Collective rotations of asymmetrically deformed many-body systems: III. Centrifugal distortion†

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Abstract. General kernel expansions beyond the Gaussian overlap and quadratic approximations are derived. An order of magnitude analysis of the integrands in the projection integrals is carried out and all integrations are performed analytically. A theorem by Watson on the number of independent centrifugal distortion coefficients is extended to the projection formalism.

1. Introduction

In the quantum mechanics of many-body systems centrifugal distortions manifest themselves as corrections to rigid rotor spectra. In both molecular and nuclear physics the subject has a long history (for reviews see Kirchoff (1972) and Bohr and Mottelson (1975)).

In molecular spectroscopy Kivelson and Wilson (1952) developed an approximate treatment of the rotational energy levels of a non-rigid asymmetric rotor. They found that in the expansion of the Eckart (1935) Hamiltonian products of four total angular momentum components are the leading terms in a perturbative description of centrifugal distortion. In general the rotational Hamiltonian may be written schematically as

$$H = H_2 + H_4 + H_6 + \ldots, \tag{1}$$

where H_{2N} represents a sum of terms involving angular momentum operators to the $2N$th power. The solution of the corresponding eigenvalue problem and the phenomenological use of Hamiltonians such as (1) was systematised by Watson (1967). He showed that among the building blocks of H_{2N}, the so-called standard forms

$$S_{klm} = \tfrac{1}{2}(J_x^k J_y^l J_z^m + J_z^m J_y^l J_x^k) \tag{2}$$

only $2N + 1$ are independent. Consequently in a phenomenological treatment of centrifugal distortion to order $2N$ there are at most $3 + 5 \ldots + 2N + 1 = N(N+2)$ adjustable parameters. This theorem clarified a number of inconsistencies which arose when the Kivelson-Wilson formalism (containing nine instead of eight spectroscopic

constants for $N = 2$) was applied to non-planar molecules (Dreizler and Dendl 1965, Dreizler and Rudolph 1965).

In nuclear physics, Hamiltonians of type (1) were developed by Bohr and Mottelson (1975). However, due to the extreme non-rigidity of nuclei, implying the absence of a reference configuration, alternative methods for the description of rotational motion were developed. One of those, namely angular momentum projection is the topic of this series of papers. For axial nuclei a first-order treatment by Peierls and Yoccoz (1967) led to the familiar $J(J+1)$ law for the energy levels and the quantal definition of a moment of inertia. In the present context it was shown by Verhaar (1963) that centrifugal distortion of axially symmetric systems corresponds to an order by order evaluation of integrals appearing in the projection operator formalism.

In paper I of this series (Lathouwers and Deumens 1982) the Peierls–Yoccoz theory was generalised to include asymmetric situations. The rotational secular equation which arises in the general non-axial case was reduced to a rigid rotor eigenvalue problem corresponding to a quantal moment of inertia tensor. In this contribution we aim to describe centrifugal distortion by working out an order of magnitude analysis which allows the systematic extension of the procedure used in I. In particular the theorem by Watson on the number of independent adjustable parameters will be generalised.

2. Angular momentum projection

The basic equations in the angular momentum projection formalism, as described in I, are the rotational secular equations

$$\sum_L [H_{KL}^J - E^J \Delta_{KL}^J] c_L^J = 0 \tag{3}$$

$$H_{KL}^J = \frac{2J+1}{8\pi^2} \int d\Omega\, D_{KL}^{J*}(\Omega) \langle \chi | HR(\Omega) | \chi \rangle \tag{4}$$

$$\Delta_{KL}^J = \frac{2J+1}{8\pi^2} \int d\Omega\, D_{KL}^{J*}(\Omega) \langle \chi | R(\Omega) | \chi \rangle \tag{5}$$

with $-J \leqslant K, L \leqslant J$. These equations arise if one decomposes an arbitrary wavefunction $\chi(x)$ into its angular momentum components, constructs superpositions of these states and determines the coefficients variationally (see e.g. MacDonald 1970). In the formulae $\mathcal{R}(\Omega)$ and $D_{KL}^L(\Omega)$ denote, respectively, the elements and corresponding irreducible representations of the rotation group. Using the conventional Euler parametrisation, in which $\Omega \equiv (\varphi, \theta, \gamma)$ with $0 \leqslant \varphi$, $\gamma \leqslant 2\pi$ and $0 \leqslant \theta \leqslant \pi$, the explicit forms of $\mathcal{R}(\Omega)$, $D_{KL}^J(\Omega)$ and the volume element $d\Omega$ are

$$\mathcal{R}(\Omega) = \exp(-i\varphi J_z) \exp(-i\theta J_y) \exp(-i\gamma J_z) \tag{6}$$

$$D_{KL}^J(\Omega) = \exp(-iK\varphi) d_{KL}^J(\theta) \exp(-iL\gamma) \tag{7}$$

$$\int d\Omega = \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\gamma \tag{8}$$

where the $d_{KL}^J(\theta)$ or Wigner functions are related to Jacobi polynomials. Aside from these purely group theoretical attributes, the integrals that generate the Hamiltonian

and overlap matrices H^J_{KL} and Δ^J_{KL} contain dynamical quantities: the so-called Hamiltonian and overlap kernels, $\langle\chi|H\mathcal{R}(\Omega)|\chi\rangle$ and $\langle\chi|\mathcal{R}(\Omega)|\chi\rangle$. Their behaviour depends upon the detailed properties of the intrinsic state $\chi(x)$. Therefore no analytical progress in the calculation of the matrix elements (4) and (5) seems possible such that, in general, a numerical evaluation of the projection integrals is required. Angular momentum projection has therefore long been regarded as a purely numerical technique incapable of generating any phenomenological insight.

