Correlated motion in atomic and molecular three-particle systems

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Abstract

High accuracy, non-relativistic, calculations are used to study the electronic and nuclear motion in the ground state of three-particle atomic and molecular systems using a series solution method with a triple orthogonal Laguerre-based wavefunction [1]. This method is adapted to calculate, in a single variational calculation, the critical mass of a third particle required for stable binding to a two-particle system [2] and the critical nuclear charge for binding of two-electrons [3] and, in part, to calculate high-precision Hartree-Fock energies and expectation values.

Accurate determination of fully correlated electron densities is important for those involved in developing correlation functionals for density functional theory (DFT). The correlated motion of electrons, including at low nuclear charge *Z*, is quantified using radial and angular densities and the Löwdin definition of electron correlation [4]. Results confirm the presence of a secondary Coulomb hole for helium, and results for the anionic systems H^- and the critical nuclear charge system, indicate that only a primary Coulomb hole exists.

In mainstream quantum chemistry, it is usual to treat molecules within the Born-Oppenheimer approximation, a molecular structure is assumed and the equilibrium structure corresponds to a local minimum structure on a potential energy surface. In the present work no such assumptions are made and atoms and molecules are treated on an equal footing as few-particle quantum systems. Results will be presented demonstrating that the nuclear motion in diatomic ions is strongly correlated; by evaluating the particle density at the centre of mass, it is shown that the spatial distribution/localisation of the like-charged particles depends on the relative masses of the nuclei rather than just their absolute mass [5], and that molecular structure arises naturally from the analysis of the all-particle wavefunction.

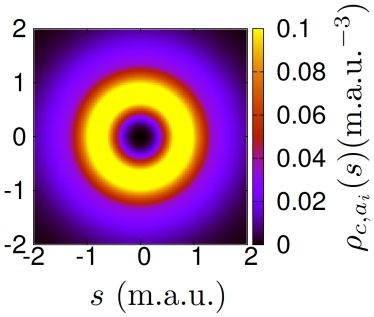


Figure 1: Centre of mass particle density plot for μDT^+.

Recent Publications

[1] A.W. King, F. Longford and H. Cox*, J. Chem. Phys*. 2013, **139**, 224306-1 – 224306-7.
[2] A.W. King, P.E. Herlihy and H. Cox*, J. Chem. Phys*. 2014, **141**, 044120-1 – 044120-5
[3] A.W. King, L. C. Rhodes, C. A. Readman and H. Cox, *Phys. Rev. A* 2015, **91**, 042512-1 – 042512-6.
[4] P. Löwdin, *Phys. Rev.* 1955, **97**, 1509-1520; *Ibid*. *Int. J. Quantum Chem*. 1995, **55**, 77 – 102.
[5] A. L. Baskerville, A.W. King and H. Cox, *Phys. Rev. A* 2016, **94**, 042512-1 – 042512-9.



Biography

Dr Hazel Cox is a Senior Lecturer in Chemistry at the University of Sussex. Her first degree is in mathematics and for her PhD she used computer algebra to solve the Schrödinger equation for three particle systems. Her research interests involve using quantum chemistry to determine the underlying chemical and physical properties responsible for the structure, reactivity and spectroscopy of metal-ligand complexes and to probe the boundaries of current methodologies by exploring the fundamental interactions in few particle Coulomb systems.

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Notes/Comments: