

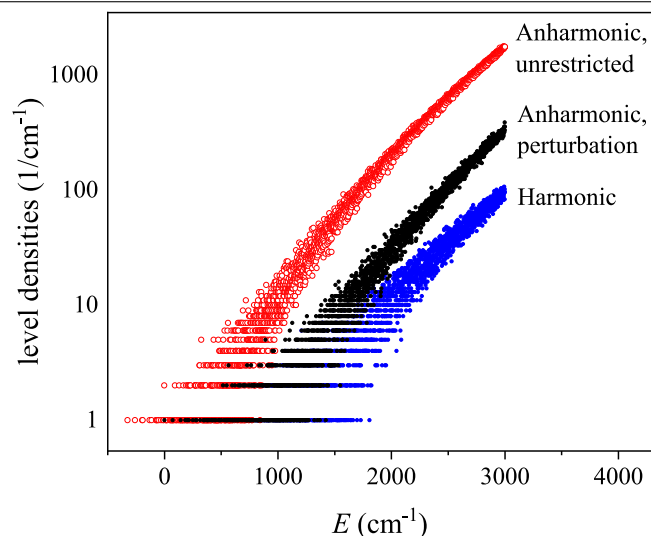


Research paper

Calculation of level densities of coupled anharmonic molecular vibrations

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GRAPHICAL ABSTRACT



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ABSTRACT

We present a method to calculate molecular vibrational densities of states (level densities) with anharmonic vibrations, crucial in many cases for describing thermal properties of molecular species. Coupling of modes is fully implemented and the method eliminates the severe numerical artefacts associated with the commonly used limitation to the second order expansion in quantum numbers with their negative coupling constants. The method proceeds by calculating the canonical partition function perturbatively and applying the inverse Laplace transform. C_7^- is used as a case study.

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1. Background

The calculation of vibrational level densities is arguably the most important single part of the description of thermal properties of matter. Although a description of vibrations as harmonic motion will capture the main part of their thermodynamics, anharmonicities contribute in a measurable and occasionally important manner. One example is given by the recent measurement of the thermionic emission rate constant of C_7^- [1]. The molecule will be used as a case study here. The description of such unimolecular reactions requires input of level densities. The choice of this anion was made because a very detailed study has been performed to determine the energy dependence of the emission rate constant as a function of energy. The study eliminated the detrimental effect of the width of energy distributions of the decaying systems. For details of the experiments, please see Ref. [1].

Both spectroscopic and quantum chemical studies can provide the input for the analysis of the effect of anharmonicities (see e.g. Refs. [2–4] and Ref. [5] for a molecule of astrophysical interest). Most of the data provide anharmonicities that contribute to the energy quadratically in the vibrational quantum numbers, i.e., with sums over products of the vibrational quantum numbers for different modes. When the anharmonicities do not couple different modes, it is easy to generalize the Beyer–Swinehart (B–S) algorithm [6], because that method is basically a convolution of the level densities of independent degrees of freedom. For such cases the vibrational energy of a molecule is given as

$$E = \sum_i E_i(n_i), \quad (1)$$

where $E_i(n_i)$ is the energy of oscillator i containing n_i quanta, and the sum runs over all values of modes. With $\rho(E, i)$ denoting the level density at total excitation energy E for the system with i modes included, the B–S convolution, becomes

$$\rho(E, i+1) = \sum_{k=0}^{k_{\max}(i+1)} \rho(E - E_{i+1}(k), i), \quad (2)$$

where the sum runs over all possible quantum states of mode $i+1$, limited by energy conservation. With $E_{i+1}(k) = \hbar\omega_{i+1}k$ this reduces correctly to the B–S algorithm. This is the procedure used in Ref. [7]. For the second order expansion considered in this paper, the diagonal-only approximation would reduce the energy functional that will be used (see Eq. (4)) to

$$E = \sum_i \left(\hbar\omega_i \left(n_i + \frac{1}{2} \right) + \chi_{i,i} \left(n_i + \frac{1}{2} \right)^2 \right). \quad (3)$$

The prescription allows a numerically exact calculation once the vibrational spectrum is known, but it clearly only works because Eq. (1) holds in this case, i.e., if the expression for the energy does not contain terms with products of quantum numbers of different modes. In Ref. [7] uncoupled Morse oscillators were assumed for that purpose.

