

2 Theoretical methods

2.1 Electronic structure methods

An accurate description of the electronic structure of a molecule needs to take into account the correlation energy, which is defined as the difference between the exact energy and the Hartree-Fock (HF) energy. The choice of the method applied to calculate the correlation energy depends on the nature of the correlation. There are in general two limiting cases:

1. **dynamic correlation:** The HF determinant is a valid approximation and all calculations of the electron correlation are based on excitations from this determinant.
2. **static correlation:** The molecule has to be described by more than one determinant and the description with only one HF determinant is qualitatively wrong.

As might be expected, most molecules are somewhere in between these limiting cases. While all methods that start from the HF determinant are referred to as single reference methods, methods that start from a description with more than one determinant are called multi-reference methods. For both types of methods, the ones applied in this thesis will be briefly presented in the following.

All electronic structure calculations have been carried out with the Molpro package of *ab initio* programs^[35] unless otherwise stated.

2.1.1 Single reference methods

Coupled-Cluster Calculations

As noted above, the electron correlation in single-reference methods is calculated by generating new terms in the wave function via excitations of electrons from the HF determinant. Depending on how many electrons are excited with respect to the HF determinant, these new determinants are classified as *single*, *double*, *triple* etc. excitations. If an excitation operator \hat{T} is defined as:^[36]

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_{N_{el}} \quad (2)$$

this operator will create all possible excitations from the HF determinant and give the correct wave function within the given basis set. However, the number of terms is extremely large even for systems with rather few electrons. In coupled cluster (CC) theory, the excitation operator is the argument of the exponential function which accounts for the fact that there are dependencies between the coefficients of the wave function expansion for different excitations. The coupled cluster wave function is then given as:

$$\Psi_{CC} = e^{\hat{T}} \Phi_{HF} \quad (3)$$

The first time that the CC ansatz was introduced into theoretical chemistry was by Čížek in 1966^[37] while an equivalent approach was used almost ten years earlier in nuclear physics.^[38] Since the number of terms generated by the cluster operator would be too large to handle computationally, the excitation operator is usually truncated. In coupled cluster with singles and doubles (CCSD) for example, the operator is truncated after the \hat{T}_2 term. The exponential form of the cluster operator however ensures that also disconnected excitations of higher order are included, that result from products of the excitation operator eq. 2 (e.g. disconnected quadruples via the $1/2\hat{T}_2^2$ operator). This inclusion of products of excitations makes the CC method size extensive while it is not variational in the commonly used projected form.^[39]

One of the most commonly used *ab initio* methods is CCSD(T),^[40] where the triple excitations are included in a perturbative manner. In the case of open-shell electronic states, either restricted or unrestricted HF reference wave functions can be used. The former method leads to both a spin unrestricted (RHF-UCCSD) and a partially spin-restricted (RHF-RCCSD) formalism. RHF-UCCSD is computationally about three times more demanding than RHF-RCCSD, which is furthermore free from spin contamination.^[41,42] Since no UHF based CC variants are available in Molpro, the interface to Kallay’s MRCC program^[43] was used for the UHF-UCCSD(T) calculations. Usually, only valence electrons are correlated in the CC calculations and results obtained with this method will be marked with the suffix fc (frozen-core), whereas calculations with all electrons being correlated will be denoted with ae (all electron).

Explicitly correlated methods

Since convergence of the correlation energy with the basis set is quite slow and CCSD(T) already has a rather unfavourable scaling of N_{basis}^7 with the basis set size, methods are required that enable to reach the CBS limit faster. One of the reasons of the slow convergence is the poor description of the electronic cusp when the wave function is expanded in functions that do not explicitly include the interelectronic distance. Hylleraas was the first to use functions that do include the interelectronic distance r_{12} (so called geminals) in 1929^[44] and later that idea was revived by Kutzelnigg and co-workers.^[45–47] Following a suggestion by Ten-no,^[48] Werner and coworkers implemented geminals of the form $F(r_{12}) = -\frac{1}{\beta} \exp(-\beta r_{12})$ in coupled-cluster calculations.^[49,50] The resulting method was presented with two different approximations with acronyms CCSD(T)-F12a and CCSD(T)-F12b, where the latter was recommended for larger basis sets and will be used in this thesis. The derivation of the theory leads to many three- and four-electron integrals whose calculation is very expensive. One possible solution is to approximate these integrals by sums of two-electron integrals by introduction of the resolution of the identity (RI).^[45] An efficient implementation then requires auxiliary basis functions, the construction of a complementary auxiliary orbital basis (CABS) and density fitting (DF)

