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Frontiers in electronic structure theory

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Current and emerging research areas in electronic structure theory promise to greatly extend the scope and quality of quantum chemical computations. Two particularly challenging problems are the accurate description of electronic near-degeneracies (as occur in bond-breaking reactions, first-row transition elements, etc.) and the description of long-range dispersion interactions in density functional theory. Additionally, even with the emergence of reduced-scaling electronic structure methods and basis set extrapolation techniques, quantum chemical computations remain very time-consuming for large molecules or large basis sets. fitting and explicit correlation methods, are makir challenges. © *2010 American Institute of Physics*. [doi

The past 15 years have seen major advances in electronic structure theory. Coupled-cluster theory or multireference methods, when joined with basis set extrapolation techniques, allow very accurate computations of small molecules. Indeed, for the smallest molecules (about six atoms or fewer), the leading small corrections to the electronic structure treatment can be added (relativistic effects, Born–Oppenheimer diagonal corrections, and higher-order correlation effects) to yield molecular properties so accurate that they have been used to match the high rovibrational levels of the water molecule as required to prove the presence of water on the sun or to model the greenhouse effect on earth.[1,2] While small-molecule computations have been achieving ever higher accuracy, at the same time, standard techniques of electronic structure theory have been extended to larger and larger molecules through the development of new approximations and better algorithms. Together, these advances

Для небольших молекул (порядка шести атомов) при описании электронной структуры можно ввести небольшие поправки к основным эффектам (релятивизм, неадиабатичность и корреляция), что позволяет воспроизводить свойства молекул и рассчитывать высоко лежащие колебательно-вращательные уровни настолько точно, насколько это требуется, например, для подтверждения наличия воды на солнце или для моделирования парникового эффекта на Земле. [1,2]

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[2] O.L. Polyansky, A.G. Császár, S.V. Shirin, N.F. Zobov, P. Barletta, J. Tennyson, D.W. Schwenke, P.J. Knowles, Science **299**, 539 (2003).