However, further insight into the structure of the rotational secular equations can be gained if one observes that the kernel values are a measure of the interaction, via the Hamiltonian or directly, between the original state $\chi(x)$ and its rotated version $\mathcal{R}(\Omega)\chi(x)$. If this interaction is weak, i.e., significant for small rotations only, the intrinsic state is said to be strongly deformed. Strong deformation can be caused by localisation of individual particles, as in molecules, or by the combined effect of a large number of delocalised particles, as in tri-axial nuclei. The case of strong deformation is therefore quite general and can cover both rigid and non-rigid situations. Assuming that the intrinsic state under consideration is strongly deformed implies that we should concentrate on regions in the parameter space corresponding to rotations $\mathcal{R}(\Omega)$ 'close' to the unit operator. However, the Euler parametrisation, used so far, is not suited for this purpose. Indeed, figure 1 makes it clear that small rotations do not necessarily correspond to small azimuthal angles φ and γ which causes the relevant integration domain to be a non-connected subset of the square $0 \leqslant \varphi, \gamma \leqslant 2\pi$.

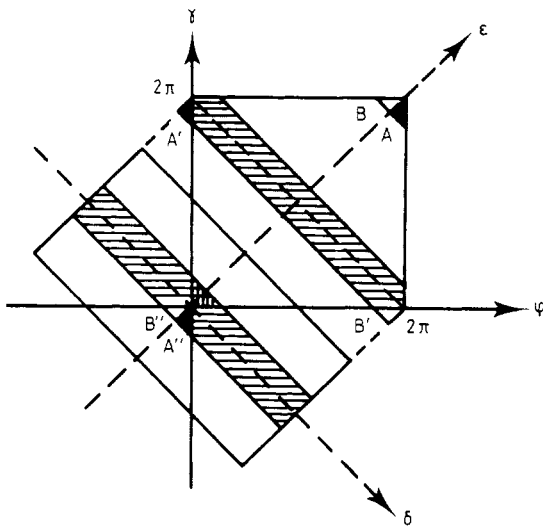**Figure 1.** Region in the (φ, γ) and (ε, δ) plane corresponding to small rotations.

Studying the topology in the (φ, γ) plane, using the invariance of the integrands under translations of 2π in the φ and γ directions, makes it clear that a more convenient parameterisation is obtained by using the sum and difference angles, $\varepsilon = \frac{1}{2}(\varphi + \gamma)$ and $\delta = \frac{1}{2}(\varphi - \gamma)$, in addition to the polar angle θ. Indeed, in the (ε, δ) plane the relevant rotations are situated in a narrow strip along the δ axis, i.e., small rotations correspond to small ε (and θ) while δ is arbitrary in this respect. It is easily shown (see I) that

the basic ingredients in the projection integrals, if transformed to the $(\varepsilon, \theta, \delta)$ parametrisation, take the form

$$\mathcal{R}(\Omega) = \exp(-i\varepsilon J_z) \exp[-i\theta(J_y \cos \delta - J_x \sin \delta)] \exp(-i\varepsilon J_z) \tag{9}$$

$$D^J_{KL}(\Omega) = \exp[-i(K+L)\varepsilon] d^J_{KL}(\theta) \exp[-i(K-L)\delta] \tag{10}$$

$$\int d\Omega = \int_{-\pi/2}^{+\pi/2} d\varepsilon \int_0^\pi \sin \theta \, d\theta \int_{-\pi}^{+\pi} d\delta. \tag{11}$$

Using these expressions and introducing the well known Gaussian overlap and quadratic approximations it was shown in I that the rotational secular equation (3) reduces to a rigid rotor eigenvalue problem corresponding to the inertia tensor Q

$$Q = FK^{-1}F \tag{12}$$

$$F_{kl} = \langle \chi | J_k J_l | \chi \rangle, \qquad K_{kl} = \langle \chi | J_k [H - E(0)] J_l | \chi \rangle \tag{13}$$

$$E(0) = \langle \chi | H | \chi \rangle. \tag{14}$$

The F_{kl} are the components of the so-called angular momentum fluctuation tensor while $E(0)$ is referred to as the intrinsic or internal energy. It is the purpose of this paper to go beyond the Gaussian overlap and quadratic approximations and to show that more general expansions lead to modifications of the rigid rotor spectra that can be interpreted as centrifugal distortion effects. Throughout the derivations it is assumed that the intrinsic state $\chi(x)$ is a given real function which is normalised to one.

3. General expansions of projection integrands

Since it has been established that infinitesimal rotations correspond to small values of the angles ε and θ, δ being completely arbitrary in this respect, the overlap kernel $\Delta(\varepsilon, \theta, \delta)$ is expected to be a sharply peaked function of ε and θ. Therefore we expand $\log \Delta(\varepsilon, \theta, \delta)$, rather than $\Delta(\varepsilon, \theta, \delta)$ itself, in a Taylor series

$$\log \Delta(\varepsilon, \theta, \delta) = \sum_{mn} L_{mn}(\delta) \theta^m \varepsilon^n. \tag{15}$$

On the other hand, since $H(\varepsilon, \theta, \delta)$ behaves similarly as $\Delta(\varepsilon, \theta, \delta)$, we may safely expand their ratio, i.e., we propose a second expansion

$$K(\varepsilon, \theta, \delta) = \frac{H(\varepsilon, \theta, \delta)}{\Delta(\varepsilon, \theta, \delta)} = \sum_{mn} K_{mn}(\delta) \theta^m \varepsilon^n. \tag{16}$$