approximations.^[49,50] Since the treatment of the perturbative triples is not straightforward in the F12 framework, they are determined conventionally which leads to a small basis set error. Werner and coworkers proposed a simple scheme to correct for that error by scaling the triples contribution^[50] according to

$$\Delta E_{(T^*)} = \Delta E_{(T)} \cdot \frac{E_{corr}^{MP2-F12}}{E_{corr}^{MP2}} \quad (4)$$

where $E_{corr}^{MP2-F12}$ and E_{corr}^{MP2} denote the correlation energy as obtained by Møller-Plesset perturbation theory of second order with and without F12 approximation, respectively while $\Delta E_{(T)}$ is the triples contribution and the scaled triples contribution is designated by the asterisk in $\Delta E_{(T^*)}$.

2.1.2 Multi-reference methods

In typical HF-SCF calculations only the occupied orbitals of a single determinant are optimized. If, however, static correlation is present, a single determinant may lead to even qualitatively wrong results and it is necessary to expand the wave function as a linear combination of several configuration state functions (CSFs) and optimize both the orbitals and the expansion coefficients.

$$\Psi = \sum_I C_I \Phi_I \quad (5)$$

This method is referred to as multi-configuration self-consistent field (MCSCF). The resulting equation for the energy is of fourth order in the orbitals making a direct minimization impracticable. Instead, an approximative expression for the energy is optimized iteratively (microiterations) resulting in better orbitals and coefficients leading to faster convergence.^[51] The implementation of this second-order optimization in Molpro by Werner and Knowles^[52,53] allows for a reduction of computational time by a factor of 10-20 compared to common Newton-Raphson procedures. In MCSCF calculations, the choice of the active space i.e. the orbitals from which excitations are considered is crucial, since an active space that is too small will only give a small fraction of the correlation energy and large active spaces can become computationally unfeasible. Orbitals that are not part of the active space will have occupation numbers of 2 or 0, whereas orbitals belonging to the active space will usually have fractional occupation numbers. If MCSCF is performed as a complete active space self-consistent field (CASSCF) calculation this means that within the active space all possible excitations are considered. CASSCF calculations can thus be considered as a full configuration interaction (CI) within the active space and in this thesis only this type of calculations will be performed.

Multi-reference configuration interaction

Analogous to CI expansions in single-reference methods it is possible to calculate dynamical correlation by including excitations from the MCSCF reference function. This leads to the multi-reference configuration interaction (MRCI) method, which is usually truncated after the double excitations and is then called multi-reference configuration interaction with singles and doubles (MRCISD). The wave function can then be written as

$$\Psi = \sum_I C_I \Phi_I + \sum_s \sum_a C_a^s \Phi_s^a + \sum_{ij,p} \sum_{ab} C_{ab}^{ij,p} \Phi_{ij,p}^{ab}, \quad (6)$$

where the configuration space is subdivided in three subspaces. Φ_I includes all internal configuration state function (CSF)s that can be constructed from all orbitals that are occupied in the reference wave function. The singly external CSFs Φ_s^a are created by single excitation from the reference. Finally, in $\Phi_{ij,p}^{ab}$ two electrons are excited to external orbitals and the index p denotes the spin state which is either singlet or triplet. As first suggested by Meyer^[54] and later implemented by Werner and Reinsch,^[55] the number of excitations can considerably be reduced if the excitation operators work on the complete reference wave function instead of working on the CSFs. This method of “internal contraction” is now commonly used and implemented in Molpro.^[56,57]

Being a truncated CI method, MRCISD is not size-extensive. Several corrections have been proposed to approximately account for higher order excitations. The most popular one by Davidson^[58] can be formulated as

$$\Delta E_D = E_{\text{corr}} \frac{1 - c_0^2}{c_0^2}, \quad (7)$$

where c_0 is the coefficient of the reference wave function in the MRCI wave function and E_{corr} is the correlation energy as obtained by MRCI. It is possible to either use the coefficient of the fixed or the relaxed reference function, but the latter choice is made throughout this thesis. When the Davidson correction is employed, the acronym is MRCI(+Q) and MRCI otherwise.

