Chapter 8

Conclusions and Outlook

Synopsis

In the present chapter, the general conclusions of this work are drawn and some suggestions for the future work are presented.

8.1 Conclusions

The purpose of this thesis project was to use the recently developed linear response formalism, which incorporates the important effects such as relativity and electron correlation, for the theoretical modeling of Mössbauer isomer shift. The theoretical description of MIS requires a reliable value of the calibration constant $\alpha$, which is usually obtained from the linear regression of theoretical contact densities against the experimental isomer shifts. It was our hope that the use of the highly accurate theoretical methods in combination with the linear response approach would provide a universally applicable value of the calibration constant $\alpha$ for $^{57}$Fe and $^{119}$Sn nuclei, which could be used in the future MIS calculations on various $^{57}$Fe and $^{119}$Sn based systems without the necessity to parametrize the calibration constant for the given method. The major conclusions drawn from this dissertation are,
Chapter 3

- The performance of various density functionals within the linear response formalism for the MIS calculations were analyzed, the results pointed out that the correlation of calculated MIS with the experimental values improves with the increased fraction of the HF exchange in the density functional.
- The use of standard contracted basis sets yields reasonable results at the HF and density functional levels of theory, however with the use of the highly correlated \textit{ab initio} methods the small basis sets lead to substantial errors, suggesting the need to use the extended basis sets in connection with high-level \textit{ab initio} methods.
- The MIS calculations carried out using a literature value of the calibration constant $\alpha$ does not produce satisfactory correlation with the experimental isomer shifts even when the hybrid functionals are used in combination with large basis sets, therefore, it is suggested to use a constant $\alpha$ obtained from the calibration of the contact densities calculated with the most accurate theoretical methods against the experimental isomer shifts.

Chapter 4

- The importance of proper description of relativity and electron correlation for the accurate determination of contact density near the nucleus is demonstrated (see Figure 4.2).
- The use of highly correlated \textit{ab initio} methods gives a better description of the electron contact density near the $^{119}\text{Sn}$ nucleus and improves the calibration constant $\alpha$.
- The calibration constant $\alpha_{\text{MP2}}(^{119}\text{Sn}) = (0.091 \pm 0.002) a_0^{-3} \text{ mm/s}$ obtained with the use of relativistically corrected MP2 calculations is in excellent agreement with the previously obtained values, and can be proposed as a reliable, universally applicable constant for future MIS
8.1. Conclusions

Calculations thus eliminating the necessity to develop method dependent parametrizations.

- The MIS calculations on CaSnO$_3$ perovskite for the pressure range 0-36 GPa yield isomer shifts in a reasonable agreement with the experimental results. This confirms that the linear response formalism is capable of describing small variations of the isomer shift resulting e.g. from the pressure variations or from phase transitions.

**Chapter 5**

- The improved correlation with the experiment obtained by the use of the highly correlated methods (which is seen in Chapter 4), motivates us to test the double hybrid density functional developed by S. Grimme [55] in the calibration of $\alpha^{(57}\text{Fe})$.
- The calibration constant, $\alpha^{B2-PLYP}_{\text{B2-PLYP}} = -0.306 \pm 0.009 \, a_0^3$ mm s$^{-1}$ obtained gives the best statistical correlation with the experimental data, and this value is in excellent agreement with the experimental estimate of $\alpha = -0.31 \pm 0.04 \, a_0^3$ mm s$^{-1}$. This suggests to use this constant for the future $^{57}\text{Fe}$ MIS calculations.

**Chapter 6**

- The presence of different iron sites observed experimentally in the $^{57}\text{Fe}$ Mössbauer spectra of Prussian blue analogue RbMn[Fe(CN)$_6$]·H$_2$O is analysed using the $^{57}\text{Fe}$ parametrization developed in Chapter 5.
- The isomer shift differences $\Delta\delta_{\text{HT-LT}}$ of $\sim 0.1$ mm/s between the HT and LT phase of the RbMn[Fe(CN)$_6$]·H$_2$O compound originate from the change of oxidation state of iron from Fe$^{\text{III}}$ to Fe$^{\text{II}}$.
- The $\Delta\delta$ differences of 0.01-0.03 mm/s of the two different iron sites within both HT and LT phases originate from the different distribution patterns of Rb$^+$ ions around the iron sites.

**Chapter 7**

- The recently discovered iron based superconductors are studied in
order to analyse the variation of the hyperfine structure parameters; the isomer shift and hyperfine coupling constant, under phase transition and upon chemical substitution of these compounds. The MIS calculations are based on the parametrization developed in Chapter 5.

- The MIS study shows that with the tetragonal-orthorhombic phase transition in these compounds, the contact density decreases (ca. 0.17 $a_0^{-3}$) and the isomer shift increases (ca. +0.05 mm/s), which is characteristic for all the iron based superconductors studied.