Non-zero off-diagonal couplings are, however, more the rule than the exception, and a restriction to zero off-diagonal anharmonicities will give too unrealistic results. This is indicated by a simple counting of anharmonicities. For a non-linear molecule of N atoms, there are $(3N-6) \times (3N-7)$ off-diagonal couplings vs. only $3N-6$ diagonal, and the off-diagonal elements are frequently numerically larger than the diagonal. A numerical example demonstrating this argument is given in Fig. 6 of Ref. [8].

The calculation of the contribution from the off-diagonal terms to the density of states is a non-trivial matter, even when the anharmonicities are limited to quadratic contributions. One method used to calculate level densities of anharmonic systems is the Wang–Landau method [9–11]. The method applies a variation of the general Metropolis algorithm, which is stochastic in nature, and has the ensuing requirement on statistics for good precision. More seriously, it encounters the problem that expressions for the energy that are truncated at the second order terms, i.e., products of quantum numbers appear at most

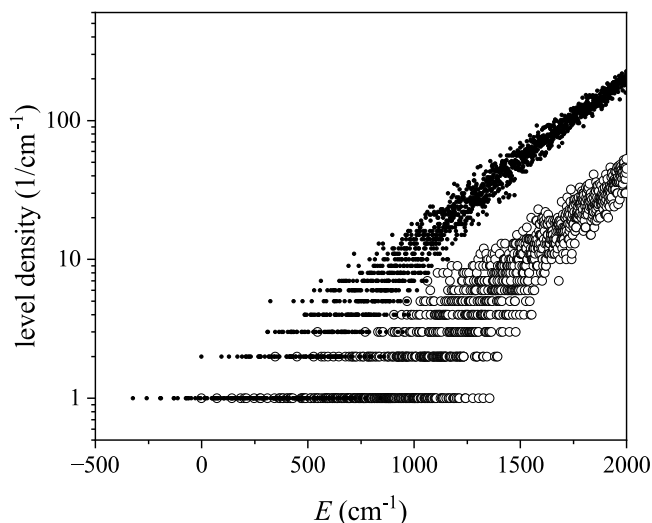


Fig. 1. The direct count low energy vibrational level density of C_7^- for two different cut-off energies as described in the main text. The 2000 cm^{-1} cutoff data are given with open circles, the 3000 cm^{-1} cutoff data with small filled black circles. The data are given as counted; no shift or normalization has been implemented, apart from setting the zero of energy to the quantum mechanical ground state, as mentioned in connection with Eq. (4).

up to second order, involve second order anharmonicity coefficients that are often negative. These negative coefficients limit the range of quantum numbers to values where the energies still increase with increasing quantum numbers. The set of quantum numbers where increases reduce the system energy clearly define a threshold above which the approximation becomes unphysical.

This limit is reached at fairly low energies, as demonstrated very clearly in Fig. 1. The figure shows the level densities for C_7^- calculated by a direct state count for two cases. In one case, the quantum numbers of the modes are limited to be below the values $2000 \text{ cm}^{-1}/\hbar\omega_i$. The other case is calculated with the upper limits set to $3000 \text{ cm}^{-1}/\hbar\omega_i$. Both data sets are generated with a count looping over all quantum numbers up their maxima set by the two limits mentioned, and no approximations or adjustments were made for either calculation. The two curves shift notably, even for energies below 1000 cm^{-1} . The 3000 cm^{-1} cut-off curve even produces states at negative energies, another signal that the second order equation has been used beyond its applicability. It should be noted that even if the cutoff energies in this numerical example appear high, oscillators will have populations in excess of these energies, even in molecules in microcanonical ensembles with significantly lower average energy per oscillator. Fig. 3 illustrates the relevance of the problem shown in Fig. 1.