Average coupled-pair functional

Another way to capture dynamical correlation and approximately achieve size extensivity is to minimize the energy functional:

$$E = E_0 + \frac{\langle \Psi_0 + \Psi_c | H - E_0 | \Psi_0 + \Psi_c \rangle}{1 + g_a \langle \Psi_a | \Psi_a \rangle + g_e \langle \Psi_e | \Psi_e \rangle} \quad (8)$$

where Ψ_0 and Ψ_c are the normalized reference and correlation wave functions, respectively, Ψ_a and Ψ_e are the internal and external parts of Ψ_c and g_a and g_e are numerical factors.

The choice of $g_a = 1$ and $g_e = 2/n$ with n being the number of correlated electrons leads to the size extensive average coupled-pair functional (ACPF) method.^[59] If $g_a = g_e = 1$, the usual MRCI solution is retained. For both MRCI and ACPF, an explicitly correlated method has been implemented in Molpro, which uses similar approximations as the F12b variant for single-reference coupled cluster.^[60]

CIPT2

In order to also include correlation effects from the core electrons, a hybrid method, CIPT2,^[61] where excitations from the active space are treated by MRCI and the remaining excitations of the core electrons are treated by multi-reference perturbation theory at second-order (MRPT2), was developed. This has the advantage of including core correlation effects at rather low cost without introducing intruder-state problems that are an issue for conventional MRPT2 calculations. Since these problems usually occur due to excitations from the active orbital subspace which is now treated by MRCI, they are effectively reduced as was shown for calculations on the chromium dimer.^[61] As is the case for MRCI, the method can be employed with and without the use of Davidson correction, leading to acronyms CIPT2(+Q) and CIPT2, respectively.

For all methods applied in this thesis, correlation consistent polarized valence basis sets of the Dunning type are employed.^[62] The acronym cc-pVnZ with n taking the values T,Q,5,6,7 will be further abbreviated to VnZ in the following. For the explicitly correlated methods, basis sets of the cc-pVnZ-F12 type (briefly termed VnZ-F12) are employed.^[63] For the RI approximation, auxiliary basis sets of the cc-pVnZ-F12/Optri^[64] type where n is the same for the atomic-orbital and the auxiliary basis set are employed. Furthermore basis sets of the aug-cc-pVnZ/MP2FIT^[65] and the cc-pVnZ/JKFIT^[66] type are used as DF basis and DF basis for the Fock and exchange matrices, respectively.

2.1.3 Inclusion of smaller effects

The methods described so far build the basis of a composite approach where especially in the case of single-reference methods some smaller effects need to be added in order to get a larger fraction of the correlation energy.

Douglas-Kroll-Hess method

The Hamiltonians employed in all of the above methods are non-relativistic. Building up on the work of Douglas and Kroll,^[67] Hess suggested the use of a transformed relativistic Hamiltonian that is bounded from below, thereby enabling variational calculations.^[68,69] The Douglas-Kroll-Hess method at second-order (DKH2) is then capable of taking into account scalar-relativistic effects and typically recovers more than 97 % of the

total relativistic energy as obtained by the fully relativistic Dirac-Hartree-Fock method in the case of atoms. The application of this method requires a specially recontracted basis set that allows for a different radial behaviour in the core region. These basis sets have been provided by de Jong and coworkers and are denoted VnZ -DK, using a similar notation as above.^[70]

The contribution of scalar relativistic effects as obtained by the DKH2 method will be denoted ΔDK .