Our first task is now to express the coefficients in these expansions in terms of quantities directly obtainable from $H(\varepsilon, \theta, \delta)$ and $\Delta(\varepsilon, \theta, \delta)$. For this purpose we first rewrite the defining equation for the kernels as

$$\langle \chi | \mathcal{R}(\Omega) | \chi \rangle \equiv \Delta(\varepsilon, \theta, \delta) = \langle \chi(\delta) | \exp(-i\varepsilon J_z) \exp(-i\theta J_y) \exp(-i\varepsilon J_z) | \chi(\delta) \rangle \tag{17}$$

$$\langle \chi | H \mathcal{R}(\Omega) | \chi \rangle \equiv H(\varepsilon, \theta, \delta) = \langle \chi(\delta) | H \exp(-i\varepsilon J_z) \exp(-i\theta J_y) \exp(-i\varepsilon J_z) | \chi(\delta) \rangle \tag{18}$$

where the state $\chi(\delta)$ is obtained by rotating all particles an angle δ around the z axis, i.e.,

$$\chi(\delta) \equiv \chi(x | \delta) = \exp(i\delta J_z) \chi(x) = \chi(A(\delta, \bar{e}_z) x). \tag{19}$$

Observe that if $\chi(x)$ is real so is $\chi(x|\delta)$. Direct expansion of the exponentials in (17)-(18) yields (we treat the overlap kernel as an example whenever the same result holds for the Hamiltonian kernel)

$$\Delta(\varepsilon, \theta, \delta) = \sum_{klm} (-i)^{k+l+m} \langle \chi(\delta) | J_z^k J_y^m J_z^l | \chi(\delta) \rangle \frac{\theta^m}{m!} \frac{\varepsilon^{k+l}}{k!l!}. \tag{20}$$

The reality of $\chi(\delta)$, implying time reversal invariance, requires that only an even number of angular momentum components leads to non-vanishing matrix elements $\langle \chi(\delta) | J_z^k J_y^m J_z^l | \chi(\delta) \rangle$. Furthermore if one moves a J_z component to the left of J_y^m past this operator all new terms which arise, if one takes into account the angular momentum commutation relations, contain an odd number of J components and therefore do not contribute. Introducing a new summation index $k + l = n$ we can then rewrite (20) as

$$\Delta(\varepsilon, \theta, \delta) = \sum_{\substack{m+n \\ \text{even}}} 2^n \frac{(-)^{(m+n)/2}}{m!n!} \langle \chi(\delta) | J_y^m J_z^n | \chi(\delta) \rangle \theta^m \varepsilon^n$$

$$\equiv \sum \Delta_{mn}(\delta) \theta^m \varepsilon^n. \tag{21}$$

Similarly, if the Hamiltonian is time reversal invariant we have

$$H(\varepsilon, \theta, \delta) = \sum_{\substack{m+n \\ \text{even}}} 2^n \frac{(-)^{(m+n)/2}}{m!n!} \langle \chi(\delta) | H J_y^m J_z^n | \chi(\delta) \rangle \theta^m \varepsilon^n$$

$$\equiv \sum H_{mn}(\delta) \theta^m \varepsilon^n. \tag{22}$$

For the overlap case we can convert the expansion of $\Delta(\varepsilon, \theta, \delta)$ into one for $\log \Delta(\varepsilon, \theta, \delta)$ by using the series

$$\log(1 + z) = \sum_{k=1}^{\infty} \frac{(-)^{k+1}}{k} z^k. \tag{23}$$

Identifying the log arguments in (15) and (23) leaves us with the calculation of

$$\Delta(\theta, \varepsilon, \delta) = \log\left(1 + \sum_{m+n \geq 2} \Delta_{mn}(\delta) \theta^m \varepsilon^n\right)$$

$$= \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k} \left(\sum_{m+n \geq 2} \Delta_{mn}(\delta) \theta^m \varepsilon^n\right)^k. \tag{24}$$

The multinomial theorem then tells us that the $\theta^m \varepsilon^n$ terms in the expansion (15) arising from the kth power in (24) are of the form

$$k! \sum_{[k]} \prod_{i=1}^{p} \frac{1}{k_i!} [\Delta_{m_i n_i}(\delta)]^{k_i} \tag{25}$$

where $[k] = [k_1, k_2, \ldots, k_p]$ denotes a partition of k, i.e., $k_1 + k_2 + \ldots + k_p = k$. The subscripts m_i and n_i are restricted by the relations

$$\sum_{i=1}^{p} k_i m_i = m, \qquad \sum_{i=1}^{p} k_i n_i = n \tag{26}$$

and no two pairs (m_i, n_i) are identical (see Abramowitz and Stegun 1965) Combining the restrictions on the indices m_i, n_i and k_i yields a maximum power k that can

contribute to the $\theta^m \varepsilon^n$ term in (15). Indeed

$$m + n = \sum_{i=1}^{p} k_i (m_i + n_i) \geq 2 \sum_{i=1}^{p} k_i = 2k. \tag{27}$$

Therefore the infinite sum over k in (24) truncates at $k = \frac{1}{2}(m+n)$ and the final result for the coefficients $L_{mn}(\delta)$ reads

$$L_{mn}(\delta) = \sum_{k=1}^{(m+n)/2} (k-1)!(-)^{k+1} \sum_{[k]} \prod_{i=1}^{p} \frac{1}{k_i!} [\Delta_{m_i n_i}(\delta)]^{k_i}. \tag{28}$$

If we define an extra expansion for the inverse of the overlap kernel by

$$1/\Delta(\varepsilon, \theta, \delta) \equiv \sum D_{mn}(\delta) \theta^m \varepsilon^n \tag{29}$$

the coefficients $D_{mn}(\delta)$ can be obtained as above by using the series

$$1/(1+z) = \sum_{k=0}^{\infty} (-1)^k z^k. \tag{30}$$

The result is only a slight modification of the way in which contributions from k partitions are summed in (28)

$$D_{mn}(\delta) = \sum_{k=1}^{(m+n)/2} k!(-)^k \sum_{[k]} \prod_{i=1}^{p} \frac{1}{k!} [\Delta_{m_i n_i}(\delta)]^{k_i}. \tag{31}$$

The ultimate expansion of the ratio $K(\varepsilon, \theta, \delta)$ is then easily derived since

$$K(\varepsilon, \theta, \delta) = H(\varepsilon, \theta, \delta)/\Delta(\varepsilon, \theta, \delta)$$
$$= \left(\sum H_{mn}(\delta) \theta^m \varepsilon^n \right) \left(\sum D_{kl}(\delta) \theta^k \varepsilon^l \right) \tag{32}$$

from which it follows immediately that

$$K_{mn}(\delta) = \sum_{k=0}^{m} \sum_{l=0}^{n} H_{m-k,n-l}(\delta) D_{kl}(d). \tag{33}$$

Observe that in view of (19) the sums in both (29) and (33) are also restricted to values of m and n for which $m + n$ is even.

