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The Subduction of Vibrational States of Molecules from the Momentum Space of Simple Harmonic Motion

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A single-particle model of molecular vibrational states is proposed in which the normal modes are projected out of the body vibrations of an infinite simple harmonic sphere. This model assigns the spurious change of mass or centre of mass and leads to removal of mass monopoles and dipoles from the system. These conservation conditions impose strict boundary conditions on the potential and basis functions. On incorporation into the model they result in a set of loop equations in which the potential is proportional to the fundamental vibration. The simplest solutions to these equations strongly resemble the Poschl–Teller generalization of the Morse potential. The solutions have been extended to incorporate the repulsive states and generate the set of net attractive states appropriate to the anharmonic potential.

The basis functions of this potential display both angular and radial node structures. The degeneracies between radial and angular mode patterns can be studied by transformation into an angular coordinate space. In this way coupling to other phenomena described in similar angular momentum space can be performed directly before subduction to real displacement space.

Key words: Subduction – Molecular vibrations – Momentum point groups.

1. Introduction

The starting point of normal mode analysis in a molecular system is the set of degrees of freedom of its constituent atoms. If present, symmetry elements are

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very useful to normalize this set by finite group projection techniques. Finally the external degrees of freedom, describing translations and rotations, are eliminated from the result [1].

In this approach the whole is realized by construction from its parts. Interestingly the mirror image of this analysis can be envisaged as a valuable alternative treatment: in this process the molecule itself is considered as a subsystem of a more integrated whole. It receives its characteristics by subduction from the properties of the parent ensemble. Especially for molecules with high, spherical-like symmetry – such as transition metal complexes or boron hydrides – this approach can be expected to offer a successful description.

Vibronic selection rules for chromium(III) compounds have been recently obtained according to these principles [2]. Similar lines of thought are much more often encountered in the description of electronic structure, ranging from ligand field theory [3] to electrons in a box or ring models.

A recent example of these cage models is the subduction of molecular orbitals for metal clusters from the modes of an electron on a sphere [4]. Orbital coefficients for the finite system receive the value of the spherical wave functions on the site of the atoms.

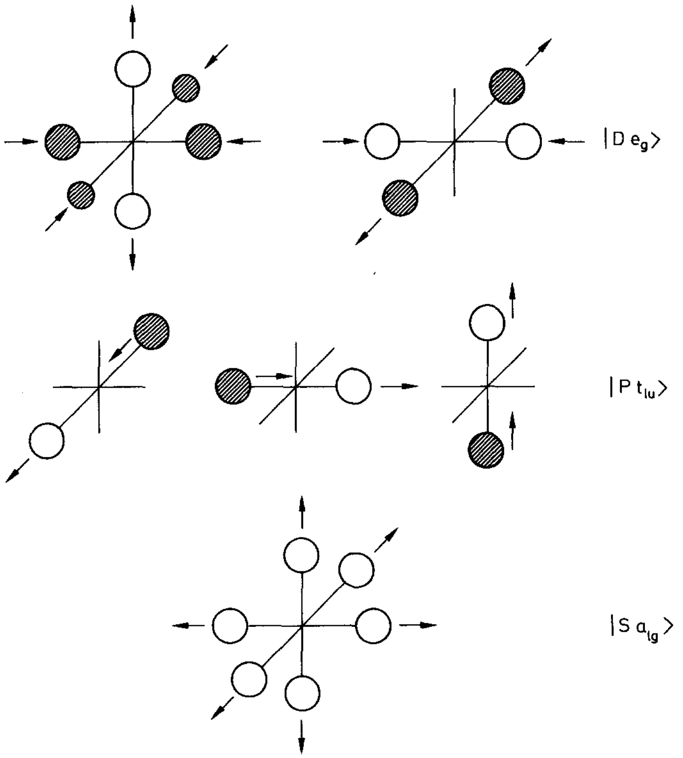

Fig. 1. The relationship between stretchings of an octahedral frame and the σ-orbitals for an octahedral cluster, as obtained in Ref. [4]

The cluster orbitals, obtained by Stone, can immediately be related to the vibrational modes of an octahedron. Fig. 1 shows the correspondence between the σ-orbitals of the cluster and octahedral stretching modes. Positive orbital coefficients are simply replaced by inward motion, arrows pointing away from the centre being attributed to negative lobes. In the same way the bending modes can be obtained from the π-symmetry orbitals, based on vector surface harmonics. (The latter also describe the rotational degrees of freedom.)

In Fig. 1 capital letters ($S, P, D \cdots$) are used to designate the spherical symmetry parentage. This paper intends to examine whether the sphere indeed offers the appropriate symmetry to characterize vibrations. Two problems are at the basis of the present analysis:

(1) the apparent dichotomy between stretching and bending modes and
(2) the observed selection rules for vibronic transitions.

2. Qualitative Considerations

Internal coordinates are often divided into two classes, stretchings and bendings, that change respectively bond lengths and bond angles. This distinction silently suggests that there are different restoring forces. As an example, in a transition metal complex force constants for stretchings are assumed to contain information on metal-ligand bond strengths, whereas bending frequencies are expected to be determined more likely by interligand repulsion.

However, in real molecules equisymmetric bending and stretching modes do interfere. A clear example is provided by the t_{1u}-asymmetric stretch and the t_{1u}-buckle mode in an octahedral complex [5]. In both cases bond lengths and bond angles vary simultaneously (see Fig. 2) so that the pure antisymmetric stretch, as represented in Fig. 1 is a unilateral idealization.