Core-core/core-valence correlation

Both the fc-CC and the multi-reference methods (excluding CIPT2) include only excitations of the valence electrons while the core electrons are still uncorrelated. The correction of this deficiency requires the use of a different class of basis sets, which allow for more flexibility in the core region and is denoted cc-pCV nZ (briefly termed CV nZ).^[71] These basis sets are also used in the few ae-CCSD(T) calculations in this thesis. The contribution of inner-shell correlation calculated as the difference between ae- and fc-CCSD(T) calculations with the same CV nZ basis set will be termed ΔCV .

Higher-order correlation

A further correction to the CC calculations can be obtained by including excitation operators higher than \hat{T}_2 in eq. 2. This leads to a hierarchy of CC methods:

$$CCSD(T) \rightarrow CCSDT \rightarrow \mathbf{CCSDT(Q)} \rightarrow \mathbf{CCSDTQ}$$

where the brackets denote a perturbative treatment of the respective excitation operator and only the methods printed in bold are considered in this thesis. The reason for the neglect of explicitly calculating the effect of the iterative triples contribution is that usually an overestimation of the correlation energy is observed and CCSD(T) performs better than CCSDT in most cases when applied to e.g. spectroscopic parameters.^[72] The contributions of higher correlation are calculated as differences. $\Delta(Q)$ -(T) denotes the effect of iterative triples and is calculated as the difference between a fc-CCSDT(Q) and a fc-CCSD(T) calculation employing the same basis set. ΔQ -(Q) is the difference of a fc-CCSDTQ and a fc-CCSDT(Q) calculation. The sum of both is termed ΔHC . The CCSDT(Q) method^[73] will be applied with a VTZ basis set while the rather small VDZ basis set is employed for the expensive CCSDTQ calculations.^[74] All higher-order correlation (HC) calculations were performed in Molpro with an interface to Kallay's MRCC program^[43].

Diagonal Born-Oppenheimer correction

An improvement over the Born-Oppenheimer approximation is achieved by means of the diagonal Born-Oppenheimer correction (DBOC).^[75] The energy contribution is given by:

$$\Delta E_{\text{DBOC}} = - \sum_{A=1}^N \sum_{i=x,y,z} \frac{1}{2M_A} \langle \Psi(\mathbf{r}; \mathbf{R}) | \nabla_{R_{Ai}}^2 | \Psi(\mathbf{r}; \mathbf{R}) \rangle \quad (9)$$

It is thus calculated as the expectation value of the electronic Born-Oppenheimer wave function $\Psi(\mathbf{r}; \mathbf{R})$ over the sum of the kinetic energy operators of the nuclei $\nabla_{R_{Ai}}^2$ with M_A denoting the masses of the nuclei, \mathbf{r} and \mathbf{R} are coordinates of the electrons and the nuclei, respectively. Eq. 9 shows that the DBOC correction is most important for light nuclei. In this thesis it is considered for coordinates involving H-atom motion only. The DBOC contribution (termed ΔDBOC) and the corresponding $\Psi(\mathbf{r}; \mathbf{R})$ wave function is calculated by means of ae-CCSD with a CVQZ basis set using the CFOUR program.^[76]

2.2 Vibrational Perturbation Theory

Watson's isomorphic rovibrational Hamiltonian for linear molecules has the form:^[77]

$$\hat{H} = \underbrace{\frac{1}{2} \sum_{k=1}^{3N-5} P_k^2 + \frac{1}{2} \mu (\pi_x^2 + \pi_y^2)}_{\hat{H}_{\text{vib}}} + \underbrace{\frac{1}{2} \mu (\Pi_x'^2 + \Pi_y'^2)}_{\hat{H}_{\text{rot}}} - \underbrace{\mu (\Pi_x' \pi_x + \Pi_y' \pi_y)}_{\hat{H}_{\text{Coriolis}}} + V, \quad (10)$$

