

University of Groningen

Electronic structure theory meets precision measurements

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DOI:
[10.33612/diss.195934645](https://doi.org/10.33612/diss.195934645)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2021

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Haase, P. (2021). *Electronic structure theory meets precision measurements*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen. <https://doi.org/10.33612/diss.195934645>

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Chapter 3

Theoretical predictions of molecular enhancement factors

The previous chapter was concluded by introducing the finite-field method used for calculating atomic and molecular properties in the framework of the relativistic coupled-cluster method. In this chapter, additional aspects, which are applicable to most electronic structure methods and thus not dependent on the exact form of the wave function, will be introduced. In Sec. 3.1, the operators needed for calculating the P, T -odd molecular enhancement factors will be derived. The operator needed for calculating HFS constants has been derived in detail in **Chapter 4**. In Sec. 3.2, different strategies to determining the uncertainty of the calculated parameters will be discussed and in Sec. 3.3, some aspects related to the connection between *ab initio* results and the (real) experimental world will be introduced.

3.1 P, T -odd interaction constants

In the introduction of this thesis the two P, T -odd interactions, which contribute to the P, T -odd molecular dipole moment in paramagnetic systems, were introduced, namely the electron electric dipole moment (eEDM) and nucleon-electron scalar-pseudoscalar (S-PS) interactions. In **Chapter 5**, the corresponding molecular enhancement factors, W_d and W_s , in BaF have been calculated and in Sec. 3.1.3, the results of W_d in YbF will be presented. These calculations were performed with the relativistic CC method introduced in the previous chapter with the aid of the finite-field method. The two properties were thus obtained from the numerical derivatives:

$$W_d = \frac{1}{\Omega} \left. \frac{dE_{\Omega}(\lambda_{d_e})}{d\lambda_{d_e}} \right|_{\lambda_{d_e}=0} \quad (3.1)$$

$$W_s = \frac{1}{\Omega} \left. \frac{dE_{\Omega}(\lambda_{k_s})}{d\lambda_{k_s}} \right|_{\lambda_{k_s}=0} \quad (3.2)$$

where the factor $\frac{1}{\Omega}$ comes from the definition of the effective Hamiltonian, Eq. (1.4). $E_{\Omega}(\lambda_{d_e})$ and $E_{\Omega}(\lambda_{k_s})$ denote the perturbed energies of a given electronic state indicated

by Ω , corresponding to the following total Hamiltonian in which the perturbation, being either the eEDM or S-PS Hamiltonian, are added with corresponding perturbation strength, λ_{d_e} and λ_{k_s} :

$$\hat{H} = \hat{H}^{(0)} + \lambda_{d_e} \hat{H}^{\text{eEDM}}/d_e \quad (3.3)$$

$$\hat{H} = \hat{H}^{(0)} + \lambda_{k_s} \hat{H}^{\text{S-PS}}/k_s \quad (3.4)$$

where the zeroth-order Hamiltonian is the field-free Dirac-Coulomb Hamiltonian:

$$\hat{H}^{(0)} = \sum_i \left[c\vec{\alpha}_i \cdot \hat{\vec{p}}_i + \beta_i c^2 - \hat{V}_{eN} \right] + \hat{V}_{ee} + \hat{V}_{NN} \quad (3.5)$$

as introduced in Eq. (2.22).

The task in the following two sections is to derive \hat{H}^{eEDM} and $\hat{H}^{\text{S-PS}}$ from fundamental theory and in Sec. 3.1.3, a computational study of W_d in YbF will be presented.