A treatment that regards molecular vibrations as fragmentary remnants of continuous functions, can therefore only be successful if in the course of the reverse process, from a finite molecule to a vibrating continuum, the bending and stretching components of one single mode will grow to respectively angular

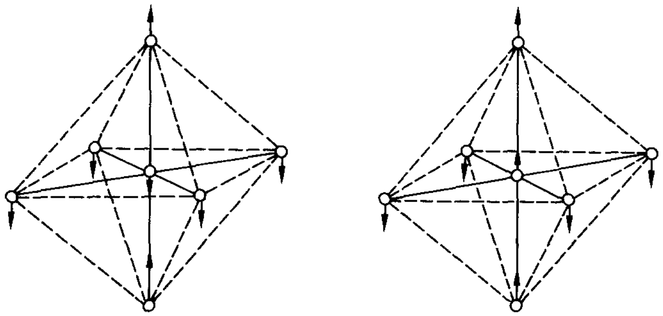

Fig. 2. Octahedral t_{1u}-normal modes. Spherical symmetry labels taken from Ref. [5]

and radial parts of one and the same function. Spherical symmetry can only characterize the angular part and is therefore but an intermediate step in the subduction chain.

To illustrate this point more clearly, and in view of the subsequent treatment, we will offer a brief description of a model continuum with spherical symmetry. Consider a thin spherical shell of gas, contained between two concentric rigid boundary layers. The density at a certain point in the shell will be denoted $\rho(\boldsymbol{r})$. All points can be considered to be at the same radial distance from the centre.

Small oscillations in density are given by

$$\rho(\boldsymbol{r}) = \rho_0 + \delta\rho(\boldsymbol{r}) \tag{1}$$

where ρ_0 denotes the average density of the medium.

It is a standard result in acoustics that these oscillations can be described by the usual spherical harmonics, Y_{lm_l}, multiplied by an amplitude, $A_{lm_l}(t)$, that changes harmonically in time

$$\delta\rho(\boldsymbol{r})\rho_0 Y_{lm_l}(\theta, \varphi) A_{lm_l}(t). \tag{2}$$

In fact this problem is completely analogous to the flooded planet case; density oscillations of a gas in a rigid cage being transformed into volume changes of an incompressible liquid on the surface of a sphere [6]. Eq. 2 can be interpreted as follows: in some regions gas is rarified while it is condensed in others, mass flowing back and forth between these. Motions are evidently wholly tangential to the sphere and therefore mimic bendings. The model is illustrative in that it also explains why bendings and stretchings are coupled. Indeed mass is alternately accumulated and removed at certain poles, exerting varying pressure on the walls. A more general model naturally would have to account for surface expansions or inflections. A model continuum that provides a unified picture of stretchings and bendings is therefore a solid body.

Vibrations of solid bodies are especially important in the theory of sound and have been studied extensively in the past, notably by Rayleigh [7] and Lamb [8]. Recently these simple dynamical models have received new attention in the study of nuclear structure [9, 10] (Liquid Drop Model), and it was suggested [2] that they might provide a useful clue for the present problem too. Classically, two types of motions are distinguished, surface modes (generated by surface tension) and compressibility waves (due to density changes). Especially the latter waves will be studied in more detail, since they provide insight in the characteristics of a vibrating continuum.

3. The Liquid Drop Model

3.1. *Surface Modes*

A vibrating nucleus is not unlike a finite liquid drop and some features of its low lying vibrational states have indeed been related to classical results [10].

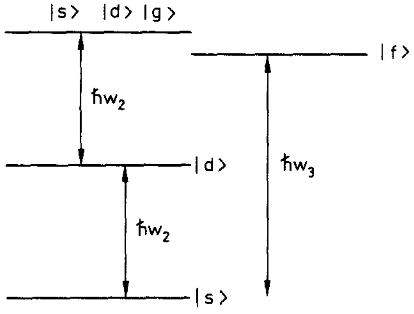

Fig. 3. Harmonic vibrations of a liquid drop (taken from Ref. [10]). The states at $2\hbar\omega_2$ energy are two-phonon excitations

An incompressible liquid drop, subject to a certain surface tension will perform surface oscillations, represented by the usual spherical harmonics. However, the p-mode corresponds to a centre-of-mass motion of the whole system and consequently the classical approximations predict for this mode zero frequency [7]. Assuming classically obtained frequencies to be a measure for energy of a particular vibration, the lowest lying states can be represented as in Fig. 3. Indeed especially the spherically symmetric nuclear ground states exhibit a pattern of low lying states that resembles Fig. 3. An assessment of electromagnetic transition rates in this scheme is difficult, though it appears that both the quadrupole and the octupole transitions will be enhanced. The dipole is absent because it corresponds to the physically spurious centre-of-mass motion. The vibrational model assumes charge and mass densities to be proportional. Oscillating charges that interact with the electromagnetic field are therefore at the surface of the nucleus. Notice that as in Fig. 3, in the flooded planet case the first excited mode is the quadrupole oscillation, as exemplified in the tidal waves.

3.2. Compressibility Waves

Besides surface modes, space filling matter also exerts compression modes [9], governed by density changes over the entire volume. The simplest possible homogeneous and isotropic medium, capable of these oscillations is a compressible liquid or gas, characterized by a single fundamental constant, the so called compressibility coefficient [6], that relates excess pressure $(\delta p(\boldsymbol{r}))$ to changes in density $(\delta\rho(\boldsymbol{r}))$.