where P_k are linear vibrational momenta conjugate to the normal coordinates Q_k , $\pi_{x,y}$ and $\Pi_{x,y}'$ are vibrational and rotational angular momenta, respectively, μ denotes the inverse inertia tensor and V is the PES represented in normal coordinates. As is the case in electronic structure calculations, there are two general ways to find the eigenstates of this Hamiltonian. The variational approach of diagonalizing the Hamiltonian in a suitable basis (e.g. products of harmonic oscillator/rigid rotor functions) or perturbation theory to arbitrary order. The former approach gives more accurate results and has widely been applied in our group on 3-atomic molecules.^[78,79] The calculations, however, become increasingly more complex with the number of atoms especially since the rovibrational basis required becomes very large. Therefore perturbation theory is commonly used for larger molecules, yielding spectroscopic parameters in reasonable agreement with experimental data in the case of semi-rigid molecules.^[30,80] Apart from model calculations, only vibrational perturbation theory at second-order (VPT2) will be applied in this thesis and discussed in more detail in the following.

When calculating the second order perturbation energy, a large number of off-diagonal matrix elements of the first-order perturbation Hamiltonian need to be evaluated. A contact transformation ensures that all these elements are zero, thereby formally reducing the problem to a first-order calculation. This is achieved by a similarity transformation

$$\hat{H}' = T\hat{H}T^{-1} \quad (11)$$

where the unitary function T takes the form:

$$T = e^{i\lambda\mathbf{S}} \quad (12)$$

T can now be expanded in powers of λ and insertion into eq. 11 and collecting same powers of λ ultimately leads to

$$\hat{H}^{(1)} = i(\hat{H}^{(0)}S - S\hat{H}^{(0)}) \quad (13)$$

when applying the condition $\hat{H}^{(1)'} = 0$. The form of the transformation function S has been discussed by Herman and Shaffer^[81] and Nielsen.^[82]

The second order transformed Hamiltonian is then given by

$$\hat{H}^{(2)'} = \sum_k \hat{H}_k^{(2)} + \sum_{tr} \frac{i}{2} [S_r \hat{H}_t^{(1)} - \hat{H}^{(1)} S_r] \quad (14)$$

where the second sum is only over terms of second-order.^[83] The remaining diagonal matrix elements were computed and are tabled in the article by Herman and Shaffer.^[81] By separately collecting terms with like powers of vibrational and rotational quantum numbers the term energy formulas:^[84]

$$T(v, J) = G(v) + F_v(J) \quad (15)$$

with

$$G(v) = \sum_r \omega_r(v_r + 0.5d_r) + \sum_{r \geq s} \chi_{rs}(v_r + 0.5d_r)(v_s + 0.5d_s) + \sum_{t \geq t'} \chi_{tlt'} l_t l_{t'} + \dots \quad (16)$$

and

$$F_v(J) = B_v(J(J+1) - l^2) - D_e(J(J+1) - l^2)^2 + H_e(J(J+1) - l^2)^3 + \dots \quad (17)$$

are obtained. In eq. 16 ω_r denotes the harmonic, χ_{rs} and $\chi_{tlt'}$ denote anharmonic vibrational constants, d_r is the degeneracy of the r -th normal mode and the index t sums over degenerate normal modes only while r and s sum over all normal modes. Finally, v is a collective variable for the set of all vibrational quantum numbers. B_v , D_e and H_e

in eq. 17 are the effective rotational constant, quartic and sextic centrifugal distortion constants, respectively.

Each of these spectroscopic parameters is now connected to the potential (see eq. 10). The following formulas as taken over from Allen *et al.*^[84] require the anharmonic force constants of the potential expanded in dimensionless normal coordinates using the unrestricted summation convention.³ The vibrational anharmonic constants are then given by:

$$\chi_{ss} = \frac{1}{16}\phi_{ssss} - \frac{1}{16}\sum_{s'}\phi_{sss'}^2\frac{8\omega_s^2 - 3\omega_{s'}^2}{\omega_{s'}(4\omega_s^2 - \omega_{s'}^2)}, \quad (18)$$

$$\chi_{tt} = \frac{1}{16}\phi_{tttt} - \frac{1}{16}\sum_s\phi_{stt}^2\frac{8\omega_t^2 - 3\omega_s^2}{\omega_s(4\omega_t^2 - \omega_s^2)} \quad (19)$$