3.1.1 eEDM enhancement

The derivation of an appropriate operator for the eEDM enhancement starts by considering the P, T -odd eEDM Lagrangian density [101, 102]:

$$\mathcal{L}^{\text{eEDM}} = -i \frac{d_e}{2} \bar{\Psi} \sigma^{\mu\nu} \gamma^5 \Psi F_{\mu\nu} \quad (3.6)$$

which is the P, T -odd analogue of the anomalous magnetic moment. Ψ ($\bar{\Psi}$) is the Dirac (conjugate) field of the electron, $\sigma^{\mu\nu} = \frac{i}{2} \gamma^\mu \gamma^\nu - \gamma^\nu \gamma^\mu$, $\gamma^{\mu, \nu}$ are the Dirac matrices, $\gamma^5 = i\gamma^0 \gamma^1 \gamma^2 \gamma^3$ and $F_{\mu\nu}$ is the electromagnetic field tensor. By inserting the expressions for $\sigma^{\mu\nu}$, γ^5 and $F_{\mu\nu}$, one obtains the eEDM Lagrangian density in terms of \vec{E} and \vec{B} :

$$\mathcal{L}^{\text{eEDM}} = d_e \bar{\Psi} (\vec{\Sigma} \cdot \vec{E} + i\vec{\alpha} \cdot \vec{B}) \Psi \quad (3.7)$$

which can be translated into the Hamiltonian (using the relations, $\bar{\Psi} = \Psi^\dagger \gamma^0$ and $\vec{\gamma} = \gamma^0 \vec{\alpha}$):

$$\hat{H}^{\text{eEDM}} = -d_e (\gamma^0 \vec{\Sigma} \cdot \vec{E} + i\vec{\gamma} \cdot \vec{B}) \quad (3.8)$$

where $\vec{\Sigma} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}$ and $\vec{\gamma} = \begin{pmatrix} 0 & \vec{\sigma} \\ -\vec{\sigma} & 0 \end{pmatrix}$. To the best of my knowledge, the only numerical calculations of the term involving \vec{B} was performed by Lindroth et al. [103] considering the eEDM enhancement in the Cs atom on the Hartree-Fock level using the Dirac-Coulomb-Breit Hamiltonian, i.e. including all terms to $\mathcal{O}(\alpha^2)$. The effect

of the entire $\mathcal{O}(\alpha^2)$ terms, i.e. due both to magnetic interaction as well as the Breit terms, on the enhancement factor in Cs was found to be -0.4% on the Hartree-Fock level. Based on the findings of Lindroth et al., all calculations of enhancement factors since then have been neglecting the interaction with a magnetic field, taking into account only the interaction with the electric field:

$$\hat{H}^{\text{eEDM}} \approx -d_e \gamma^0 \vec{\Sigma} \cdot \vec{E} \quad (3.9)$$

The same will be done here, but further studies of the effect of the magnetic interaction, in particular for heavier systems or systems of significant different nature than Cs, would be desirable.

The operator in Eq. (3.9) takes into account the interaction between the eEDM and both internal and external electric fields, $\vec{E} = \vec{E}_{\text{int}} + \vec{E}_{\text{ext}}$. The internal electric field acting on electron i is due to the nuclei, I , and other electrons, j [104]:

$$\vec{E}_{\text{int},i} = \sum_I \frac{\vec{r}_{iI}}{r_{iI}^3} - \sum_{j \neq i} \frac{\vec{r}_i - \vec{r}_j}{r_{ij}^3} \quad (3.10)$$

The second term is a two-electron operator which poses additional challenges to the implementation (see Ref. 42 for a discussion hereof). Consequently, it is advantageous to rewrite the operator into a one-electron form as was first introduced in Ref. 104:

$$\hat{H}^{\text{eEDM}} = \sum_i 2icd_e \beta_i \gamma_i^5 \hat{p}_i^2 \quad (3.11)$$

For the derivation of the operator, the reader is referred to Ref. 104, but one aspect is worth noting. In order to rewrite Eq. (3.8) into Eq. (3.11), the external electric field, \vec{E}_{ext} , should be included in the zeroth order Hamiltonian. In the method described so far, this is not the case, since $\hat{H}^{(0)}$ is the field-free Dirac-Coulomb Hamiltonian, Eq. (3.5). However, even if the external electric field was included in $\hat{H}^{(0)}$, the resulting interaction would not be complete due to the lack of rotational degrees of freedom as a consequence of the Born-Oppenheimer approximation (see Sec. 3.3.1). In order to justify the use of Eq. (3.11), the interaction with an external electric field will be treated in a second step using the Stark Hamiltonian as will be shown in **Chapter 5**. This leads to the polarization factor which was discussed in the introduction.