The coefficient will be denoted γ

$$\delta p/\delta\rho = \gamma p_0/\rho_0. \tag{3}$$

The compression modes of a drop correspond to sound waves in a spherical cavity. There is no need to comment on the thermodynamic validity of Eq. (3). The reference to acoustical waves in a medium only serves as a simple physical background for the model. All that really matters is that any change in density provokes a pressure variation, causing a *local* restoring force. The constants of Eq. (3) will always appear as a product with the dimensions of a velocity to the second power. It will be represented by $(u_c)^2$, classically considered as the velocity of sound

$$u_c^2 = \gamma p_p/\rho_0. \tag{4}$$

Compression modes have received less attention in nuclear physics, since they occur at much higher energies, where other phenomena are important. A more elaborate treatment is therefore presented.

The density variations will be written as a product:

$$\delta\rho(\boldsymbol{r}) = \rho_0 A(t)\Phi(\boldsymbol{r}). \tag{5}$$

The only factor that interests us here, is the $\boldsymbol{r}$-dependent function Φ. We have already considered the case of a spherical shell, where Φ was a spherical harmonic (Eq. 2). Here Φ is obtained as a result of the wave equation in three dimensions

$$\nabla^2\Phi + (2\pi\nu/u_c)^2\Phi = 0 \tag{6}$$

where ∇^2 is the Laplacian and ν the frequency. The solutions of this equation are the half integer Bessel functions $\mathcal{J}_{l+1/2}$ of order $l+1/2$

$$\Phi = Y_{lm_l}(\theta, \varphi)r^{-1/2}\mathcal{J}_{l+1/2}(r2\pi\nu/u_c). \tag{7}$$

The boundary conditions at the surface of the cavity will only allow a quantized set of frequencies. Thus a new radial quantum number n is introduced. Several boundary conditions can be envisaged.

Since no density changes can be found outside the cavity, a boundary condition that matches continuity will require that $\Phi(r)$ becomes zero when r reaches the surface $(r = a)$

$$\Phi(\boldsymbol{r})|_{r=a} = 0. \tag{8}$$

From Eq. (8) a spectrum of quantized frequencies results, determined by the positive zero's of the appropriate Bessel functions. (The same eigenvalues are also obtained in the quantum mechanical description of a particle in a spherical box, see Ref. [6]).

For an s-mode $(l = 0)$, we obtain from Eq. (8):

$$2\pi\nu/u_c = n\pi/a \qquad (n = 1, 2, 3 \cdots). \tag{9}$$

(Subsequently we will use a shorthand notation $k = 2\pi\nu/u_c$.)

The resulting wave functions confront us with a paradox. It can be shown that none of these conserves mass. Indeed at any time the mass conservation condition requires:

$$\int_V \rho\, dV = \rho_0 V \tag{10}$$

where integration is over the volume of the cavity.

Combining Eqs. (1), (5) and (10) we obtain a more convenient form of mass conservation

$$\int_V \Phi_{nlm_l}(\boldsymbol{r})\,dV = 0. \tag{11}$$

This equation states that the total change of mass in the cavity equals zero. Whenever $l \geq 1$, i.e. for all solutions having angular nodes, this equation is certainly obeyed, since the angular part of the integral vanishes. Only for s-modes, conservation of mass depends on the radial part of the volume integral. Realizing that the radial part of Φ is a solution of the radial wave equation, we can easily perform integration

$$\begin{aligned}\int_0^a r^2 r^{-1/2}\mathcal{J}_{1/2}(kr)\,dr &= -1/k^2\cdot\left[r^2\frac{\delta}{\delta r}r^{-1/2}\mathcal{J}_{1/2}(kr)\right]_0^a\\ &= -1/k^2\cdot r^2\frac{\delta}{\delta r}r^{-1/2}\mathcal{J}_{1/2}(kr)\Big|_{r=a}.\end{aligned} \tag{12}$$

Eq. (12) is only a special case of Green's theorem that a volume integral can be replaced by a surface condition. Using the recurrence relations for Bessel functions, thus surface condition takes a very simple form:

$$\frac{\delta}{\delta r}r^{-1/2}\mathcal{J}_{1/2}(kr) = -kr^{-1/2}\mathcal{J}_{3/2}(kr). \tag{13}$$

Hence the mass conservation of the s-modes depends on the value of the p-modes at the boundary. Obviously, if the k-values are chosen according to Eq. (9), so that the s-modes go to zero at the surface, the p-modes with the same frequencies will not have roots at $r = a$, since the positive zeros of Bessel functions with subsequent orders are interlaced [11]. This clearly demonstrates that none of the s-modes, as obtained from the usual boundary condition in Eq. (8), will conserve mass.

The Liquid Drop Model removed this contradiction by taking into account small surface displacements, as a consequence of the non-vanishing radial flux of Φ at the boundary [9]. The boundary condition as such thus did not reflect the required conservation properties. Since it is our aim to study continuous potentials that can replace the actual boundary requirements, explicit incorporation of the conservation properties in the space of interest is needed. In keeping the domain of the wave function well defined, mass can only be conserved by altering the boundary condition for the s-modes, so that:

$$\frac{\delta}{\delta r}\Phi_{n00}\Big|_{r=a} = 0. \tag{14}$$

This condition states that there is no mass flow through the boundary, which would be the case for a gas in a rigid container. The above condition can be generalized, so as to conserve not only mass, but any λth-order moment of the system (for mass $\lambda = 0$, for the centre of mass $\lambda = 1$ etc. . . .).