It will be shown in the next section that a systematic evaluation of the projection integrals also involves the expansion into Taylor series of the (θ, ε) part of the Wigner functions. This presents no problem for the ε dependence since only exponentials are involved. However, since it will be important to distinguish between even and odd powers we put

$$\exp[i(K+L)\varepsilon] = \cos(K+L)\varepsilon + i \sin(K+L)\varepsilon$$
$$= \sum_p c_p(K+L)\varepsilon^{2p} + i \sum_p s_p(K+L)\varepsilon^{2p+1} \tag{34}$$

$$c_p(K+L) = (-)^p (K+L)^{2p}/(2p)!, \qquad s_n(K+L) = (-)^p (K+L)^{2p+1}/(2p+1)!. \tag{35}$$

For the derivation of power series for the $d^J_{KL}(\theta)$ one can start from the defining equation

$$d^J_{KL}(\theta) = \langle JK| \exp(-i\theta J_y)|JL\rangle = \sum_p \frac{(-i\theta)^p}{p!} \langle JK|J_y^p|JL\rangle. \tag{36}$$

Assuming $K \geq L$ and using the properties of the angular momentum shift operators $J_{\pm} = \frac{1}{2}(J_x \pm iJ_y)$ one can check that

$$d^J_{KL}(\theta) = \sum_p d_p(JKL)\theta^{K-L+2p} \tag{37}$$

$$d_p(JKL) = (-\tfrac{1}{2})^{K-L}\left[\binom{J+K}{J+L}\binom{J-L}{J-K}\right]^{1/2} \langle JK|J_y^{2p}|JK\rangle \tag{38}$$

Observe that $d^J_{KL}(\theta)$ contains only even or odd θ-powers depending on whether $K-L$ is even or odd. The matrix elements $\langle JK|J_y^{2p}|JK\rangle$ can easily be calculated using elementary angular momentum theory (see e.g. Brink and Satchler 1968). This completes an admittedly highly technical but necessary step in a systematic evaluation of the projection integrals. We now have at our disposal power series, for both kernels and D functions, adapted to the topology of the $(\varepsilon, \theta, \delta)$ parameter space of the rotation group, i.e., expansions in ε and θ with conservation of the full δ dependence of the expanded quantities.

4. Order of magnitude analysis

The strong deformation of the intrinsic state implies good convergence for small θ and ε of the power series derived in the previous section. In turn this can be translated into stating that all coefficients $K_{mn}(\delta)$ and $L_{mn}(\delta)$ are of the same order of magnitude. However, the quantities $K(\varepsilon, \theta, \delta)$ and $\log \Delta(\varepsilon, \theta, \delta)$ are not the ones which enter into the integrals (4) and (5). It is therefore necessary to give expressions for $H(\varepsilon, \theta, \delta)$ and $\Delta(\varepsilon, \theta, \delta)$ which reflect the feature of strong deformation and to which successive approximations can be defined. In the language of perturbation theory: we need an unperturbed problem and a set of perturbations to which one can assign an order of magnitude in terms of an expansion parameter. In I we presented a zeroth-order version of the present scheme such that our first problem, the definition of a suitable unperturbed problem, is already solved. A short summary adapted to the present context will therefore suffice.

If we exponentiate (15) we obtain an expression of $\Delta(\varepsilon, \theta, \delta)$ in terms of the logarithmic coefficients $L_{mn}(\delta)$

$$\Delta(\varepsilon, \theta, \delta) = \exp\left(\sum_{m+n \geq 2} L_{mn}(\delta)\theta^m\varepsilon^n\right) \tag{39}$$

it will be useful to subdivide the terms in the exponent into groups for which $m+n = 2N$ with $N = 1, 2, 3, \ldots$, i.e., and rewrite (39) as

$$\Delta(\varepsilon, \theta, \delta) = \exp\left(\sum_{m+n=2} L_{mn}(\delta)\theta^m\varepsilon^n\right)\exp\left(\sum_{m+n=4} L_{mn}(\delta)\theta^m\varepsilon^n\right)\ldots. \tag{40}$$

It is clear that since all $L_{mn}(\delta)$, independently of the value of $m+n$, are of the same order of magnitude, the exponentials with $m+n \geq 4$ will vary slowly compared to the term with $m+n = 2$. Therefore the latter will determine the gross features of the overlap kernel. The $L_{mn}(\delta)$ with $m+n = 2$ are easily computed from (21) and (28)

$$L_{20}(\delta) = -\tfrac{1}{2}\langle\chi(\delta)|J_y^2|\chi(\delta)\rangle = -\tfrac{1}{2}(\langle J_x^2\rangle \sin^2\delta + \langle J_y^2\rangle \cos^2\delta - \langle J_xJ_y\rangle \sin 2\delta)$$

$$L_{11}(\delta) = -2\langle\chi(\delta)|J_yJ_z|\chi(\delta)\rangle = 2(\langle J_xJ_z\rangle \sin\delta - \langle J_yJ_z\rangle \cos\delta) \tag{41}$$

$$L_{02}(\delta) = -2\langle\chi(\delta)|J_z^2|\chi(\delta)\rangle = -2\langle J_z^2\rangle.$$