We suggest here a method to avoid the problem by a calculation of the level densities with a perturbative expansion in the second order anharmonic terms, applied to the experimentally relevant C_7^- [1]. The data used in the analysis are the input fundamental vibrational frequencies and the coefficients to the second order terms provided by quantum chemical calculations. The frequencies and anharmonicities are listed in Appendix A. We will not treat the problem of the partitioning of the states on the symmetry species of the molecule, which can be of interest for some applications. That problem was treated in Ref. [12] and we refer the interested reader to the general results in that paper.

2. Setting

The energy including the quadratic contribution will be represented by the form

$$E = \sum_i \hbar\omega_i \left(n_i + \frac{1}{2}\right) + \sum_{j \geq k} \chi_{j,k} \left(n_j + \frac{1}{2}\right) \left(n_k + \frac{1}{2}\right), \quad (n_j, n_k = 0, 1, 2, \dots) \quad (4)$$

where $\hbar\omega_i$ describes the harmonic part of the quantum energy, $\chi_{j,k}$ are the anharmonicity coefficients, and the sums run over all modes, as indicated. A form where the terms $1/2$ were left out would be both less cumbersome and more physical, but we will conform to the conventional usage. The non-zero off-diagonal elements of the matrix $\chi_{j,k}$ ($\chi_{j,k} \neq 0, j \neq k$) in the second term couple modes and therefore prevent a simple separation of variables. Although higher order terms in Eq. (4) can be considered, as in Ref. [8], the coefficients need to be at least of fourth order to avoid the convergence problems discussed below. That would require the determination of a large number of independent coefficients (3860 in addition to the 15 fundamental frequencies for C_7^-). We will not consider those situations here.

For analytical work it is more convenient to write Eq. (4) as

$$E = \sum_i \hbar\omega_i n_i + \sum_{j \geq k} \chi_{j,k} n_j n_k + \frac{1}{2} \sum_{j \geq k} \chi_{j,k} (n_j + n_k) + \frac{1}{2} \sum_i \hbar\omega_i + \frac{1}{4} \sum_{j \geq k} \chi_{j,k}. \quad (5)$$

We will use the shorthand $E_{gs} \equiv \frac{1}{2} \sum_i \hbar\omega_i + \frac{1}{4} \sum_{j \geq k} \chi_{j,k}$ for the quantum mechanical ground state energy.

The values of the C_7^- -harmonic frequencies and anharmonic coefficients used here were calculated with the ORCA 5.04 software package [13] using the B3LYP functions together with the ma-def2-SVP basis set and D3BJ dispersion corrections. The anharmonic effects on the vibrational frequencies were computed with vibrational second-order perturbation theory (VPT2), as implemented in ORCA, using very tight convergence criteria for the geometry and the SCF optimization cycles. From the values in Tables A.1,A.2 in Appendix A it is clear that the second order terms are predominantly negative, as one might expect by analogy with the Morse potential and other empirical interatomic potentials.

3. Perturbation-inversion

The method that will be developed is based on the inverse Laplace transform of the canonical partition function. The technique has proven to be a powerful tool to obtain level densities [14]. The expressions in Ref. [14], given in Eqs. (6), (7), are a development of the steepest descend method which already gives good results, both for nuclear densities of states and vibrational level densities [15–17]. A procedure very similar to the one derived in Ref. [14] was later derived in Ref. [18], where it was used to calculate anharmonic but separable motion level densities, i.e., level densities where all off-diagonal elements of the χ matrix are zero. As mentioned, the level densities for such situations can also be calculated exactly with the modified B–S algorithm.

The basic equations of the method are (with $\beta \equiv 1/k_B T$) [14,19]

$$\rho(E)dE = \frac{1}{\sqrt{2\pi C/k_B T}} Z(T) e^{\beta E} dE \quad (6)$$

$$\bar{E}(T) = E + k_B T \quad (7)$$

where C is the heat capacity and Z is the canonical partition function of the system, calculated at the temperature determined by Eq. (7). As Helmholtz free energy, $F = E - TS$, is given by $Z = \exp(-\beta F)$, Eq. (6) essentially states that the level density is the exponential of the entropy, but with a reciprocal square root factor that accounts for the width of the thermal distribution over which the entropy is calculated. Eq. (7) defines the temperature which is used in Eq. (6). The inclusion

of the term $k_B T$ on the right hand side of Eq. (7) for the inversion point, derived in Ref. [14], gives an excellent agreement for level densities, as documented in Ref. [20], and makes the method far superior to other quasi-analytical expressions.