$$\chi_{ltlt} = -\frac{1}{48}\phi_{tttt} - \frac{1}{16}\sum_s\phi_{stt}^2\frac{\omega_s}{4\omega_t^2 - \omega_s^2}, \quad (20)$$

in case of the diagonal elements and

$$\chi_{ss'} = \frac{1}{4}\phi_{ss's's'} - \frac{1}{4}\sum_{s''}\phi_{ss's''}\phi_{s''s's'}\frac{1}{\omega_{s''}} - \frac{1}{2}\sum_{s''}\phi_{ss's''}^2\frac{\omega_{s''}(\omega_{s''}^2 - \omega_s^2 - \omega_{s'}^2)}{\Delta_{ss's''}}, \quad (21)$$

$$\chi_{st} = \frac{1}{4}\phi_{sstt} - \frac{1}{4}\sum_{s'}\phi_{ss's'}\phi_{s'tt}\frac{1}{\omega_{s'}} - \frac{1}{2}\sum_{t'}\phi_{stt'}^2\frac{\omega_{t'}(\omega_{t'}^2 - \omega_s^2 - \omega_t^2)}{\Delta_{stt'}} + B_e\zeta_{st}^2\left(\frac{\omega_s}{\omega_t} + \frac{\omega_t}{\omega_s}\right), \quad (22)$$

$$\chi_{tt'} = \frac{1}{8}(\phi_{t_x t_x t_x' t_x'} + \phi_{t_x t_x t_x' t_y'}) - \frac{1}{4}\sum_s\phi_{stt}\phi_{st't'}\frac{1}{\omega_s} - \frac{1}{4}\sum_s\phi_{stt'}^2\frac{\omega_s(\omega_s^2 - \omega_t^2 - \omega_{t'}^2)}{\Delta_{stt'}}, \quad (23)$$

$$\chi_{ltlt'} = \frac{1}{2}\sum_s\phi_{stt'}\frac{\omega_s\omega_t\omega_{t'}}{\Delta_{stt'}} \quad (24)$$

in case of the off-diagonal elements. The index s runs only over non-degenerate modes and the index t runs only over degenerate modes while the denominator $\Delta_{rr'r''}$ is given by

$$\Delta_{rr'r''} = (\omega_r + \omega_{r'} + \omega_{r''})(\omega_r + \omega_{r'} - \omega_{r''})(\omega_r - \omega_{r'} + \omega_{r''})(\omega_r - \omega_{r'} - \omega_{r''}). \quad (25)$$

B_e is the rotational constant at equilibrium and ζ_{st} are the Coriolis interaction constants whose calculation is described in the appendix.

The effective rotational constant B_v in eq. 17 is given by

$$B_v = B_e - \underbrace{\sum_r \alpha_r(v_r + 0.5d_r)}_{-\Delta B_0} + \dots \quad (26)$$

³Note that this choice results in formulas that differ from the ones originally obtained by Nielsen^[82,85] by multiplicative factors.

and analogous formulas hold for the centrifugal distortion constants. In eq. 26, α_r are the vibration-rotation interaction constants with respect to the r -th normal mode and read

$$\alpha_s = -\frac{2B_e^2}{\omega_s} \left[\frac{3a_s^2}{4I_e} + \sum_t \zeta_{st}^2 \frac{3\omega_s^2 + \omega_t^2}{\omega_s^2 - \omega_t^2} + \pi \left(\frac{c}{h} \right)^{1/2} \sum_{s'} \phi_{ss's'} a_{s'} \frac{\omega_s}{\omega_{s'}^{3/2}} \right] \quad (27)$$

$$\alpha_t = -\frac{2B_e^2}{\omega_t} \left[\frac{1}{2} \sum_s \zeta_{st}^2 \frac{3\omega_t^2 + \omega_s^2}{\omega_t^2 - \omega_s^2} + \pi \left(\frac{c}{h} \right)^{1/2} \sum_s \phi_{stt} a_s \frac{\omega_t}{\omega_s^{3/2}} \right]. \quad (28)$$