In general the conservation condition for the λth-order moment takes the following form:

$$\int_V Y^*_{\lambda m_\lambda} r^\lambda \Phi_{nlm_l}\, dV = \delta_{\lambda l}\delta_{m_\lambda m_l}\int_0^a r^{\lambda+2} r^{-1/2}\mathcal{J}_{l+1/2}(kr)\, dr = 0. \tag{15}$$

If the Kronecker deltas in this expression are equal to one, the radial part becomes the determinant of the integration.

$$\int_0^a r^{\lambda+2} r^{-1/2}\mathcal{J}_{\lambda+1/2}(kr)\, dr = -r^{\lambda+2}\Big/ k^2\left(\frac{\delta}{\delta r}-\frac{\lambda}{r}\right) r^{-1/2}\mathcal{J}_{\lambda+1/2}\Big|_{r=a} = 0. \tag{16}$$

The boundary condition that will conserve the λth -moment thus requires that the radial part of the s-modes obeys Eq. (16). The usual classical boundary condition for a medium in a rigid container only considers the term in $\delta/\delta r$ [12]. The operator in Eq. (16) is a generalized momentum operator, also taking into account the centrifugal forces to be associated with a wave that carries angular momentum.

Furthermore these generalized momentum operators act as shift operators [13]. From the Bessel equation the following relations are easily found:

$$\begin{aligned} -1/k\left(\frac{\delta}{\delta r}-\frac{l}{r}\right) r^{-1/2}\mathcal{J}_{l+1/2} &= r^{-1/2}\mathcal{J}_{l+3/2} \\ 1/k\left(\frac{\delta}{\delta r}+\frac{l+1}{r}\right) r^{-1/2}\mathcal{J}_{l+1/2} &= r^{-1/2}\mathcal{J}_{l-1/2}. \end{aligned} \tag{17}$$

The operator which occurs in Eq. (16) is thus recognized as a ladder operator, increasing the order of the Bessel function by one. Hence as a general result one can state:

"*The λth-order moment is conserved if radial quantum numbers of the λ-modes are determined by the positive zeros of the (λ + 1)-modes.*"

3.3. Results

From the foregoing treatment two different types of boundary conditions resulted, the radial quantum number of the λth-mode being determined by the roots of either $\mathcal{J}_{l+1/2}$, or $\mathcal{J}_{l+3/2}$.

The resulting energies of the l-modes in the latter scheme are thus exactly degenerate with the $(l+1)$-mode energies in the former scheme.

What scheme shall we adopt? The consideration of the degree-of-freedom rule provides the answer.

First of all, mass has to be conserved, therefore, the totally symmetric modes obey the second criterion. Furthermore, there is no restoring force for translations. Hence the p-modes also have to obey the second criterion, in order to conserve the first moment, i.e. the centre of mass. But now all external degrees of freedom have been removed. The higher moments are left as internal degrees

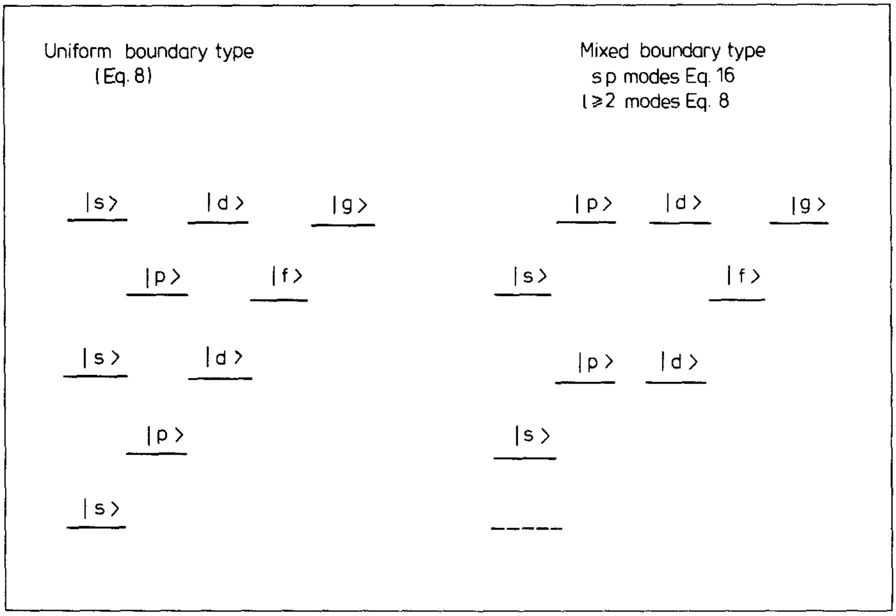

Fig. 4. Frequency pattern for two types of boundary conditions. $s, d, g \cdots$ modes have even parity, $p, f, h \cdots$ modes are odd. Only one-phonon states are shown. The $|s\rangle$ and $|p\rangle$ states from the right-hand side diagram are degenerate with $|p\rangle$, resp. $|d\rangle$ states in the uniform-boundary type

of freedom and therefore follow the first boundary condition. The result is thus of the mixed boundary type.

Fig. 4 displays the change in frequencies upon removal of zeroth and first moments. Its left-hand side shows the frequency pattern for a uniform boundary requirement, where all modes vanish at the surface. In the right-hand side of the figure zeroth and first moments have been removed so that s- and p-modes are shifted in frequency to the level of respectively p- and d-modes of the uniform scheme. The result is not too different from the surface mode distribution in Fig. 3.

The uniform pattern in Fig. 4 shows remarkable agreement with the spectrum of the spherical harmonic oscillator [14] with symmetry group $U(3)$. Although the degeneracies of this group are not exactly reproduced in a finite cavity, all even modes tend to have frequencies which are whole integral multiples of the fundamental, whereas the odd modes approach half integral multiples of the fundamental [6].