The values of these coefficients are completely determined by the elements of the angular momentum fluctuation tensor F_{kl} defined in (13). A further simplification of the expressions (41) can therefore be obtained by diagonalising F_{kl} which amounts to a rotation of the intrinsic state (see I). Adopting this conventional orientation of $\chi(x)$ one sees that $L_{11}(\delta)$ vanishes while $L_{20}(\delta)$ reduces to

$$L_{20}(\delta) = -\tfrac{1}{2}(\langle J_x^2 \rangle \sin^2 \delta + \langle J_y^2 \rangle \cos^2 \delta). \tag{42}$$

In view of the fact that the $m + n = 2$ terms constitute the dominating part of the overlap kernel we define its unperturbed or zeroth-order form by

$$\Delta_0(\varepsilon, \theta, \delta) = \exp[-\tfrac{1}{2}(\langle J_x^2 \rangle \sin^2 \delta + \langle J_y^2 \rangle \cos^2 \delta)\theta^2 - 2\langle J_z^2 \rangle \varepsilon^2]. \tag{43}$$

Observe that (43) is indeed a sharply peaked function of ε, θ for all δ provided $\langle J_k^2 \rangle \gg 1$, i.e., provided the eigenvalues of the angular momentum fluctuation tensor are large. That this is indeed the signature of strong deformation in all directions was established in I.

Since the remainder of the overlap kernel, i.e., the right-hand side exponentials in (40), varies slowly compared with $\Delta_0(\varepsilon, \theta, \delta)$ it may be expanded in a Taylor series

$$\exp\left(\sum_{m+n \geqslant 4} L_{mn}(\delta)\theta^m \varepsilon^n\right) = 1 + \sum_{k=1}^{\infty} \frac{1}{k!}\left(\sum_{m+n \geqslant 4} L_{mn}(\delta)\theta^m \varepsilon^n\right)^k. \tag{44}$$

In order to estimate the importance of these terms relative to $\Delta_0(\varepsilon, \theta, \delta)$ we introduce the order parameter λ by putting

$$1/\lambda = \sum_{k=1}^{3} \langle J_k^2 \rangle / 3. \tag{45}$$

For this definition to be consistent with that of the zeroth-order overlap kernel the exponent in (43) should be of zeroth-order in λ, i.e.,

$$L_{20}(\delta)\theta^2 + L_{02}(\delta)\varepsilon^2 = O(\lambda^0). \tag{46}$$

Since both $L_{20}(\delta)$ and $L_{02}(\theta)$ are of order $1/\lambda$ this implies that θ and ε are to be considered as quantities of order $\lambda^{1/2}$. We must therefore carry out the order magnitude analysis of (44) on the basis of the estimates

$$L_{mn}(\delta) = O(1/\lambda) \qquad \text{and} \qquad \theta^m \varepsilon^n = O(\lambda^{(m+n)/2}). \tag{47}$$

With these guidelines a general perturbation expansion of the full overlap kernel can now be obtained by regrouping the terms in (44) into parts of equal order in λ, i.e.

$$\Delta = \Delta_0\left(1 + \sum_{N=1}^{\infty} W_N\right) \qquad \text{with} \qquad W_N(\varepsilon, \theta, \delta) = O(\lambda^N). \tag{48}$$

By repeatedly using the multinomial theorem we can work out the powers in (44) while the estimates (47) allow us to decide upon the order of magnitude of the individual contributions. Some combinatorics then yields the following result for the overlap perturbation of order N

$$W_N(\varepsilon, \theta, \delta) = \sum W_{mn}^N(\delta)\theta^m \varepsilon^n \tag{49}$$

$$W_{mn}^N(\delta) = \sum_{[k]} \prod_{i=1}^{p} \frac{1}{k_i!}[L_{m_i n_i}(\delta)]^{k_i} \tag{50}$$

where m and n are defined as in (26) and the sum in (49) is restricted by the condition $4 \leq m + n \leq 4N$. Requiring each term in (49) to be of order N fixes the number k in (50). Indeed one easily checks using (48) that this implies that $k = \frac{1}{2}(m + n) - N$.

For the derivation of a Hamiltonian counterpart of (48) we first observe that since $K_{mn}(\delta)$ are of the same order of magnitude they can be considered of order $1/\lambda$ by chosing appropriate energy units. Secondly, the first term in (33) is nothing but the intrinsic energy, i.e.,

$$K_{00} = \langle \chi | H | \chi \rangle = E(0) \tag{51}$$

which can be taken as the origin of the energy scale. We therefore start the K expansion at $m + n = 2$ which amounts to computing purely rotational energies $E - E(0)$. The zeroth-order Hamiltonian kernel is then given by

$$H_0(\varepsilon, \theta, \delta) = \Delta_0(\varepsilon, \theta, \delta) K_0(\varepsilon, \theta, \delta) \tag{52}$$

$$K_0(\varepsilon, \theta, \delta) = \sum_{m+n=2} K_{mn}(\delta) \theta^n \varepsilon^n. \tag{53}$$

Explicit expressions for $K_{20}(\delta)$, $K_{11}(\delta)$ and $K_{02}(\delta)$ are easily computed from (31) and (33) and have been listed in I. For the full H kernel we have

$$H = \Delta K = \Delta_0 \left(1 + \sum_{N=1}^{\infty} W_N \right) \left(K_0 + \sum_{N=1}^{\infty} K_N \right) \tag{54}$$

$$K_N(\varepsilon, \theta, \delta) = \sum_{m+n=2N+2} K_{mn}(\delta) \theta^m \varepsilon^n. \tag{55}$$

Observing that the order of a product of two kernel parts is the sum of their individual orders we obtain the perturbation expansion of the Hamiltonian kernel

$$H = \Delta_0 \left(K_0 + \sum_{N=1}^{\infty} V_N \right) \tag{56}$$

$$V_N(\varepsilon, \theta, \delta) = \sum_{M=0}^{N} K_{N-M}(\varepsilon, \theta, \delta) W_M(\varepsilon, \theta, \delta). \tag{57}$$

In the forms (48) and (56) the projection kernels are now ready to be integrated with the irreducible representations of the rotation group.