The prescription in Eqs. (6), (7) generates ρ as a smooth function of energy which is obviously not exact for a discrete spectrum. It does, however, often provide an advantage for applications at low energies when ratios of level densities are used and where an exact sum of delta functions can lead to complications due to division by zero.

An obstacle to the application of this technique is that, as for the B–S algorithm, the canonical excitation energy and entropy cannot be calculated exactly when modes are coupled by higher order terms. One possible solution of this problem is a calculation with a perturbative expansion. For small couplings, $\hbar\omega \gg |\chi|$, this is a viable procedure and this is the choice made here.

The partition function, Z , for the set of oscillator frequencies $\{\omega_i\}$ and quadratic anharmonicity coefficients $\{\chi_{j,k}\}$ is

$$Z = \sum_{\{n_i\}} \exp \left(-\beta \sum_i \hbar\omega_i n_i - \beta \sum_{j \geq k} \chi_{j,k} n_j n_k - \frac{\beta}{2} \sum_{j \geq k} \chi_{j,k} (n_j + n_k) - \beta E_{gs} \right), \quad (8)$$

where $\sum_{\{n_i\}}$ indicates summation over all sets of non-negative integers. This sum diverges. The divergence is avoided with an expansion of the exponential in the anharmonic terms:

$$Z \approx e^{-\beta E_{gs}} \sum_{\{n_i\}} e^{-\beta \sum_i \hbar\omega_i n_i} \left\{ 1 - \beta \sum_{j \geq k} \chi_{j,k} n_j n_k - \frac{\beta}{2} \sum_{j \geq k} \chi_{j,k} (n_j + n_k) \right\}. \quad (9)$$

To perform the sums over the χ 's, terms need to be separated into diagonal and off-diagonal terms. Symbolically:

$$\sum_{j \geq k} n_j n_k = \sum_j n_j^2 + \sum_{j > k} n_j n_k. \quad (10)$$

The result is a sum of several sums that can all be done. Appendix B gives the calculations. The result is

$$Z \approx e^{-\beta E_{gs}} \prod_i (1 - e^{-\beta \hbar\omega_i})^{-1} \times \left(1 - 2\beta \sum_j \chi_{j,j} \frac{e^{\beta \hbar\omega_j}}{(e^{\beta \hbar\omega_j} - 1)^2} - \sum_{j > k} \chi_{j,k} \frac{\beta(e^{\beta \hbar\omega_j} + e^{\beta \hbar\omega_k})}{2(e^{\beta \hbar\omega_j} - 1)(e^{\beta \hbar\omega_k} - 1)} \right). \quad (11)$$

The canonical energy of this partition function is

$$\begin{aligned} \langle E \rangle &= -\frac{\partial \ln Z}{\partial \beta} \\ &= E_{gs} + \sum_i \frac{\hbar\omega_i}{e^{\beta \hbar\omega_i} - 1} - 2 \sum_j \chi_{j,j} \frac{e^{\beta \hbar\omega_j} [\beta \hbar\omega_j + e^{\beta \hbar\omega_j} (\beta \hbar\omega_j - 1) + 1]}{(e^{\beta \hbar\omega_j} - 1)^3} \\ &\quad + \sum_{j > k} \chi_{j,k} \frac{(1 - \beta \hbar\omega_k) e^{\beta \hbar(\omega_j + \omega_k)} + (1 - \beta \hbar\omega_j) e^{\beta \hbar(\omega_j + 2\omega_k)} - 2e^{\beta \hbar(\omega_j + \omega_k)}}{2(e^{\beta \hbar\omega_j} - 1)^2 (e^{\beta \hbar\omega_k} - 1)^2} \\ &\quad + \sum_{j > k} \chi_{j,k} \frac{(\beta \hbar\omega_j + 1) e^{\beta \hbar\omega_j} + (\beta \hbar\omega_k + 1) e^{\beta \hbar\omega_k} - e^{2\beta \hbar\omega_j} - e^{2\beta \hbar\omega_k}}{2(e^{\beta \hbar\omega_j} - 1)^2 (e^{\beta \hbar\omega_k} - 1)^2}. \end{aligned} \quad (12)$$