3.4. Discussion

(1) Degrees of Freedom

The adaptation of the s-modes corresponds to the scalar degree of freedom. Its analog in the conventional treatment of an N-atom molecule is the number of particles involved.

The *vectorial* property associated with the p-modes, refers to the three translational degrees of freedom.

The representation of the *rotor* $(\hat{\mathscr{L}}_x\hat{\mathscr{L}}_y\hat{\mathscr{L}}_z)$ which is a gerade p-mode is lacking in the energy scheme. Indeed a sphere is rotationally invariant. Transversal modes, which travel around an axis of revolution are exactly degenerate with those that travel in the opposite direction. Therefore, they can be transformed into standing waves, without altering their energy. This is not the case for longitudinal waves which incorporate translations.

The spurious states were thus seen to be embedded in the entire manifold of s- and p-modes. The boundary condition acted as a projection operator. It removed the degrees of freedom required, simultaneously reorthogonalizing the remaining basis functions, as will be shown in the next section.

(2) Dimensions of the Solution Space

Consider the set of all Bessel functions of a particular order that are obtained by the requirement that Φ vanishes at the surface. We can denote this set as follows:

$$\{\mathscr{J}_{l+1/2}(kr)|^{\mathscr{J}_{l+1/2}(ka)=0}\}. \tag{18}$$

The ka values are the positive zeros of $\mathscr{J}_{l+1/2}(kr)$. This set is known to form a complete space, i.e. any arbitrary $f(r)$, which is well behaved in the interval $[0, a]$, can be described through an expansion in this space. The above set is therefore often called a *Fourier–Bessel* series.

The root defining condition, which acts as a transcendental equation accompanying the wave equation, was put in a more general form by Dini (see Ref. [11]). Using the notation of Watson, we can denote Dini's series as follows:

$$\{\mathscr{J}_{\nu(kr)}|^{k\mathscr{J}'_\nu(k)+H\mathscr{J}_\nu(k)=0}\} \tag{19}$$

where ν stands for the order of the Bessel function, the prime denotes the first derivative with respect to k and H as a constant. These authors have put the boundary at $r=1$.

Generalizing the equation for a boundary at $r=a$, we obtain the condition:

$$r\frac{\delta}{\delta r}\mathscr{J}_\nu(kr)+H\mathscr{J}_\nu(kr)\Big|_{r=a}=0. \tag{20}$$

On the other hand the boundary condition (Eq. (16)), which was used for s- and p-modes, can be written as follows:

$$\left(\frac{\delta}{\delta r}-\frac{l}{r}\right)r^{-1/2}\mathscr{J}_{l+1/2}(kr)=r^{-3/2}\left[r\frac{\delta}{\delta r}\mathscr{J}_{l+1/2}(kr)-(l+1/2)\mathscr{J}_{l+1/2}(kr)\right]. \tag{21}$$

Comparing Eqs. (20) and (21) we can at once identify H as being equal to $-\nu$ in the present problem. Quoting Watson [11], "in this case a peculiar phenomenon occurs, which has no analogue in the theory of Fourier–Bessel expansions". Indeed in this case $k=0$ is also a root of the transcendental equation, which is not considered in the set of Eq. (19). The series obtained by this type of boundary condition are therefore almost complete; one term still has to be added to make an arbitrary function describable in this set of solutions. This term can of course at once be determined as the degree of freedom, which was removed by this type of boundary requirement. The appropriate expression is given by Watson.

Generalizing his result to a boundary at $r=a$, this initial term takes the form:

$$\frac{2(\nu+1)}{a^{\nu+2}} r^{\nu} \int_0^a t^{\nu+1} f(t/a)\, dt \tag{22}$$

where $f(r)$ stands for the arbitrary function to be expanded. If one wants to conserve the λth-order moment, this function takes the form $r^{\lambda+1/2}$ (see Eq. 15). With $\nu=\lambda+1/2$, one can calculate the above initial term:

$$\frac{2(\nu+1)r^{\nu}}{a^{\nu+2}} \int_0^a t^{\nu+1} \frac{t^{\nu}}{a^{\nu}}\, dt = r^{\nu} \equiv f(r). \tag{23}$$

As can be seen from Eq. (23), the initial term already carries the whole function. There is no remainder left to interact with Dini-Space.

In this sense none of the p-modes will show interference with a dipole. The conclusions of Fig. 3 thus seem to prevail also in this case: the scattering of waves will occur through the quadrupole mode, while "resonant" absorptions correspond to the octupole.

Finally the above analysis points out that the spurious mode is not really "removed". It corresponds to a root at the origin, i.e. at zero energy, where the system is at rest.

4. The Quantum Mechanical Model

4.1. General Features

The Liquid Drop Model represents a mixture of classical and quantum mechanical terminology. Waves are interpreted in a classical way as density changes in a continuous medium, but their frequency pattern is transformed to an energy spectrum.

It is tempting to eliminate this ambiguity by associating a quantum mechanical pseudo article – a vibron as we may call it – with density waves. Moreover a suitable potential function, $V(r)$, could be introduced to remove the boundary conditions of the previous treatment. To carry the acoustical metaphore one step further, one could think of a distance – dependence in the velocity of sound, so that the transmittance of sound gradually fades towards limiting distances.

The constants, encountered so far, have their analogs in the quantum mechanical treatment. The medium dependent constant, u_c, which proved to be a scaling factor for frequency, is now replaced by $\hbar^2/2m$, which is the scaling factor for energy. The surface radius, a, which could be looked upon as the scaling factor for space will similarly have its analog in the parameters that help define the potential energy function.

