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Application of the Time-Dependent Density Functional Theory to the Study of Chiroptical Properties of Organic and Inorganic Compounds

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Abstract

Although several rigorous quantum-chemical *ab initio* methods, such as the coupled-cluster response theory, multi-configuration time-dependent Hartree-Fock method, and time-dependent Møller-Plesset pertubation theory, have become available in recent years for the calculation of excitation properties of molecules, these wavefuction-based approaches are still restricted to relatively small molecules because of their computational costs. However, due to the progress in the development of corresponding techniques and the demands of studying large molecules, the time-dependent density functional theory has also become popular as a cost-efficient general procedure in quantum chemistry.

In Chapter 1 of this thesis, a brief introduction to the background and the formalism of time-dependent density functional theory (TDDFT) for excited-states, as well as to density functional theory (DFT) for ground-state, is presented. Due to its high efficiency and the potential ability to cope with large molecular systems, the theory has been used in this thesis to interpret the chiroptical properties of both organic and inorganic molecules, and to predict their absolute configurations and conformations not only in the gas phase but also in solution.

In Chapter 2, the TDDFT method has been applied to determine the absolute configuration of *rubroflavin*. For this purpose up to thirty plausible isomers (including the quinoid, phenolic and other forms) have been taken into consideration. Their structures have been optimized at the DFT/TZVP/BP86 level. One quinoid isomer, which is separated from all other structures by an energy gap of about 4 kcal/mol was found to be the most stable species and to dominate the CD spectrum. Based on the geometries of the most stable isomer obtained in presence and absence of the solvent, the excitation energies and oscillator as well as rotational strengths have then been calculated using the TDDFT method. Comparison of the measured CD spectrum with that calculated for the energetically lowest isomer shows that especially the long wavelength parts of the spectra agree fairly well as far as the wavelengths and the signs of the Cotton effects are concerned. A detailed analysis of the spectra led us to the conclusion that the absolute configuration of *rubroflavin* at the –S(=O)CH$_3$ group is (S). This result supports earlier assignments based on semiempirical and *ab initio* studies on a thermal decomposition product of the *rubroflavin*.

In order to get an insight into the structures of proteins the higher excited states of disulfides have been analysed in Chapter 3. Although the two lowest energy excited states of disulfide chromophores in proteins have been studied extensively, there is little reliable information about their higher excited states. In this work, the TDDFT method has been used to predicting the spectroscopic properties of dimethyl disulfide. The principal results are: For the first

two transitions, the TDDFT calculations confirm the features predicted in earlier semiempirical MO calculations, *i.e.*, the strength of the longest wavelength band obeys a quadrant rule. However, although the two lowest energy transitions have rotational strengths of opposite sign and almost cancel for right-handed disulfides with dihedral angles near 90°, they have a small positive resultant at such dihedral angles. In addition, a set of four closely spaced transitions with a strong net positive rotational strength for right-handed disulfides is predicted close to 210 nm for $\delta \sim 90°$. This group of transitions remains positive over a significant range of dihedral angles near 90°, and thus does not show the quadrant behavior of the first long-wavelength band. These transitions should be valuable for assigning the absolute configuration of disulfides. Moreover, if a protein has a significant bias toward disulfides of a given chirality, these transitions can make a substantial contribution to the far-UV CD spectrum.

In Chapter 4, the structures and chiroptical properties of the tris(didentate) chelates [Se/Te(O CR^{1}R^{2}CR^{3}R^{4}O)$_3$], have been studied. These chelates display both configurational [Δ or Λ; (R) or (S)] and conformational (δ or λ) chirality. The relative stability of the chelates have been obtained at the DFT/TZVP/BP86 level. In order to assess the contributions of these three chiral arrays to the Cotton effects of the chelates and to elucidate their stereochemistry in the gas phase and in solution, calculations of the UV and CD spectra (down to 180 nm) have been performed using the TDDFT method. An extensive conformational analysis has supplied additional information on the relevant conformers in the conformational manifold. It was found that the dominant CD effect reflects mostly the δ/λ twists of the three five-membered ligand rings, and less so the influence of the Δ/Λ core configuration, while the contributions of any (R)/(S) chiral carbon atoms of the ligand rings are negligible. The sign, the intensity, and the energy of this dominant CD band are found to depend on the stereochemistry of the chelates in a predictable way. Among the conformers, those with equatorially disposed methyl substituents are much preferred. These results make it possible to determine the absolute configuration (Δ/Λ) and conformation (δ/λ) of the chelates from the CD data.

In Chapter 5, the CD spectra of bisporphyrins have theoretically been examined with a *coupled circular oscillator* (CCO) model. The geometry of the compound has been optimized at the RI-DFT/SVP/BP86 level, but due to its size (149 atoms) the excitation energies and rotational strengths have not been obtained. For this reason, the CCO model has been used. The model can uniquely be represented by four variables R_{AB}, α, β and δ. The angular dependences of the energy ordering and the signs of rotational strengths for the four transitions in bisporphyrins were analysed. The δ-dependence was shown to strictly fulfil a *6-Sector Rule*. In addition, we found that the second and the third transitions usually dominate the CD spectra of bisporphrins, and in this case the sign of *A*-value obeys a *4-Sector Rule*.