The operator in Eq. (3.11) is P, T -odd which means that it can only be evaluated by a Kramer-unrestricted method. In the framework of the DIRAC program, it can consequently be evaluated at the coupled-cluster level only since the Hartree-Fock and DFT implementations utilize Kramers-restriction which is not the case for the coupled-cluster implementation. The same goes for the operator introduced in the following section.

3.1.2 Nucleon-electron scalar-pseudoscalar interaction

The P, T -odd interaction between electrons and nuclei takes various forms [102, 105]. In paramagnetic systems, the scalar-pseudoscalar nucleon-electron (S-PS) interaction is the dominating term which takes the form:

$$\mathcal{L}^{\text{S-PS}} = \bar{N} N \cdot \bar{\Psi} \gamma^5 \Psi \quad (3.12)$$

This term can be re-written in an effective Hamiltonian for nucleus I by taking the non-relativistic limit for the nucleons:

$$\hat{H}_I^{\text{S-PS}} = \frac{iG_F}{\sqrt{2}} Z_I k_s \gamma^0 \gamma^5 \rho(\vec{r}_I) \quad (3.13)$$

where G_F is the Fermi coupling constant which indicates the weak nature of this interaction and which in atomic units is 2.2225×10^{-14} a.u., Z_I is the atomic number of nucleus I and ρ is the nuclear charge density. k_s is the magnitude of P, T -odd interaction which was introduced in the effective Hamiltonian in Eq. (1.4). Sometimes the S-PS interaction is parametrized by C_S which is related to k_s by $C_S = \frac{Z}{A} k_s$ where A is the total number of nucleons. In principle, the S-PS enhancement should be calculated for every nucleus in the system, but in practice only the heavy element(s) will contribute due to the Z^3 scaling.

3.1.3 Computational study of W_d in YbF

Paper 3 *Enhancement factor for the electric dipole moment of the electron in the BaOH and YbOH molecules, M. Denis, P. A. B. Haase, R. G. E. Timmermans, E. Eliav, N. R. Hutzler, and A. Borschevsky, Phys. Rev. A 99, 42512 (2019)*

Contributions: *Calculations of W_d in YbF for comparison with the results for YbOH.*

In addition to the results presented in **Chapter 5**, the results of W_d in YbF from a collaboration with Malika Denis [106] will be discussed here. The main focus of this work was to calculate W_d in the triatomic systems BaOH and YbOH since the additional vibrational degrees of freedom potentially give rise to enhanced experimental sensitivity. An interesting question to ask in this context is how the molecular enhancement factor differs between the triatomic and diatomic (isoelectronic) analogues, i.e BaF and YbF. My contribution to this work was to calculate W_d in the diatomic species and in the following an additional computational analysis compared to the results included in Ref. 106 will be presented.

Due to the complicated electronic structure associated with the Yb atom, the single-reference CC method does not give reliable results, indicated by large T1-diagnostic values which is a measure for the quality of the CC wave function [107]. Instead, the multi-reference FSCC method was used. In the case of YbF, both sector (0,1) and

Table 3.1 W_d in YbF [$10^{25} \frac{\text{Hz}}{e_{cm}}$], calculated at the FSCC level with different basis sets and using the 4-component and X2C Hamiltonians.

basis set	W_d
4C	
vdz	1.057
vtz	1.144
vqz	1.156
X2C	
vqz	1.144
aeqz	1.144
s-aug-vqz	1.144

(1,0) were tested, starting from YbF^+ and YbF^- , respectively. Before discussing the effects of basis set and relativity on the calculated W_d , the suitability of the FSCC method for treating YbF should be determined.