We will adopt the convention to express all energies (the potential function included) in units of $\hbar^2/2m$, so that we can write the wave equation as follows:

$$\nabla^2\Phi - V\Phi + E\Phi = 0. \tag{24}$$

Having established the correspondence between the two terminologies, attention should be focused on the differences. If we want to construct a system with only internal degrees of freedom, the conservation conditions of the preceding section have to be restated in a quantum mechanical language. It should be realized that their classical form makes implicit reference to a ground state at rest. This state is the completely valid fundamental description of the system. Its mass is defined and so is its motion with respect to an external coordinate system. The conditions of conservation made certain that not a single excited state will alter these characteristics.

Excited states are not allowed to show net density changes or centre-of-mass shifts, with respect to the ground state. Hence they are defined in an internal coordinate system. In quantum mechanics a zero-point energy remains present in the fundamental mode. Therefore in a quantum mechanical sense, this ground state, being denoted $|0\rangle$, must explicitly feature in the conservation conditions. Writing excited states as $|\Phi\rangle$, the removal of the λth-order must be written:

$$\langle\Phi|Y_{\lambda m_\lambda} r^\lambda|0\rangle = 0. \tag{25}$$

Since all excited states are orthogonal to the ground state, the zeroth-order moment has not changed. However, the dipole transition moment must be eliminated in order to transform the system to translationally invariant internal coordinates. Indeed translation of mass in a dipole causes translation of the centre-of-mass (see Ref. [1]).

4.2. *The Harmonic Oscillator*

As noticed before [1, 15], all vibrations of a solid body can be accommodated in the unitary group in three dimensions $U(3)$, which is represented by the spherical harmonic oscillator. The removal of the centre-of-mass motion in this group poses no problems. Indeed the product $r|0\rangle$, featuring in Eq. (25) for $\lambda = 1$, is the radial function of the fundamental p-mode. Evidently all other p-modes will obey Eq. (25), since they are orthogonal to the origin of the p-series. In other words: the whole dipole strength for transitions from the ground state is concentrated in the first quantum jump. After removal of this fundamental p-mode, no reorthogonalization of the remaining basis is needed.

The assignment of the first p-mode as the physically spurious state fully coincides with more elaborate nuclear shell models [10]. Similarly, according to these models, removal of this mode eliminates dipole transitions in the low energy region, and the main oscillator strength is attributed to the octupole transitions.

Moreover, using Eq. [25], a simple assessment can be made of Irvine's remark that "the removal of spurious centre-of-mass motion in any single particle representation, other than that of harmonic oscillators, is extremely complicated" (quoted from Ref. [10], page 263).

Indeed, consider a simple linear oscillator

$$\left(-\frac{d^2}{dx^2}+V(x)-E\right)|\Phi\rangle=0. \tag{26}$$

Once again the condition for centre-of-mass conservation can be looked upon as an orthogonality requirement. Suppose therefore that the product $x|0\rangle$ obeys the same wave equation as $|\Phi\rangle$, with a different eigenvalue, say E'. After factorization this equation becomes:

$$\left(-\frac{d^2}{dx^2}-\frac{2}{x}\frac{d}{dx}+V(x)-E'\right)|0\rangle=0. \tag{27}$$

But $|0\rangle$ also obeys the basic equation, Eq. (26), being the fundamental mode with eigenvalue E^0. Combining both differential equations, one obtains:

$$\left(\frac{2}{x}\frac{d}{dx}-E^0+E'\right)|0\rangle=0$$

or:

$$|0\rangle\sim\exp\left(-(E'-E^0)x^2/4\right). \tag{28}$$

This solution is recognized as the fundamental mode of the harmonic oscillator. Hence only in this case is orthogonality of the remaining basis automatically achieved.

In summary, the $U(3)$ group, less its first p-mode, represents the single-particle model of a vibrating system. Its states can be thought of as orbitals, corresponding to the normal modes of a many-particle system. *De facto,* all these normal modes will be internalized, since the spurious centre-of-mass motion has been removed. The resulting system will not contain a mass-dipole-moment.

Now, as far as electromagnetic transition processes are involved, two extremes must be considered. If charge and mass densities are proportional, the absence of a mass dipole will include the absence of a charge dipole moment, hence the first ungerade internal transition moment available is the octupole moment. This is the case for low lying nuclear vibrational states, and confirms the predictions of the Liquid Drop Model. On the other hand, if charge and mass density distributions do not follow each other, internal modes that leave the centre-of-mass density unchanged, could well correspond to polarization of charge density according to a charge dipole moment. Indeed dipole transitions are observed in nuclear vibrational spectra too, though they occur at much higher energies [10].

These two extremes, which are distinguishable in nuclear spectra, can provide a new perspective on the problem of molecular vibrational intensities. In a molecule certainly mass and charge densities do not map onto each other, and conservation of the centre-of-mass therefore does not imply the absence of dipole transitions. However, energy considerations may indicate that in the case of strong vibronic coupling only weak polarizations could result, in comparison to octupole moments, though the latter modes are orders of magnitude less intense, for a similar extent of polarization. These considerations do stress the important role of the many-electron density distribution in the calculation of vibrational transition intensities and offer some insight into the difficulties these calculations involve.

5. The Loop Equations

5.1. Deviations from Hooke's Law

The harmonic oscillator provides the highest symmetry group for a vibrating body and therefore acts as parent group. On the other hand it is equally true that all real oscillators are to a certain extent anharmonic. However, as an apparent rule, the shape of their potential is remarkably common to all oscillators, no matter what the actual value of the force constants involved may be.

