

Towards Improving the Fitting Ability of NDDO Semiempirical Methods with q-Multipole-Multipole Interactions

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INTRODUCTION

Present semiempirical methods have an important characteristic, which makes them applicable to very large systems: the NDDO approximation, which makes them scale, with traditional algorithms, with N^2 , in contrast with the N^4 scaling of Hartree-Fock-Roothaan for the calculation of the electron repulsion integrals, where N is the number of electrons. These diatomic integrals in NDDO methods are then expressed in terms of multipole-multipole interaction terms, all containing inverse square roots in their formulae².

q-Operations emerge from nonextensive statistical mechanics¹ and have been a source of investigation in deformed algebraic structures. In particular, q-deformed functions have been proven to be much more flexible and adaptable³, which makes them suitable for applications to problems where fitting is essential, such as in the development of semiempirical methods.

METHOD

We wrote a complete NDDO software from scratch, which allowed us to investigate the usage of (i) generalized q-exponentials, replacing exponentials in the overlap and core-core repulsions; (ii) q-Gaussians replacing the Gaussians in the core-core repulsion terms, and (iii) q-inverse square roots replacing inverse square roots in the multipole-multipole interactions.

As very preliminary test systems, we considered the closed shell hydrogen systems: H_2 , H_3^+ , H_4 and H_5^+ . The reference properties: total energies, fully optimized geometries, and vertical ionization potentials, were determined via GAMESS CCSD calculations with the aug-cc-pVTZ basis set.

RESULTS AND DISCUSSION

Initially, we derived the definition of the q-inverse square root, which, to the best of our knowledge, is seemingly not otherwise available, as being:

$$\left(\frac{1}{\sqrt{x}}\right)_q = \left(\frac{3}{2} - \frac{x^{1-q}}{2}\right)^{\frac{1}{1-q}}$$

and, of course,

$$\lim_{q \rightarrow 1} \left(\frac{1}{\sqrt{x}}\right)_q = \lim_{q \rightarrow 1} \left(\frac{3}{2} - \frac{x^{1-q}}{2}\right)^{\frac{1}{1-q}} = \frac{1}{\sqrt{x}}$$

In this preliminary work, we considered a regular NDDO method, together with all fourteen different NDDO methods resulting from combinations of q-functions in the overlap, core-core repulsions (exponentials and Gaussians) and the monopole-monopole interaction term.

We parameterized all these fifteen methods for the total energies, ionization potentials and geometries of only H_2 and H_3^+ , which we took as the parameterization set. Subsequently, we used the parameters to compute the corresponding properties of H_4 , and H_5^+ systems to check the transferability of the parameters and the robustness of the methods.

Results indicated that the replacement of only the inverse square root in the monopole-monopole interaction by the q-inverse square root had a positive and significant effect on the transferability of the parameters from H_2 and H_3^+ to H_4 and H_5^+ .

CONCLUSION

Further investigation of the applicability of q-square root functions in the multipole-multipole expansions of NDDO methods for other chemical systems is therefore warranted, and is presently being carried out in our laboratories.

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¹ Tsallis, C., J. Stat. Phys. **52**, 479 (1988).

² Dewar, M.J.S. and Thiel, W., Theoret. Chim. Acta **46**, 89 (1977).

³ Mundim, K.C. Physica A **350**, 338 (2005).