The obvious way to assess the quality of a CC wave function is to look at the convergence of the results when increasing the excitation rank. The current FSCC implementation is however limited to single and double excitations and such a study is thus not feasible. Instead, we consider two alternative strategies, namely the comparison of the results obtained with sector (0,1) to those from sector (1,0) as well as the size of the employed model space. The difference in W_d when using the two sectors was found to be 1.3% on the X2C/vqz level. The similarity of the (0,1) and (1,0) results indicate that the FSCC method provides stable results and is more suitable than the single-reference approach. The dependence on the chosen model space was tested by comparing a model space containing only the valence σ orbital to one containing 5 additional virtual orbitals, resulting in a difference of 1.1%. This difference indicates that the result using the smaller model space is sufficiently converged to perform the basis set study at this level, but for highest accuracy the larger model space should of course be used. Extending the model space even further is not expected to have any significant effect.

The next aspect to discuss is the effect of the basis set on W_d . In Tab. 3.1, W_d is shown using different quality of basis sets at the FSCC (0,1) level. Due to the high computational cost of the aeqz and s-aug-vqz basis sets, these calculations, along with the vqz for comparison, were performed at the X2C level. It turns out that neither additional tight nor additional diffuse functions have any significant influence on the value of W_d . It should be noted here that the vqz basis set in the case of the Yb atom has more tight functions than for example in the case of the Ba atom. The reason for this is that there is no logical separation between the valence and core-valence space in the case of Yb. Compared to the s-block elements, one would consider the valence

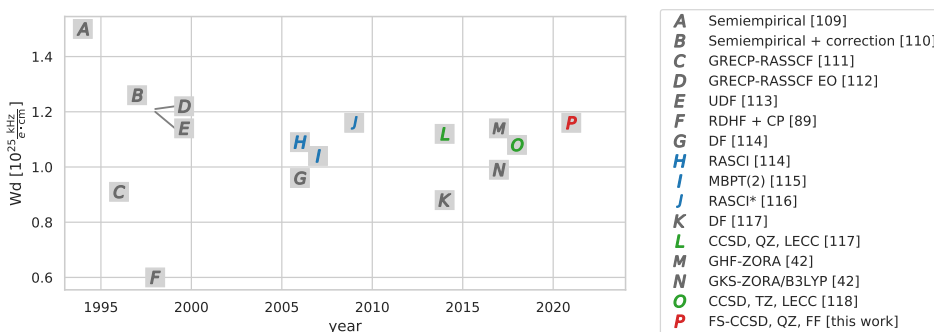


Figure 3.1 Graphical representation of reference values for W_d in YbF as a function of year published.

region as consisting of 6s, 4f and 5d and the core-valence with the additional 5s, 5p and 4d shells. However, due to the compact nature of the 4f shell, the 4f and 5s5p4d shells should be treated together [108] and all mentioned orbitals are considered as part of the valence space.

Considering now the general quality of the basis set we see a converging behavior when increasing the cardinal number. This is different to the behavior of W_d in BaF which showed a zig-zag dependence, see **Chapter 5**. The difference between the results obtained with the vqz and vtz basis sets is 1.0% which, together with the results from the additional tight and diffuse functions, indicates that the basis set is reasonably converged at the vqz level.

Lastly, the results obtained with the 4-component and X2C methods should be compared. The difference at the vqz level is 1.0% and is slightly larger than in the case of W_d in BaF (0.4%), **Chapter 5**, which is to be expected due to Yb being heavier. In the study on BaF, we also tested the effect of including the Gaunt interaction, i.e. taking into account higher order relativistic effects in the electron-electron interaction compared to the Coulomb interaction. This interaction can be calculated at the Hartree-Fock level only and we consequently chose not to consider this effect here, since the Hartree-Fock wave function provides a poor description of the multi-reference YbF system.