Two formidable questions can be raised in this respect:

(1) Does the apparent rule of a rather specific anharmonic behaviour – perhaps best described by the Morse potential – point to a simple physical requirement, inherent to oscillators?
(2) How can a complete description of real oscillators be realized by a descent in symmetry from the parent group? How should $U(3)$ quantum numbers be used to characterize anharmonic functions?

The development of a general description for anharmonic oscillators would undoubtedly greatly benefit from eventual insight into the observed deviations from Hooke's Law. In our view the emerging picture seems to be that *the shape of the anharmonic potentials reflects the imposition of conservation conditions of monopole and dipole quantities.* We have no other guideline to express these conditions than the classical intuition, presented in section 3. However, it would seem worthwhile to examine whether the special type of well-boundary, encountered in that section, can be expressed in a continuous potential function. Such a treatment cannot be expected to offer a full solution, but it appears to provide meaningful claims on the form of the potential outside the bottom of the well.

First consider the example of the conservation of the zeroth-moment in one dimension. We will refer to this case as $\mathscr{C}_0(1)$. The index denotes the order of the moment, and the argument the dimension of space.

The classical requirement that the integrated wave equals zero (cf. Eq. (11)) can now be combined with the integrated form of the wave equation. One obtains for the interval $[x_1, x_2]$:

$$E\int_{x_1}^{x_2} \Phi \, dx = -\left[\frac{d\Phi}{dx}\right]_{x_1}^{x_2} + \int_{x_1}^{x_2} V\Phi \, dx. \tag{29}$$

Two issues are possible at this point. If one deals with a constant potential between infinite boundaries, as in the model of Sect. 3, Eq. (29) can be rearranged so as to show that $\mathscr{C}_0(1)$ depends on the values the derivative takes at the boundaries. This confirms our previous conclusions.

If on the other hand the interval $[x_1, x_2]$ is stretched to infinity and some potential function is introduced, Eq. 23 takes the following form:

$$E\int \Phi \, dx = \langle V|\Phi\rangle. \tag{30}$$

This equation implies that the first derivative of the wave function vanishes at infinity and states that the integrated wave will only vanish when the wave function is orthogonal to the potential.

For ungerade modes, both integrals vanish by symmetry. Hence the conservation condition tends to force gerade modes to adopt a radial node pattern, which is equivalent to the inversion symmetry of the ungerade modes. However, it is evident that such a "displaced" oscillator can only be realized for a constant potential between infinite walls. Indeed if a wave has a radial node so that its integral equals zero, the product of that wave function with a nodeless and continuous potential function will not display the same peculiar radial symmetry any more, unless the potential is constant.

Orthogonality of a wave function to the potential is therefore a limiting case. Indeed it would be reached if the fundamental mode itself is congruent to the potential, assuming that the potential itself obeys the same Sturm–Liouville boundary condition as the wave functions [6]. In a quantum mechanical system the fundamental mode of a vibrating system can be said to probe this potential at a certain point in energy.

However, the limit where the potential is proportional to one of its own eigenfunctions offers a novel perspective since it allows one to characterize the potential itself by a differential equation. Using the parameter form

$$V = a + b\psi(x) \tag{31}$$

where a and b are independent parameters and $\psi(x)$ is the functional form, the statement that ψ itself is an eigenfunction leads to

$$-\frac{d^2}{dx^2}\psi + (a + b\psi)\psi - E\psi = 0. \tag{32}$$

In this equation a can be omitted without loss of generality since this merely shifts energies. Thus a second order non-linear differential equation is generated, containing one parameter b and an eigenvalue E. Once ψ is obtained, a normal hamiltonian is available and other eigenfunctions can be generated.

The space of eigenfunctions is thus divided into a singleton, the potential function ψ itself, and a remainder space built on this potential. The singleton is separable because it has the unique reflective property of an eigenfunction, which is its own potential.

We propose to call this equation the loop equation in quantum mechanics, recognizing the widespread interest of the purely mathematical principle of a concept that applies to itself, and in the hope that, although a limiting case, it will be helpful in designing anharmonic potentials.

5.2. Solutions of the Loop Equation

Closed form integration of Eq. (32) is possible, since the independent variable x is absent. In fact a similar equation was solved by Einstein in his treatment of the problem of perihelion shift (see Ref. [16]). Multiplying Eq. (32) by $2d\psi/dx$ one obtains after integration:

$$\left(\frac{d\psi}{dx}\right)^2 = \tfrac{2}{3}b\psi^3 - E\psi^2 + c. \tag{33}$$

The constant c is the integration constant, to be determined from boundary conditions on $d\psi/dx$.

Eq. (33) is a special case of the general elliptic equation, where the highest power present is the cube. It can be solved in general by means of elliptic functions of Jacobi [16]. As a first condition, we require $d\psi/dx$ to be equal to zero at the origin. This simply means that the potential behaves harmonically at the origin. A linear anharmonicity would imply that the origin is unstable, as is the case for Jahn–Teller instabilities, which will not be discussed here.