The order of magnitude analysis of the expanded form of the Wigner functions is possible provided the total angular momentum is not too high. Indeed, it is well known that the $d^J_{KL}(\theta)$ consist of exponential-like part near $\theta = 0$ and have an oscillatory behaviour of the type $\cos(J + \frac{1}{2})\theta$ for larger arguments. Therefore, for the expansion (37) to be valid it is necessary that the nodes of the $d^J_{KL}(\theta)$ remain outside the cut-off range provided by the unperturbed overlap kernel. This will be the case provided

$$J \ll \langle J_k^2 \rangle^{1/2}. \tag{58}$$

Under this condition the coefficients in the Taylor expansions (34) and (37) can be considered of order λ^0 and the order of magnitude of the terms is determined by the total $(\theta\varepsilon)$ power. In view of this we also need to include the extra $\sin \theta$ from the θ-volume element into our expansions. Anticipating the fact that the analytical evaluation of the resulting θ integrals will necessitate a change of variables from θ to θ^2 we put

$$\sin \theta \, d\theta = \frac{1}{2} \left(\sum_p \frac{(-)^p \theta^{2p}}{(2p+1)!} \right) d\theta^2 \tag{59}$$

The terms in large brackets can be included in the expansion of $d^J_{KL}(\theta)$, i.e., we replace (37) by

$$\sum_{p=0}^{\infty} f_p(JKL)\theta^{K-L+2p} \tag{60}$$

$$f_p(JKL) = \sum_{q=0}^{p} d_{p-q}(JKL)\frac{(-)^q}{(2q+1)!}. \tag{61}$$

It will be shown that also in the D-function part of the integrand the total $(\theta\varepsilon)$ power must be even. We therefore sort out contributions of order λ^N and define

$$D_N(\theta, \varepsilon \mid JKL) = \sum_{pq} f_p(JKL)c_q(K+L)\theta^{2p+K-L}\varepsilon^{2q} \tag{62}$$

$$D_N(\theta, \theta \mid JKL) = i\sum_{pq} f_p(JKL)s_q(K+L)\theta^{2p+K-L}\varepsilon^{2q+1} \tag{63}$$

for $K-L$ even and odd respectively. These functions $D_N(\theta, \varepsilon \mid JKL)$ are indeed of order λ^N if the summation over p and q is restricted by $p+q = N - I[\frac{1}{2}(K-L+1)]$, where $I[\frac{1}{2}(K-L+1)]$ stands for the integral part of $\frac{1}{2}(K-L+1)$.

The ingredients for the projection have now been collected into groups that can be assigned a label indicating the order of magnitude, measured in powers of λ, of its elements.

5. Order by order projection

In this section we aim to perform the integrations over ε, θ and δ in such a way that the resulting matrix elements H^J_{KL} and Δ^J_{KL} consist of terms to which one can still assign a definite order of the parameter λ.

As a result of the diagonal form of F_{kl} the unperturbed overlap kernel factorises as follows

$$\Delta_0(\varepsilon, \theta, \delta) = \exp(-c\varepsilon^2) \exp(-c_+\theta^2) \exp(c_-\theta^2 \cos^2 \delta) \tag{64}$$

$$c = 2\langle J_z^2\rangle \qquad c_\pm = \frac{1}{4}(\langle J_x^2\rangle \pm \langle J_y^2\rangle). \tag{65}$$

This makes the analytical evaluation of the projection integrals feasible provided they are performed in the proper order. Clearly, the angle δ must be integrated out exactly. On the one hand this is a complication because the δ dependence of the kernels is extremely complex but on the other hand, this integration does not affect the order of magnitude analysis since δ has nothing to do with a rotation being small or large. It will therefore suffice to demonstrate that the δ integrations can be performed analytically, without explicitly going through the entire process, and to establish possible correlations with the θ and ε integrals.

The net effect of integrating out δ is to replace the full kernels by a set of reduced kernels, one for each subdiagonal, i.e.,

$$\Delta(\varepsilon, \theta \mid K-L) = \int_{-\pi}^{+\pi} d\delta \, \Delta(\varepsilon, \theta, \delta) \exp[i(K-L)\delta]. \tag{66}$$

Inserting the decomposition (48) of the overlap we can further specify the $\Delta(\varepsilon, \theta \,|\, K - L)$ as

$$\Delta(\varepsilon, \theta \,|\, K - L) = \sum_{N=0}^{\infty} \Delta_N(\varepsilon, \theta \,|\, K - L) \tag{67}$$

$$\Delta_N(\varepsilon, \theta \,|\, K - L) = \exp(-c\varepsilon^2) \exp(-c_+\theta^2)$$

$$\times \int_{-\pi}^{+\pi} d\delta \, \exp[c_-\theta^2 \cos 2\delta + i(K - L)\delta] W_N(\varepsilon, \theta, \delta) \tag{68}$$

with analogous expressions for the Hamiltonian kernel. Taking into account the perturbative kernel expansions established in the previous section, one can see that the most general δ integral is of the form

$$\int_{-\pi}^{+\pi} d\delta \, \exp[c_-\theta^2 \cos 2\delta + i(K - L)\delta]$$

$$\times \langle \chi(\delta) | H J_y^m J_z^n | \chi(\delta) \rangle \prod_i \langle \chi(\delta) | J_y^{m_i} J_z^{n_i} | \chi(\delta) \rangle^{k_i}. \tag{69}$$