The computational study presented so far indicates that the result of W_d in YbF at the 4c/FSCC/vqz level should be reliable to within approximately 5-10%. Without any reliable estimation of higher order relativistic effects, which should be larger in YbF compared to for example BaF, it is difficult to make this uncertainty estimate more specific.

This section will be concluded by comparing the presented result to the results

which can be found in the literature calculated with a variety of different methods [42, 89, 109–118]. These results are shown in Fig. 3.1 and grouped according to the level of theory. The green points correspond to CC results, the light blue points correspond to RASCI and MBPT(2) methods, the grey points correspond to methods with a more approximate treatment of electron correlation and the red point is the result of the present study. Comparing only the methods treating electron correlation at CI-level a spread of around 20% can be seen whereas the CC results have a smaller spread of around 10%. It should however be noted that the two earlier CC results were obtained using a single-reference method. When inspecting the results in Fig. 3.1 it is tempting to take the spread in the results as a common uncertainty. However, these methods vary substantially in the level of sophistication and such a conclusion is not representative of the quality of the more sophisticated methods and probably not reliable for the less sophisticated ones. A better alternative is to establish a reliable theoretical uncertainty for each performed calculation. This will be the subject of the following section.

3.2 Establishing the accuracy of theoretical predictions

Now that the framework of the relativistic coupled-cluster method for calculating P, T -odd properties has been established, it is time to discuss the uncertainty of this method. Within electronic structure methods, it is not customary to put error bars on *ab initio* results as is done in experimental physics. The main reason for this is probably that there is no obvious way to do so which fits all *ab initio* methods. Another reason could be related to the fact that researchers within the field often have a good feeling of inherent uncertainties associated with the different methods, but when collaborating with experimentalists, or in general non-specialists, reliable uncertainty estimations can be very useful. In the scope of this thesis, uncertainties on the calculated W_d and W_s parameters are necessary since they are used in the interpretation of a precision experiment where excellent control and knowledge of all sources of errors is crucial.

In order to determine a reliable uncertainty estimate, two strategies can be followed; 1) comparison with experimental data and 2) establishing an uncertainty estimate based purely on a systematic computational study. These two strategies will be discussed in the following two sections.

3.2.1 Comparison with experimental results

The usual way to determine the accuracy of a given theoretical method is to do a so-called benchmark study where the results obtained with a (often times new) theoretical method are compared to either experimental or higher level theoretical data.

Ideally, such a benchmark study should be performed on a large set of representative systems as was done for example in Ref. 119. The result of such a study then serves as an indication of the overall accuracy, but it does not allow for uncertainties on individual results.

When an uncertainty is needed on a particular result, the difference between a theoretical and experimental determined appropriate property can serve as uncertainty estimation. There are however cases where the property of interest cannot be measured and where comparison with a related property or system can be used. For example when studying properties of superheavy elements for which experimental data is scarce, the results for lighter homologues are then compared to experimental data and the discrepancy is used as the uncertainty on the result for the superheavy element. Another example is the interpretation of atomic parity violation in Cs where the comparison between calculated and experimental hyperfine structure (HFS) constants dictated the uncertainty on the calculated parity violating matrix element, which cannot be measured, needed to extract the weak charge from measurements [35, 120].

In the search for molecular P, T -violation, the situation is similar to that of atomic parity violation, in the sense that the molecular enhancement factors W_d and W_s are necessary to relate a measurement to the fundamental P, T -odd properties. However, W_d and W_s cannot be measured and the motivation for the work presented in **Chapter 4** on HFS constants in ^{137}BaF (i.e. coupling to ^{137}Ba nucleus) was to compare the calculated HFS constants to experiment in order to get an indication of the uncertainty of the calculated P, T -odd enhancement factors [121]. The reason for using the HFS constant to benchmark W_d and W_s is that it probes the electronic wave function in the vicinity of the Ba nucleus. This is also the part of the wave function that W_d and W_s are most sensitive to due to relativistic effects and the strong electric field associated with the large nuclear charge of Ba.

