NDDO revisited: one-trick ponies, transfer Hamiltonians and hydrogen bonds

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Quite generally, MNDO-like NDDO-based semiempirical MO-techniques can be parametrized quite accurately for a limited range of properties or a small class of molecules, but less well for general applications on a wide variety of molecules. This property has been used to generate Hamiltonians for specific limited applications, such as Bartlett's "transfer Hamiltonian"[1] or "one-trick pony" Hamiltonians for treating a single class of reactions.[2]

One of the traditionally most difficult interactions for MNDO-like theories is the hydrogen bond. MNDO does not reproduce hydrogen bonds at all. AM1 gives spurious bridging hydrogen bonds and PM3 gives reasonable geometries but incorrect energies. The latter two Hamiltonians suffer from these weaknesses despite being augmented by classical two-center potentials designed specifically to improve performance for hydrogen bonds.[3]

The OMx methods,[4] which include not only orthogonalization corrections but also additional penetration integrals and pseudopotentials, can perform quite well for water (including proton transfer), as can techniques based on machine learning.[5] However, it is not very clear why these methods perform better than standard MNDO.

We have now parametrized several variations of an essentially standard MNDO augmented by polarization functions and our Feynmann dispersion correction[6] for water, and only water.[7] The results suggest that, contrary to our original expectations, *d*-polarization functions on oxygen are more beneficial than *p*-functions on hydrogen, and that the Feynman correction to the nucleus-electron interaction is being misused to mimic the pseudopotentials and penetration integrals present in OMx. The performance of the new Hamiltonian is impressive enough that it can be used for molecular dynamics simulations of periodic water boxes to give an O-O radial distribution function that agrees well with experiment.

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