Transferring the δ dependence of the intrinsic state into a rotation of the J_y powers, the kernel part of the above integrand becomes

$$\langle \chi | H (J_y \cos \delta - J_x \sin \delta)^m J_z^n | \chi \rangle \prod_i \langle \chi | (J_y \cos \delta - J_x \sin \delta)^{m_i} J_z^{n_i} | \chi \rangle^{k_i} \tag{70}$$

$$= \left(\sum_{q=0}^{m} \langle \chi | H J_x^{m-q} J_y^q J_z^n | \chi \rangle \binom{m}{q} (\cos \delta)^q (\sin \delta)^{m-q} \right)$$

$$\times \prod_i \left(\sum_{q_i=0}^{m_i} \langle \chi | J_x^{m_i - q_i} J_y^{q_i} J_z^{m_i} | \chi \rangle \binom{m_i}{q_i} (\cos \delta)^{q_i} (\sin \delta)^{m_i - q_i} \right)^{k_i}. \tag{71}$$

Observe that this is not a mere application of the binomial theorem since J_x and J_y do not commute. However, after averaging over χ, all terms from $(J_y \cos \delta - J_x \sin \delta)^m$ with the same number of J_x and J_y operators are equal due to time reversal invariance hence $(70) = (71)$ holds. Performing δ integrals thus amounts to making linear combinations of expectation values of standard forms with coefficients given by

$$\int_{-\pi}^{+\pi} d\delta \, \exp[c_-\theta^2 \cos 2\delta + i(K - L)\delta](\cos \delta)^k (\sin \delta)^l \tag{72}$$

where $k + l = m + \Sigma_i \, k_i m_i$ is the total number of θ powers multiplying (71) in the kernel expansions. The integrals (72) establish a link between this number and the order of the subdiagonal, i.e. $K - L$, one is computing. Indeed it is clear that

$$\int_{-\pi}^{+\pi} d\delta \, \exp(c_-\theta^2 \cos 2\delta) \ldots = [1 + (-)^{K-L+k+l}] \int_0^{\pi} d\delta \, \exp(c_-\theta^2 \cos 2\delta) \ldots \tag{73}$$

which implies that the even and odd θ powers in the kernel expansions contribute, respectively, to even and odd subdiagonals in the projected matrix elements H_{KL}^J and Δ_{KL}^J. Introducing the definitions of $\sin \delta$ and $\cos \delta$ in terms of $\exp(\pm i\delta)$ into (72) one can evaluate these integrals analytically as sums of Bessel functions of imaginary

argument

$$I_t(z) = \frac{1}{\pi} \int_0^\pi d\phi \, \exp(z \cos \phi) \cos t\phi = (\tfrac{1}{2}z)^t \sum_{k=0}^\infty \frac{(\tfrac{1}{2}z)^{2k}}{k!(k+t)!}. \tag{74}$$

Identification with (72) shows that we must put $\phi = 2\delta$ and $z = c_-\theta^2$. As far as the order of magnitude is concerned, it is important to notice that since $c_-\theta^2 = O(\lambda^0)$ all numerical coefficients which arise from the δ integration are of zeroth order. Therefore, as we have already argued intuitively, the δ integration does not affect the order of magnitude analysis, i.e. the reduced kernel parts $\Delta_N(\varepsilon, \theta | K - L)$ are indeed of the same order of magnitude as the perturbations $W_N(\varepsilon, \theta, \delta)$ they originate from. This is a very convenient result since we can continue using the order of magnitude analysis for the ε and θ integrations without explicitly computing the δ integrals. However, this remains a necessary step in practical applications.

So far we have not truncated any of the integrand expansions. However, having performed the δ integration, at least in principle, we must for practical applications adopt a proper truncation scheme. It is important to do this in a way which introduces a balanced approximation of the different ingredients entering the projection integrals. Therefore the following convention in proposed. We truncate the λ-ordered expansions of both kernels and Wigner functions at the same maximum value $N_{\max} = T$, i.e.,

$$H(\varepsilon, \theta | K - L) \simeq \sum_{N=0}^T H_N(\theta, \varepsilon | K - L) \qquad \Delta(\varepsilon, \theta | K - L) \simeq \sum_{N=0}^T \Delta_N(\theta, \varepsilon | K - L) \tag{75}$$

and the summations in the D function parts (62) and (63) are restricted by $p + q \leq T - I[\frac{1}{2}(K - L + 1)]$. Hereby we make sure that equal importance is given to geometrical (rotation group representations) and dynamical (kernels corresponding to the chosen internal or intrinsic state) aspects of the projection. Inserting the resulting series into the projection integrals we finally obtain ordered expressions for the matrix elements H_{KL}^J and Δ_{KL}^J, e.g.,

$$\Delta_{KL}^J \simeq \sum_{N=I[\frac{1}{2}(K-L+1)]}^{2T} \Delta_{KL}^J(N) \tag{76}$$

$$\Delta_{KL}^J(N) = \sum_{M=I[\frac{1}{2}(K-L+1)]}^T \tfrac{1}{2} \int_0^\pi d\theta^2 \int_{-\pi/2}^{+\pi/2} d\varepsilon \, D_M(\theta, \varepsilon | JKL) \Delta_{N-M}(\theta, \varepsilon | K - L). \tag{77}$$

Thus a truncation at order T, as defined above, yields projected elements that have a band structure. Since the minimum value of N in (76) is $I[\frac{1}{2}(K - L + 1)]$ the values of matrix elements decreases with increasing subdiagonal index $K - L$. They are neglected completely for $K - L > 2T$ in case $2T$ is smaller than the maximum value of $K - L$, i.e., $2J$.