3.2.2 Theoretical uncertainty estimate

A theoretical uncertainty estimate is not at all common practice when using *ab initio* methods. One reason for this is that it takes a very systematic method to establish a reliable scheme. However, the most popular theoretical method is based on density functional theory (DFT) where correlation is taken into account by the exchange-correlation functional, the form of which is unknown and is thus not systematically improvable. Another reason is that such an uncertainty estimate relies on an extensive computational study which is not feasible especially if many systems are being treated or expensive methods are being used.

However, this subject recently seemed to get more attention for example in the group of Christoph Jacob where, until now, uncertainties due to the employed molecular geometry were investigated using sophisticated methods for uncertainty quantification [122]. Also in the field of atomic and molecular physics, theoretical uncertainties on

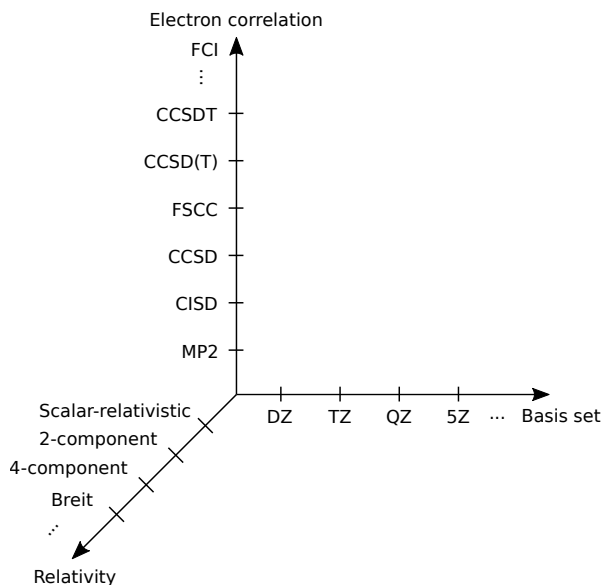


Figure 3.2 Illustration of a quality assessment of standard *ab initio* methods inspired by Fig. 1 in Ref. [74]. The origin corresponds to a non-relativistic Hartree-fock method with a minimal basis set.

calculated properties sometimes appear, even though the method for obtaining these is often not obvious [42, 44, 123–127].

For the past few years, in our group we have been working on a scheme for calculating reliable uncertainty estimates in a systematic fashion. This scheme can best be explained by considering the graphical illustration of a standard *ab initio* method depicted in Fig. 3.2 which shows the three cornerstones of such a method: The basis set, treatment of electron correlation and of relativity. When moving along each axis, the quality of the treatment improves. In the case of electron correlation and basis set the step-wise improvement is systematic when CC theory and cardinal number optimized basis sets are used. The step-wise inclusion of relativistic effects is less systematic and the associated uncertainty is thus the hardest to estimate, as will become clear later. The idea of the scheme is to estimate what is still missing relative to a given point on each of the axes. If for example a QZ basis set is used, the effect of going to 5Z and higher can then be estimated by considering the difference between the TZ and QZ result. We usually take half of this difference as the uncertainty estimate since a converging behavior can be expected. Note that the illustration in Fig. 3.2 could in principle have more dimensions representing for example the treatment of the nuclear structure, nuclear motion, for which an example will be shown in **Chapter 5**,

solvent effects, etc.

