Hybrid approach to numerical molecular orbitals

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Molecular systems beyond diatomics are less amenable to numerical methods than atomic systems because of their complicated geometries. This is a significant problem for density functional theory methods which require the evaluation of spatial functions. One aspect of the problem is that the electron wave functions vary rapidly in the neighborhood of the nuclei, requiring a greater density of mesh points near the nuclei.

Recent work [1] has focussed on going beyond the GTO approach to the LCAO method for molecular orbitals, by numerically optimizing the radial orbitals entering the LCAO calculation. These methods provide good HF results using much smaller basis sets than are conventionally required. However, it is difficult to improve the accuracy by including polarization orbitals because of the well-known slow convergence of the angular momentum expansions.

A momentum space approach to the molecular orbital problem has been proposed by Alexander et al [2]. In this approach a global cartesian mesh is introduced in momentum space and the HF equations solved iteratively, invoking the fact that the kinetic energy operator is diagonal. This approach is feasible only because the FFT method can be applied to transform between position and momentum space.

This momentum space approach can be applied to evaluate the small corrections to the HF solutions obtained from numerical optimization. Since the cusp behavior at the nuclei is properly described, the correction functions are smoothly varying in both position and momentum space. In this poster the procedure will be described, and results for some small molecules presented.

[1] J.D. Talman, Phys. Rev. Lett. **84**, 855 (2000); Int. J. Quantum Chem. **95**, 442 (2003). See also D. Andrae, Mol. Phys. **99**, 327 (2001).

[2] S.A. Alexander and H.J. Monkhorst, Int. J. Quantum Chem. 32, 361 (1987).