The expression for the heat capacity corresponding to this energy is rather unwieldy and will be approximated by the leading order (harmonic) term:

$$C = \sum_i (\beta \hbar\omega_i)^2 \frac{e^{-\beta \hbar\omega_i}}{(1 - e^{-\beta \hbar\omega_i})^2}. \quad (13)$$

If the contribution from the anharmonicity terms is needed, a numerical derivative of the energy is a convenient alternative. The main numerical work in the procedure is the solution for the temperature that solves Eq. (7). In most cases standard methods will converge after a few iterations.

Fig. 2 shows the level densities of C_7^- , calculated with and without anharmonicities to first order in χ 's. The two curves differ by an order of magnitude at the energies 4.0–4.3 eV, which is the relevant range for a comparison with the experimental results in Ref. [1].

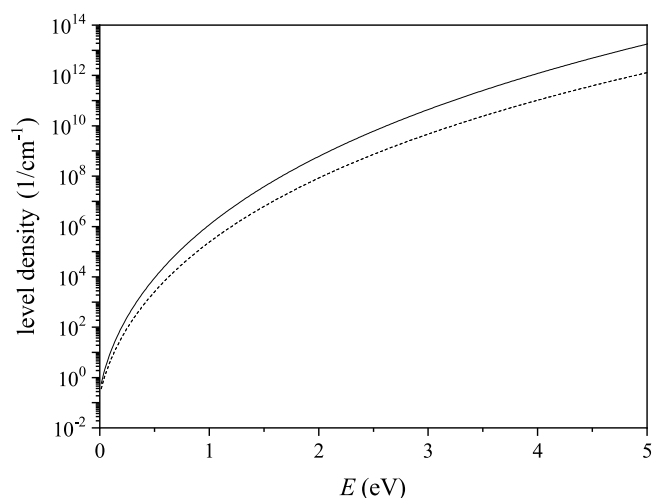


Fig. 2. The level densities of C_7^- with (full line) and without (dashed line) anharmonicities, calculated with Eqs. (6), (7), (12), (13) and the data in Appendix A. As the energy varies from 0.05 eV to 5.00 eV, the ratio of the two level densities reaches an order of magnitude.

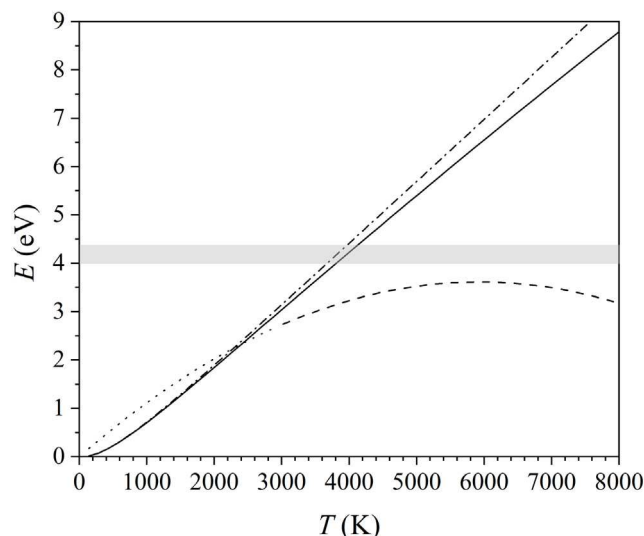


Fig. 3. The comparison of the thermal energies calculated with Eq. (12) (full line) and Eq. (4), with the latter corrected for the zero of energy. The curve for Eq. (4) is given by a dashed part and a dotted part at low temperature (see the main text for explanation). The gray area indicates the experimentally relevant region for the experiments in Ref. [1]. The dashed-dotted line is the energy in the harmonic approximation.