In the above formulas I_e is the moment of inertia taken at equilibrium position and a_s are the inertial derivatives over the normal coordinates defined as:

$$a_s = (\partial I_{xx} / \partial Q_s)_e = (\partial I_{yy} / \partial Q_s)_e. \quad (29)$$

In the expansion eq. 17 the quartic centrifugal distortion constant is given by

$$D_e = \frac{1}{2} \sum_s \frac{B_s^2}{\omega_s}, \quad (30)$$

where the summation runs over totally symmetric normal modes only and the rotational derivatives B_s are defined as:

$$B_s = -\frac{\hbar^3}{2h^{3/2} c^{3/2} \omega_s^{1/2} I_e^2} a_s. \quad (31)$$

The sextic centrifugal distortion constant H_e is then given by

$$H_e = \frac{4D_e^2}{B_e} - 2B_e^2 \sum_s \frac{B_s^2}{\omega_s^3} - \frac{1}{6} \sum_{ss's''} \phi_{ss's''} \frac{B_s B_{s'} B_{s''}}{\omega_s \omega_{s'} \omega_{s''}}, \quad (32)$$

where the summation again runs over totally symmetric normal modes only.

Further spectroscopic parameters to be considered are the rotational and vibrational l -type doubling constants. The former can be approximated by:

$$q_t \approx q_t^e + q_t^J J(J+1) + q_t^K (K \pm 1)^2 \quad (33)$$

but in this study only the harmonic part q_t^e will be calculated and is given by

$$q_t^e = -\frac{2B_e^2}{\omega_t} \sum_s \zeta_{st}^2 \frac{3\omega_t^2 + \omega_s^2}{\omega_t^2 - \omega_s^2}. \quad (34)$$

The vibrational l -type doubling constants are given by

$$r_{tt'} = -\frac{1}{2} \sum_s \phi_{stt'}^2 \frac{\omega_s(\omega_s^2 - \omega_t^2 - \omega_{t'}^2)}{\Delta_{stt'}} + \frac{1}{4} (\phi_{t_x t_x t'_x t'_y} - \phi_{t_x t_x t'_y t'_x}). \quad (35)$$

All of the spectroscopic parameters mentioned above are calculated by the VPT2 program **4Lin** which will be presented in the appendix.

In case of an anharmonic resonance $2\omega_a \approx \omega_b$ (Fermi type 1) or $\omega_a + \omega_b \approx \omega_c$ (Fermi type 2), some terms in the denominator of the formulas for the anharmonic constants are close to zero, making these terms unphysically large. These resonant terms are then removed and the anharmonic vibrational wavenumbers are calculated without these terms.^[83,86,87] The Fermi interaction is then accounted for by setting up a 2×2 matrix with the diagonal elements given by the new anharmonic wavenumbers and the off-diagonal elements are given by the coupling elements of the two states over the first order perturbation Hamiltonian. The matrix elements for this first order treatment are tabulated e.g. in Califano p. 269 and p. 296.^[83] For the most abundant isotopologues of the two molecules discussed in this thesis only one Fermi type 2 resonance occurs between the combination band $(\nu_2 + \nu_3)$ and the ν_1 stretching fundamental of l-C₃H⁺. The secular determinant of the resulting matrix reads:

$$\begin{vmatrix} (\nu_2 + \nu_3) - E & \sqrt{\frac{1}{8}}\phi_{123} \\ \sqrt{\frac{1}{8}}\phi_{123} & \nu_1 - E \end{vmatrix} = 0 \quad (36)$$

leading to the equation:

$$E_{\text{up/low}} = \frac{(\nu_2 + \nu_3) + \nu_1}{2} \pm \sqrt{\left(\frac{(\nu_2 + \nu_3) + \nu_1}{2}\right)^2 - \nu_1(\nu_2 + \nu_3) + \frac{\phi_{123}^2}{8}} \quad (37)$$

for the upper E_{up} and the lower E_{low} component of this Fermi diad.

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