- The hyperfine coupling constants calculated with the inclusion of the spin-orbit corrections give distinct variations among different classes of the iron based superconductors. The spin density near the $^{57}$Fe nucleus increases with the increase in the inter layer separation in the geometry, ie when going from 011 to 1111 types of compounds.

- The dependence of MIS and HFC on doping/chemical substitutions shows that its influence is stronger when the chemical substitution occurs in the immediate coordination sphere of $^{57}$Fe and it is less noticeable with the doping/chemical substitution in the inter layers such as Li/Ba/SmO in 111, 122, 1111 types of compounds.

- The Mössbauer parameters, MIS and HFC, are evaluated to be good tools to study the variation of the electronic structure and magnetic spin densities under phase transition and upon doping/chemical substitutions in the coordination sphere of $^{57}$Fe for the studied iron based superconductors, and can be suggested for monitoring the structural changes in these compounds.

Based on the analysis of the performance of different quantum chemical computational schemes in the calibration of the MIS, reliable and universally applicable values of the calibration constant $\alpha$ for $^{57}$Fe and $^{119}$Sn are obtained. The use of these values should eliminate the necessity for a tedious parametrization procedure when studying
the parameters of Mössbauer spectra. The application of the obtained calibration constants in combination with accurate quantum chemical methods helped us to obtain interesting results in the study of the Prussian blue analogues and of the iron-containing superconductors.

8.2 Outlook

As possible directions for the future work, the following points can be suggested,

**Parametrizations of other elements.**

The reliable values of the calibration constant \( \alpha \) for \(^{57}\text{Fe}\) and \(^{119}\text{Sn}\) obtained in this project, suggest to use the linear response formalism for the determination of accurate values of \( \alpha \) for other Mössbauer active nuclei in the periodic table, to name a few, \( \text{Ta, Eu, Au, Hg, I, U etc.} \)

Generally, the theory level for the MIS calculations are chosen by analysing the linear regression of the calculated isomer shifts within a particular theoretical method against the experimental shifts of the chosen compounds. The initial task in this direction is to yield a calibration constant \( \alpha \) from the empirical fit of the contact densities against the experimental isomer shifts. Therefore, if an accurate, method independent calibration constant \( \alpha \) is available then one can use it directly and avoid the parametrization of the calibration constant for every particular method of calculation, which saves considerable time.

**Development of basis sets for MIS calculations.**

All the calculations in this dissertation are carried out using the standard large uncontracted basis sets. However, the calculation using these basis sets are complex and time consuming. Therefore, it is es-
sential to investigate the possibility to construct more compact, yet accurate basis sets for the MIS calculations. That such a possibility exists is suggested by the results of Chapter 3, where good results were obtained with the standard contracted basis sets of small and medium size. The development of the compact basis sets for MIS calculations will enable us to save the computational work and to study bigger systems.

**Applications in the fields of Materials science and Biological Sciences.**

- **Materials Science**
  There are a number of aspects which can be studied using Mössbauer technique, in materials containing Mössbauer active nuclei. They include, the valence state determination, structural and bonding properties, solid state reactions, spin crossover, magnetic crossover etc.

  Mössbauer spectroscopy is extensively used to study the valence fluctuations and temperature dependent electron transfer between different metals in mixed valence metallic compounds. The capability of MIS to predict the valence state in such systems is clear from the analysis of the Prussian blue analogue, RbMn[Fe(CN)$_6$]·H$_2$O, described in Chapter 6. The Mössbauer parameters can effectively be used for the study of the electronic structure of newly discovered materials, for example the iron based superconductors, which is explained in Chapter 7 of this dissertation.

- **Biochemistry and Biocatalysis**
  There are numerous proteins which contain iron as their active site, the functional properties of these proteins are determined mostly by the iron electronic structure. Therefore, the small changes in the iron electronic structure under various conditions can be detected by Mössbauer spectroscopy. For instance the analysis of oxyhemoglobins
from various types of leukemia patients show a slight increase of the Mössbauer parameters, the isomer shift and quadrupole splitting, in comparison with the normal adults [146]. Moreover, several diseases are caused by the synthesis of anomalous biomolecules or from the disturbance in the biosynthesis of any other proteins. In these cases, the Mössbauer spectroscopy is helpful to study the electronic structural variations of these iron containing proteins.

Iron-oxo species are the key reactive intermediates in the catalysis of oxygen-activating enzymes and synthetic catalysts, such as cytochrome P450 and methane monooxygenase (MMO). High valent iron-oxo intermediates are used in biological systems to carry out challenging oxidations in many scenarios. The analysis of the Mössbauer properties of these intermediate states in the reaction cycle, brings an understanding of the oxidation activation in these enzymes.

There are several metabolic reactions/pathways, which can be studied using Mössbauer spectroscopy. Certain disturbances in the metabolic pathways can cause several anomalies, for example the overload of iron, resulting in diseases such as β-thalassemia, hemochromatosis etc. Therefore, the electronic and magnetic structure of Mössbauer elements in the metabolic reactions/pathways can give information on the molecular nature of the diseases and pathological processes occurring in the living organisms.