Fig. 3 shows the difference between the thermal energies calculated with the modified partition function in Eq. (12) and the unmodified in Eq. (4). As mentioned, the latter will diverge in a direct calculation. As an alternative approximate procedure, the energy is calculated with the complete energy functional and mode quantum numbers given by the harmonic, semiclassical mean values $n_i = k_B T / \hbar \omega_i$. This misrepresents the quantum effects at low temperatures, and the curve provides a good estimate of the energy functional only above the temperature given by the highest vibrational quantum energy, $k_B T = \hbar \omega_{\max}$. The curve is given as a dashed line above this temperature, and below as a dotted line, for reference.

4. Discussion

The main result of this work is Eq. (12) combined with Eqs. (6), (7). These equations provide an expression for the level densities of molecular oscillators that are described as anharmonic to second order in the vibrational quantum numbers. The method eliminates the effects of the unphysical decrease of energy with increasing quantum numbers. If unattended, this would lead to a serious overestimate of the level densities at low energies and a corresponding underestimate at high energies, and will even produce states at negative energies, as shown in Fig. 1.

The equations are used on the spectra for the experimentally studied ion C_7^- with spectral parameters calculated with quantum chemistry. The change induced by the anharmonicities is an increase by an order of magnitude at 5 eV excitation energy, explaining some of the experimentally observed reduction of the electron emission constant of two orders of magnitude relative to a purely harmonic calculation.

The equations derived here hold to first order in the anharmonicities in the expansion of the canonical partition function. From the introduction it should be clear that although higher order terms will improve the numerical accuracy, there is a fundamental limitation in the physical description of the system. An improved numerical accuracy will therefore not necessarily improve the reliability of the data, and in fact, as it has also been shown in Fig. 1, the ultimate accuracy is bound to give unphysical results. The limited numerical accuracy is therefore a suitable result, in the absence of better parametrizations of the energy functional. We also note that the method used pushes the onset of the unphysical region above the physically relevant values, at least for the example of C_7^- .

CRediT authorship contribution statement

Rui Zhang: Writing – review & editing, Investigation. **Klavs Hansen:** Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization, Writing – review & editing. **John W. Niman:** Writing – review & editing, Investigation, Conceptualization. **Piero Ferrari:** Writing – review & editing, Investigation. **Shimpei Iida:** Investigation, Writing – review & editing. **Haruo Shiromaru:** Investigation, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: J.W. Niman reports financial support was provided by US National Science Foundation. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A

Table A.1
Harmonic frequencies in cm^{-1} .

Mode	$\hbar\omega$
0	93.655
1	221.095
2	221.783
3	358.772
4	407.384
5	544.460
6	577.362
7	636.032
8	738.211
9	849.450
10	1090.829
11	1609.572
12	1835.090
13	1983.342
14	2079.877

Appendix B

In order to make the calculation clear, the terms of Eq. (9) are marked separately: let $Z_{\text{gs}} = e^{-\beta E_{\text{gs}}}$. Then the relevant thermal properties are the ones derived from Z/Z_{gs} . The first term of Z/Z_{gs} gives the standard harmonic result,

$$Z_0 = \sum_{\{n_i\}} e^{-\beta \sum_i \hbar\omega_i n_i} = \prod_i (1 - e^{-\beta \hbar\omega_i})^{-1} \equiv \prod_i z_i, \quad (14)$$

where z_i is defined as the partition function of the harmonic energy term of oscillator i .