In the remaining chapters of this thesis, theoretical uncertainty estimates have been determined for P, T -odd molecular enhancement factors, **Chapter 5**, and HFS constants, **Chapters 4 and 6**. In the case of the latter, comparison with experimental results was performed in order to test the validity of the estimated uncertainty. In the case of ground state HFS constants, **Chapter 4**, the estimated uncertainties were between two and five times larger than the deviation from experimental results. This indicates that the estimated uncertainties are on the conservative side which was the intention in the first place. In the case of excited state HFS constants, **Chapter 6**, the uncertainty estimate was only 1.5 times larger. This smaller margin is partly due to not including the higher order relativistic effects in the uncertainty estimate for the excited states since the Gaunt interaction cannot be evaluated on the FSCC level.

Even though the scheme presented in this section seems to give reliable uncertainty estimates there is definitely room for improvement, for example by applying more sophisticated uncertainty quantification methods, as in Ref. 122, to the basis set and electron correlation uncertainties. In addition, the uncertainty stemming from the treatment of relativity remains a challenge since the Breit and QED interactions are generally not available in molecular electronic structure codes. In the case of QED effects, this has however very recently changed [128, 129] and it will be interesting to see what the effects are on the properties studied in this thesis.

3.3 Connecting theoretical results with experiment

At this point, the relevant aspects of predicting molecular properties with *ab initio* methods have been covered. The input of such a calculation, in addition to the choice of method, basis set and required property, is a molecular structure, i.e. a set of coordinates which specifies the location of the individual atoms. During the calculation, unless a geometry optimization takes place, these coordinates are kept fixed and the molecule is static, i.e. it cannot vibrate, rotate or translate. Compared to the situation in the lab, this is of course a very crude approximation. It furthermore prevents complete studies on for example the interaction of a molecule in a given rotational state with an external electric field due to the lack of rotational degrees of freedom in the calculation. The motivation for treating the electronic degrees of freedom separately, known as the Born-Oppenheimer approximation, will be briefly introduced in the following section and in Sec. 3.3.2 the framework which takes care of the connection between *ab initio* parameters and for example the rotational degrees of freedom, namely effective Hamiltonian theory, will be discussed.

3.3.1 The Born-Oppenheimer approximation

The degrees of freedom in a molecule can be divided into two groups: Electronic (elec) and nuclear (nuc). By realizing the huge difference in mass between the electrons and nuclei, one can in most cases assume that the electrons will respond practically instantaneously to any change in the position of the nuclei. This is known as the Born-Oppenheimer approximation. Consequently, the wave functions of these two groups can be treated separately and the total wave function of the system can be written as the product:

$$\psi_{\text{tot}}(\{\vec{r}_i\}, \{\vec{R}_N\}) = \psi_{\text{elec}}(\{\vec{r}_i\}; \{\vec{R}_N\})\psi_{\text{nuc}}(\{\vec{R}_N\}) \quad (3.14)$$

and the total energy as the sum:

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{nuc}} \quad (3.15)$$

Above, $\{\vec{r}_i\}$ denotes the coordinates of all the electrons in the systems and $\{\vec{R}_N\}$ of all the nuclei. The electronic wave function, ψ_{elec} depends parametrically on the positions of the nuclei as indicated by the ";". This separation of variables allows one to divide the total Schrödinger equation (assuming for now a non-relativistic treatment) into an electronic and nuclear Schrödinger equation which can be solved separately.

The *ab initio* method discussed so far deals with the solution of the electronic part only, but there are many cases where also vibrational and rotational degrees of freedom, which belong to ψ_{nuc} , need to be taken into account. One example has already been mentioned, namely the study of *P*-violation in chiral molecules, where differential *P*-violating shifts of vibrational transitions were studied with *ab initio* methods (**Paper 10**). Another example will appear in **Chapter 5** where vibrational effects on *P*, *T*-violating molecular enhancement factors were calculated and included in the uncertainty estimate. In both of these cases, the vibrational analysis was performed in a two-step fashion; First the potential energy surface (PES) of a given vibrational mode was obtained with *ab initio* methods and in a second step, the vibrational Schrödinger equation was solved within this PES. Another way of treating vibrational effects on molecular properties is by using response theory [96].

