Research Interests, Frank Jensen.

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Our primary interest is in developing and testing new methodologies within the general field of computational chemistry. We are also open towards collaborative projects, where the focus usually is on solving a specific problem, often using existing methodologies. Application type projects usually consist of running calculations with a specific program and analyze the results, while development projects usually requires some type of programming, modifying existing code or writing your own code. The projects below illustrate the general research interests, but are by no means conclusive, feel free to drop me an email (frj@chem.au.dk) if you are interested in discussing possible projects. You can also take a look at our publications, to see the past projects undertaken, which gives a clue to the breath of topics we engage in.

https://tildeweb.au.dk/au23758/pub.html

Developing Improved Force Fields.

Force fields are empirical energy functions that describe how the molecular energy depends on the molecular geometry, and they are the essential components for performing molecular dynamics simulations. All force fields for production type simulations, like CHARMM, AMBER, GROMOS, OPLS, employ fixed partial atomic charges for representing the electrostatic interactions. The neglect of atomic anisotropy and polarization is known to be a major source of error in simulations. This, among other things, leads to inaccurate binding affinities, relative energies for conformations and associated conformational transition states, which affects both the structure and the dynamics when using these for simulating for example proteins.

We have recently proposed a *Bond Capacity* model where the atomic anisotropy is modelled by off-nuclei charges (representing lone-pairs and pi-bonds) and polarization is modelled by allowing the atomic charges to flow along bonds. The initial tests suggest that this is capable of reproducing molecular anisotropic polarizability to within ~10%. There are a large number of possible sub-projects here, for example using results from electronic structure calculation to analyze how the charge-flow depends on the molecule and it geometry, how to model charge-transfer effects, how to model short-range exchange-repulsion and dispersion effects, and what from a force field point of view is the best definition of an atom within a molecule. It may also be possible to “teach” such force fields to model bond breaking/formation, and this would allow a direct modelling of enzymatic reactions occurring within a protein environment, and thus casting light on how enzymes catalyze chemical reactions.

Developing New Basis Sets for Electronic Structure Methods.

All electronic structure calculations, using either wave or density functional theory methods, require a set of basis functions for representing the molecular orbitals. The goal here is to design basis sets that provide the lowest error for a given computational cost. This criterion leads to different optimum basis sets depending on the method (wave or density function) and the target molecular property. Most people have heard of the 6-31G* basis set, and some considered this as the solution to all problems, but the modern approach is to perform a series of calculations that systematically reduce the error, such that one can assign ‘error-bars’ to the calculated quantity, i.e. can the value be trusted?

The electron correlation converges as an inverse power series in the highest angular momentum L included in the basis set.

$$\Delta E_{corr} = \frac{A}{L^3} + \frac{B}{L^4} + \frac{C}{L^5} + \cdots$$

The corresponding convergence of Hartree-Fock (HF) and Density Functional Theory (DFT) energies is exponential-square-root.

$$\Delta E_{HF/DFT} = Ae^{-B\sqrt{L}}$$

This difference in convergence means that optimum basis sets for electron correlation and independent particle models (HF/DFT) are different. We have developed a hierarchy of new basis sets aimed at DFT methods, denoted *polarization consistent* (pc-*n*), where *n* (= 0,1,2,3,4) indicates the level of polarization beyond the isolated atom. The pc-*n* basis sets can be considered as HF/DFT equivalents of the correlation consistent basis sets cc-pVXZ for electron correlation methods. The most recent version of these employ a segmented contraction for improving computational efficiency, with the acronym pcseg-*n*.

The pc-*n* basis set have been used for constructing basis sets optimized for various molecular properties: pcSseg-n for NMR shielding constants, pcJ-n for NMR spin-spin coupling constants, pcX-n for X-ray spectroscopy, pcH-n for ESR hyperfine coupling constants. There may be other properties that could be of interest to construct optimized basis sets for.

The main use of spectroscopy is for obtaining information about the molecular structure. This has traditionally been done by empirical correlations, e.g. resonances around 7 ppm in the H-NMR spectrum indicates hydrogen bound to an aromatic ring. The ability to directly calculate spectra from molecular structures by electronic structure methods is increasingly becoming a routine tool, and potentially allows differentiating for example between diastereomeric structures differing by only a few ppm in C-NMR spectra. Achieving such accuracies, however, is difficult, and reducing basis set errors is only one component. There may be projects investigating how the error can be reduced in some of the other components.

Collaborative Projects.

We are currently engaged in collaborations with Prof. H. Stapelfeldt (modelling Coulomb explosion experiments), Prof. P. R. Ogilby (modelling the deactivation of $^1O_2$ in solution), Assoc. Prof. T. Weidner (LASER spectroscopy and excited state chemical reactions), Prof. L. B. Madsen (atto-sec spectroscopy and calculation of molecular structure factors) and have in the past collaborated with other groups by calculating molecular spectra and reaction mechanisms.