the most popular solution to this problem, condensing the high dimensionality. But when quantitative accuracy is required above all else, the set of approximations that DFT relies on means the results cannot be said to be truly exact. Thus it is still necessary to develop wavefunction based methods which allow for, theoretically, exact results. Monte Carlo Configuration Interaction[2, 3, 3, 4, 5, 6] (MCCI) and Full Configuration Interaction Quantum Monte Carlo[7, 8, 7, 9, 8, 10, 11, 12] (FCIQMC) are two such methods that employ random walkers to find the optimal set of Slater determinants to recover FCI energies.

Zombie states[13] are a possible new method for obtaining electronic structure that maintain the exactness of wavefunciton controlled post-Hartree Fock methods while being freed from the binary rule of a conventional Slater Determinant. Zombie states have already been shown to be able to recover FCI energies for Li_2 and LiH[13, 14]. It will be shown how this work has been extended by utilising machine learning tools so zombie states can recover FCI energies using extremely small basis set sizes for a variety of molecules. This is a key step in building zombie states into a practicable method for electronic structure calculations.

References

[1] W. A. Al-Saidi, S. Zhang, and H. Krakauer, The Journal of Chemical Physics **124**, 224101 (2006).
[2] L. Tong, M. Nolan, T. Cheng, and J. Greer, Computer Physics Communications **131**, 142 (2000).
[3] J. C. Greer, The Journal of Chemical Physics **103**, 1821 (1995).
[4] J. P. Coe, D. J. Taylor, and M. J. Paterson, The Journal of Chemical Physics **137**, 194111 (2012).
[5] J. P. Coe, D. J. Taylor, and M. J. Paterson, Journal of Computational Chemistry **34**, 1083 (2013).
[6] J. P. Coe and M. J. Paterson, The Journal of Chemical Physics **137**, 204108 (2012).
[7] G. H. Booth, A. J. W. Thom, and A. Alavi, The Journal of Chemical Physics **131**, 054106 (2009).
[8] D. Cleland, G. H. Booth, and A. Alavi, The Journal of Chemical Physics **132**, 041103 (2010).
[9] G. H. Booth and A. Alavi, The Journal of Chemical Physics **132**, 174104 (2010).
[10] D. M. Cleland, G. H. Booth, and A. Alavi, The Journal of Chemical Physics **134**, 024112 (2011).
[11] G. H. Booth, D. Cleland, A. J. W. Thom, and A. Alavi, The Journal of Chemical Physics **135**, 084104 (2011).
[12] E. Vitale, A. Alavi, and D. Kats, Journal of Chemical Theory and Computation **16**, 5621 (2020), PMID: 32786911.
[13] D. V. Shalashilin, The Journal of Chemical Physics **148**, 194109 (2018).
[14] O. A. Bramley, T. J. H. Hele, and D. V. Shalashilin, The Journal of Chemical Physics **156**, 174116 (2022).