3.3.2 Effective Hamiltonian theory

Effective Hamiltonian theory is a useful, in my opinion crucial, tool to relate properties calculated with *ab initio* theory methods to those measured in experiments. This relation is sometimes straightforward, as can be seen for ground state HFS constants presented in **Chapter 4**, but can be more complicated, for example in the case of excited states, and in **Chapter 6** an entire section is devoted to the relation between the effective Hamiltonian used in *ab initio* theory and the one usually used in experimental molecular physics. In the following, the basic idea of effective Hamiltonian theory will

be introduced. Even though the concept of an effective Hamiltonian is being used in many areas of chemistry and physics one needs to look far for a rigorous treatment of the subject. In the following I will follow the approach of McWeeny [130, 131].

Consider the perturbed Hamiltonian:

$$\hat{H} = \hat{H}^{(0)} + \hat{H}' \quad (3.16)$$

where $\hat{H}^{(0)}$ is the field-free electronic Hamiltonian, with eigenfunctions $\{\Phi_j\}$, and \hat{H}' is the operator for the perturbation of interest. The eigenfunctions, i.e. perturbed wave functions, of \hat{H} can then be expanded in terms of the unperturbed wave functions:

$$\Psi_i = \sum_j c_{ij} \Phi_j \quad (3.17)$$

and the expansion coefficients can be obtained by solving the secular equation (here in matrix form):

$$\mathbf{H}\mathbf{c} = E\mathbf{c} \quad (3.18)$$

where \mathbf{c} is the vector of expansion coefficients, $\{c_{ij}\}$.

The essence of effective Hamiltonian theory is now to reduce this complete space spanned by \mathbf{c} to a form which contains only the relevant degrees of freedom needed to describe a given situation:

$$\mathbf{H}_{\text{eff}}\mathbf{a} = E\mathbf{a} \quad (3.19)$$

where \mathbf{c} has now been divided into a part containing the states of interest, \mathbf{a} , and the rest, \mathbf{b} . Note that the eigenvalues of \hat{H}_{eff} for the \mathbf{a} states are the exact energies for these states while the eigenfunctions are approximate. The effective Hamiltonian takes the interaction with the \mathbf{b} states into account in orders of the perturbation \hat{H}' . To first order, the expectation value of \hat{H}_{eff} is:

$$\langle \Phi_{a,i} | \hat{H}_{\text{eff}} | \Phi_{a,i} \rangle \approx \langle \Psi_i | \hat{H}' | \Psi_i \rangle \quad (3.20)$$

where Φ_a denotes an \mathbf{a} state.

So far, the advantage of using an effective Hamiltonian has been concerned with the reduction of the complete space to a much smaller one, containing only the relevant states. But also the operators in the effective Hamiltonian are often simplified compared to the correct quantum mechanical operator \hat{H}' . The resulting effective Hamiltonian then consists of simple angular momentum operators with well defined eigenfunctions as well as a set of numerical parameters. Also electric and magnetic fields can be included.

A few examples of terms in the effective Hamiltonian, which will return in **Chapters 4 and 5**, are the HFS Hamiltonian, $\vec{I}\mathbf{A}\vec{S}$, and the Stark Hamiltonian, $-\vec{d} \cdot \vec{E}_{\text{ext}}$, where

\vec{I} and \vec{S} are the nuclear and electron spin, \mathbf{A} is the HFS tensor and \vec{d} is the molecular dipole moment. There are two strategies for determining \mathbf{A} and \vec{d} . In experimental research these parameters are usually fitted by comparing the energy spectrum of the effective Hamiltonian in an appropriate basis to the measured energy spectrum. However, these parameters can also be calculated with electronic structure methods as derivatives of the electronic energy with respect to the perturbation. The effective (spin) Hamiltonian consequently provides the necessary link between experimental and theoretical research.