The second and third terms in the sum in Eq. (9) can be calculated as:

$$\begin{aligned} & - \sum_{\{n_i\}} \beta \sum_{j \geq k} \chi_{j,k} \left[n_j n_k + \frac{1}{2} (n_j + n_k) \right] e^{-\beta \sum_i \hbar\omega_i n_i} \\ &= - \sum_{\{n_i\}} \beta \left\{ \sum_j \chi_{j,j} (n_j^2 + n_j) + \sum_{j > k} \chi_{j,k} \left[n_j n_k + \frac{1}{2} (n_j + n_k) \right] \right\} e^{-\beta \sum_i \hbar\omega_i n_i}. \end{aligned} \quad (15)$$

The first sum in the bracket is a sum containing coefficients that depend on the diagonal elements $\chi_{j,j}$. This is calculated to:

$$\begin{aligned} Z_{11} &= - \sum_{\{n_i\}} \beta \sum_j \chi_{j,j} (n_j^2 + n_j) e^{-\beta \sum_i \hbar\omega_i n_i} \\ &= -2Z_0 \beta \sum_j \chi_{j,j} \frac{e^{\beta \hbar\omega_j}}{(e^{\beta \hbar\omega_j} - 1)^2} \end{aligned} \quad (16)$$

The second sum in the bracket in Eq. (15) runs over products of independent quantum numbers and can be calculated as products of averages values. This gives:

$$\begin{aligned} Z_{12} &= - \sum_{\{n_i\}} \beta \sum_{j > k} \chi_{j,k} \left[n_j n_k + \frac{1}{2} (n_j + n_k) \right] e^{-\beta \sum_i \hbar\omega_i n_i} \\ &= -Z_0 \sum_{j > k} \chi_{j,k} \left[\frac{\beta}{(e^{\beta \hbar\omega_j} - 1)(e^{\beta \hbar\omega_k} - 1)} + \frac{\beta}{2} \left(\frac{1}{e^{\beta \hbar\omega_j} - 1} + \frac{1}{e^{\beta \hbar\omega_k} - 1} \right) \right] \\ &= -Z_0 \sum_{j > k} \chi_{j,k} \frac{\beta(e^{\beta \hbar\omega_j} + e^{\beta \hbar\omega_k})}{2(e^{\beta \hbar\omega_j} - 1)(e^{\beta \hbar\omega_k} - 1)}. \end{aligned} \quad (17)$$

The partition function is now

$$Z = Z_{\text{gs}}(Z_0 + Z_{11} + Z_{12}), \quad (18)$$

giving us the energy

$$\begin{aligned} \bar{E} &= - \frac{\partial \ln Z}{\partial \beta} = - \frac{\partial \ln [Z_{\text{gs}}(Z_0 + Z_{11} + Z_{12})]}{\partial \beta} \\ &= - \frac{\partial \ln (1 + \frac{Z_{11}}{Z_0} + \frac{Z_{12}}{Z_0})}{\partial \beta} + \sum_i \frac{\hbar\omega_i}{e^{\beta \hbar\omega_i} - 1} + E_{\text{gs}}. \end{aligned} \quad (19)$$

Table A.2

Anharmonic constants in cm^{-1} . A few of the entries were estimated from analogy to other values because the calculated values were a couple of orders of magnitude larger than typical values and clearly unrealistic. The estimated values are given with two digits..