For each of the constituents in (77) we have derived a finite expansion in powers of θ and ε which combined with the result of the δ integration leads to the following definite integrals

$$\int_{-\pi/2}^{+\pi/2} d\varepsilon \, \exp(-c\varepsilon^2)\varepsilon^n \times \begin{cases} \varepsilon^{2q} & \text{for } K - L \text{ and } n \text{ even} \\ \varepsilon^{2q+1} & \text{for } K - L \text{ and } n \text{ odd} \end{cases} \tag{78}$$

$$\int_0^\pi d\theta^2 \, \exp(-c_+\theta^2)\theta^{K-L+m+2p} I_t(c_-\theta^2). \tag{79}$$

The rules for the ε integrals follows from the established fact that both m and n have the same parity as the subdiagonal index $K - L$. Therefore the terms contributing to (77) are those for which the θ and ε powers for both D functions and kernels are all even or all odd. We already used this result in setting up (62) and (63).

A final approximation is now called for in order to evaluate (78) and (79) analytically. Since both c and c_+ are much larger than unity we can extend the integration ranges to 0, $+\infty$ and $+\infty$, $+\infty$, for θ and ε integrals respectively, without changing the order of magnitude of the results. Having done so (78) and (79) reduce to

$$\int_{-\infty}^{+\infty} dx \, \exp(-ax^2)x^{2r} = \frac{(2r+1)!!}{(2a)^r}\left(\frac{\pi}{a}\right)^{1/2} \tag{80}$$

$$\int_0^\infty dy \, \exp(-by)y^s I_t(y) = \Gamma(s+t+1)\left(\frac{1}{b_-}\right)^{s+1} P_s^{-t}\left(\frac{b}{b_-}\right) \tag{81}$$

where $b = c_+/c_-$, $b_- = (b^2 - 1)^{1/2}$ and P_s^{-t} the associated Legendre polynomials.

With the above information one can assemble the projected Hamiltonian and overlap matrices H_{KL}^J and Δ_{KL}^J. For low truncation order, say T equal to 1 or 2, this is still feasible by hand. However, for higher-order approximations the development of a computerised assembly code is necessary.

6. Extension of Watson's theorem

Carrying out the above program to order T requires knowledge of the matrix elements $\langle\chi|HJ_x^k J_y^l J_z^m|\chi\rangle$ and $\langle\chi|J_x^k J_y^l J_z^m|\chi\rangle$ for $k + l + m = 2N \leq 2T$ (see (71)). However, due to the angular momentum commutation rules certain relationships exist between these quantities. In order to minimise the number of integrals to be evaluated we should therefore determine exactly how many of these matrix elements are mutually independent. In molecular spectroscopy of asymmetric-top molecules this problem was solved by Watson (1967). He observed that since the spectrum of a general rotational Hamiltonian is invariant under a unitary transformation the latter can be chosen to simplify the theory. Expressing both the Hamiltonian and the unitary transformations in terms of standard forms (2) he then showed that the part of the rotational Hamiltonians consisting of standard forms of order $2N$ contains at most $2N + 1$ independent coefficients. We will refer to this result as Watson's theorem. The proof of Watson's theorem is long and complex. In addition, it applies only to semi-rigid molecules. Here we will show how the basic results obtained by Watson can be used to obtain an analogous theorem in the projection formalism, thereby essentially extending the original proof to non-rigid situations.

The starting point in the projection technique is the intrinsic state $\chi(x)$ obtained by applying a variational principle to the Hamiltonian H thus yielding the intrinsic energy $E(0) = \langle\chi|H|\chi\rangle$. Clearly, if we were to apply the same procedure to the Hamiltonian $\bar{H} = UHU^+$, with $U^+ = U^{-1}$, the state $\bar{\chi}(x) = U\chi(x)$ is associated with the same intrinsic energy. The approximate angular projection, outlined above, applied for $\bar{H}$ and $\bar{\chi}(x)$ then contains expectation values for which we can write

$$\langle\bar{\chi}|S_{klm}|\bar{\chi}\rangle = \langle\chi|U^+ S_{klm}U|\chi\rangle \tag{82}$$

$$\langle\bar{\chi}|\bar{H}S_{klm}|\bar{\chi}\rangle = \langle\chi|HU^+ S_{klm}U|\chi\rangle \tag{83}$$

where $k + l + m$ is an even integer. This follows from (1), (71) and the reality of $\chi(x)$. If the unitary transformation U is put in the form

$$U = \exp(iS) \qquad \text{with} \qquad S = \sum_{pqr} s_{pqr} S_{pqr} \tag{84}$$

S needs to be Hermitian. On the other hand if $\bar{H}$ is to be time reversal invariant, U must share this property which in turn requires S to change sign under time reversal. Both conditions can be satisfied by taking real coefficients s_{pqr} and restricting the indices to have an odd sum, i.e., $p + q + r$ is an odd integer. Aside from these restrictions the s_{pqr} are arbitrary. The essence of Watson's theorem is then that the s_{pqr} can be chosen such that among the $(N + 1)(2N + 1)$ possible operators, $U^+ S_{klm} U$ with $k + l + m = 2N$, only $2N + 1$ are non-vanishing. This implies that among the expectation values (78) or (79) only $2N + 1$ are mutually independent†. Since the intrinsic state $\chi(x)$ is fixed so are the expectation values (82). Thus the only remaining adjustable quantities are a set of $2N + 1$ independent Hamiltonian matrix elements (83). From a phenomenological point of view this means that the angular momentum projection formalism contains at order N at most $2N + 1$ adjustable parameters, i.e., Watson's theorem is readily extendable. Therefore centrifugal distortion in rigid and non-rigid systems can be treated by the same methods and differs only in the magnitude of the order parameter λ. For a semi-rigid molecule $\lambda = \kappa^4 \simeq 10^{-4}$, where κ is the Born-Oppenheimer perturbation parameter (Watson 1967). In non-rigid systems λ can be much larger implying a much slower convergence of the perturbation expansions. The magnitude of centrifugal distortion coefficients of Van der Waals molecules and their anomalous behaviour under isotopic substitution provides a clear demonstration (Leopold 1984).

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† For $N = 1$ the unitary transformation U reduces to a rotation. This invariance property has already been used in I by adopting a suitable orientation of the intrinsic state.