r	s	$\chi_{r,s}$	r	s	$\chi_{r,s}$
0	0	-0.89178	1	0	-8.24539
1	1	-0.98246	2	0	0.80843
2	1	-1.5	2	2	-2.01417
3	0	0.86667	3	1	0.65577
3	2	-4.03581	3	3	0.29628
4	0	-4.96009	4	1	-20.58234
4	2	0.47912	4	3	0.16
4	4	0.03718	5	0	-4.26471
5	1	-1.38701	5	2	-5.21469
5	3	0.00941	5	4	-3.18520
5	5	-0.07392	6	0	-0.17226
6	1	0.32419	6	2	0.22624
6	3	-2.33489	6	4	-1.15169
6	5	-0.93211	6	6	-0.29762
7	0	0.22206	7	1	-6.27552
7	2	-1.07441	7	3	-4.05511
7	4	-0.73673	7	5	-0.17
7	6	-0.69470	7	7	-0.27080
8	0	-1.32290	8	1	-5.02924
8	2	0.31465	8	3	-0.33895
8	4	-1.03386	8	5	-0.89119
8	6	0.31388	8	7	-0.38211
8	8	-0.10615	9	0	-2.25862
9	1	-0.04524	9	2	-3.13677
9	3	-1.54324	9	4	-1.13130
9	5	-0.43295	9	6	0.22059
9	7	-2.93443	9	8	-0.12
9	9	-0.14373	10	0	-2.01083
10	1	-1.20496	10	2	-1.24766
10	3	1.14751	10	4	0.57753
10	5	-0.47182	10	6	-3.27986
10	7	0.54590	10	8	-2.31195
10	9	-1.85067	10	10	0.43265
11	0	-3.42895	11	1	-2.79462
11	2	-2.72642	11	3	-1.78182
11	4	-1.43411	11	5	-2.47176
11	6	0.08269	11	7	-2.08104
11	8	-3.60335	11	9	-3.98896
11	10	-3.04134	11	11	-3.40417
12	0	-6.51309	12	1	-17.14643
12	2	-6.31240	12	3	-4.91900
12	4	-10.76492	12	5	-4.74646
12	6	-4.13317	12	7	-4.07986
12	8	-7.14188	12	9	-5.04136
12	10	-6.21649	12	11	-18.04071
12	12	-10.83863	13	0	-3.75399
13	1	-2.99974	13	2	-2.59029
13	3	-3.82730	13	4	-3.31663
13	5	-3.52368	13	6	-7.70883
13	7	-2.61560	13	8	-11.87761
13	9	-9.64089	13	10	-4.32678
13	11	-27.86400	13	12	-16.77331
13	13	-18.38643	14	0	-4.09691
14	1	-4.39684	14	2	-4.88354
14	3	-4.52145	14	4	-4.01816
14	5	-5.26196	14	6	-5.77972
14	7	-4.20216	14	8	-5.43520
14	9	-4.91242	14	10	-31.14807
14	11	-16.37599	14	12	-44.23590
14	13	-11.39418	14	14	-10.12723

The first term is equal to:

$$\begin{aligned} & - \frac{\partial \ln (1 + \frac{Z_{11}}{Z_0} + \frac{Z_{12}}{Z_0})}{\partial \beta} = - \frac{1}{1 + \frac{Z_{11}}{Z_0} + \frac{Z_{12}}{Z_0}} \frac{\partial (\frac{Z_{11}}{Z_0} + \frac{Z_{12}}{Z_0})}{\partial \beta} \\ &= \frac{1}{1 + \frac{Z_{11}}{Z_0} + \frac{Z_{12}}{Z_0}} \left[-2 \sum_j \chi_{j,j} \frac{e^{\beta \hbar\omega_j} [\beta \hbar\omega_j + e^{\beta \hbar\omega_j} (\beta \hbar\omega_j - 1) + 1]}{(e^{\beta \hbar\omega_j} - 1)^3} \right] \end{aligned} \quad (20)$$

$$\begin{aligned}
& + \sum_{j>k} \chi_{j,k} \frac{(1 - \beta \hbar \omega_k) e^{\beta \hbar (2\omega_j + \omega_k)} + (1 - \beta \hbar \omega_j) e^{\beta \hbar (\omega_j + 2\omega_k)} - 2e^{\beta \hbar (\omega_j + \omega_k)}}{2(e^{\beta \hbar \omega_j} - 1)^2 (e^{\beta \hbar \omega_k} - 1)^2} \\
& + \sum_{j>k} \chi_{j,k} \frac{(\beta \hbar \omega_j + 1) e^{\beta \hbar \omega_j} + (\beta \hbar \omega_k + 1) e^{\beta \hbar \omega_k} - e^{2\beta \hbar \omega_j} - e^{2\beta \hbar \omega_k}}{2(e^{\beta \hbar \omega_j} - 1)^2 (e^{\beta \hbar \omega_k} - 1)^2} \Big].
\end{aligned}$$

The factor of $1/(1 + Z_{11}/Z_0 + Z_{12}/Z_0)$ in front of the square bracket has little effect, and could be left out because it amounts to a second order contribution in the χ 's. It is retained in the numerical calculations, though.

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