Using ψ_0 as the value of ψ at the origin, c can now be eliminated.

$$\left(\frac{d\psi}{dx}\right)^2 = \tfrac{2}{3}b(\psi^3 - \psi_0^3) - E(\psi^2 - \psi_0^2). \tag{34}$$

The fundamental $1s$-mode, having no radial nodes nor a periodic structure, is realized for the eigenvalue $E = \tfrac{2}{3}b\psi_0$. In that case the result has the following form:

$$\psi = \psi_0 \operatorname{sech}^2(kx) \tag{35}$$

where the scaling parameter k is a function of b, given by:

$$b = -6k^2/\psi_0 \quad \text{or} \quad E = -4k^2. \tag{36}$$

Hence the potential takes the form:

$$V = b\psi = -6k^2 \operatorname{sech}^2(kx). \tag{37}$$

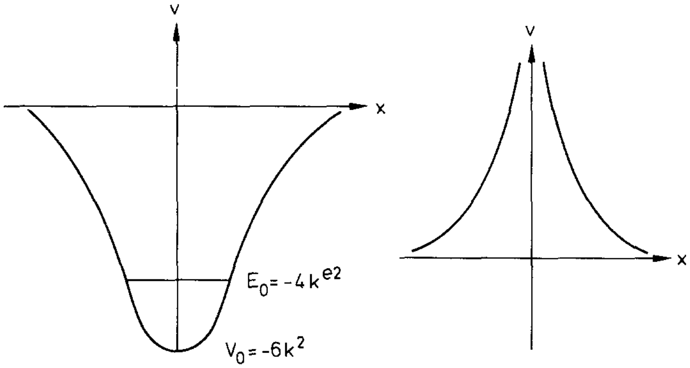

Fig. 5. Fundamental bounded and unbounded s-modes of the loop equation $\mathscr{C}_0(1)$ (cf. Eqs. (37), (38)

If we would have put $c = 0$ in Eq. (33), the same eigenvalue $E = -4k^2$ would have yielded the unbound s-mode, with positive b

$$V = 6k^2 \operatorname{cosech}^2(kx). \tag{38}$$

Fig. 5 presents the graphs of both functions. The potentials displayed in this figure bear great resemblance to trial functions studied by Pöschl and Teller around 1930, in an evaluation of anharmonic oscillators [17]. Also Rosen and Morse [18] have devoted interest to this type of potentials. A more detailed survey will be presented in Sect. 6.

5.3. The Generalized Loop Equation

In conclusion to this section, the generalized loop equation in three dimensions for any λth-order moment, is presented. Using the earlier notation, this case is denoted $\mathscr{C}_\lambda(3)$.

Adopting spherical symmetry, the starting point is the radial wave equation for modes with angular quantum number λ.

Multiplying this equation with the radial operator r^λ and integrating over the interval $[0, \infty]$, one obtains:

$$\begin{aligned} E\int r^{\lambda+2}\psi\, dr = -\int r^{\lambda+2}\frac{d^2\psi}{dr^2}\, dr - 2\int r^{\lambda+1}\frac{d\psi}{dr}\, dr \\ -\lambda(\lambda+1)\int r^\lambda \psi\, dr + \int r^{\lambda+2} V\psi\, dr. \end{aligned} \tag{39}$$

By partial integration this expression reduces to:

$$E\int r^{\lambda+2}\psi\, dr = -\left[r^{\lambda+2}\left(\frac{d}{dr}-\frac{\lambda}{r}\right)\psi\right]_0^\infty + \langle r^\lambda V|\psi\rangle. \tag{40}$$

Once again the generalized radial momentum operator appears (cf. Eq. (16)). Assuming the usual boundary behaviour Eq. (40) leads to the orthogonality of Φ to the product $r^\lambda V$. The loop equation that will match this requirement simplifies to:

$$-\frac{d^2}{dr^2}\psi - \frac{2(\lambda+1)}{r}\frac{d\psi}{dr} + b\psi^2 - E\psi = 0. \tag{41}$$

This is the general form of the loop equation in three-dimensional spherical symmetric space. Also one-dimensional conservation conditions follow this equation: $\mathscr{C}_0(1)$ corresponding to $\lambda = -1$, and $\mathscr{C}_1(1)$ to $\lambda = 0$. Cylindrical symmetries might be incorporated as well. General solutions for this equation do not seem to be available in the literature. For $\lambda = 0$, the differential operator in Eq. (41) has the usual form for radial spherical problems and the loop equation in that case is recognized as an example of the Lane–Emden equation in astrophysics [16]. However, no closed form integration of this equation seems to be published to date.

Only for $\lambda = -1$ solutions could be obtained (see Sect. 5.2). However, this is also the only case where the singularity at the origin is avoided.

6. Anharmonic Oscillators

6.1. The Pöschl–Teller Potentials

The potential considered by Pöschl and Teller [17, 19] (P.T.) is a linear combination of both *s*-mode solutions of the loop equation. Using units of $\hbar^2/2m$ it can be expressed as follows:

$$V = \kappa(\kappa-1)k^2 \operatorname{cosech}^2(kx) - \lambda(\lambda+1)k^2 \operatorname{sech}^2(kx). \tag{42}$$

The constants κ and λ characterize respectively the repulsive and attractive parts of the potential. k is a typical scaling factor for the independent variable.

The loop equation produces specific values of κ and λ which we will identify as $\kappa = -2$, $\lambda = +2$.

The P.T.-potential is a displaceable oscillator in that the eigenvalues of the resulting wave functions only depend on the difference between κ and λ. Keeping this difference fixed while changing the parameters will not affect eigenvalues, whereas eigenfunctions can be modified at will. In the limiting case, where both κ and λ are very large, while keeping a finite net attractive difference between the two, the P.T.-potential shape is displaced towards the Morse curve [17]. (The actual Morse potential is the leading term in the exponential expansion of Eq. (42).)

Apparently previous reasons for studying these functions are related to the fact that closed form integration of the resulting wave equation poses no difficulties. Detailed treatments of the various P.T.-type potentials are offered by Flügge [20].

However, these solutions also are attractive from another point of view. They can be related to harmonic functions. The distortional event that modifies harmonic oscillators to anharmonic potentials can thus be described more adequately.

6.2. The Attraction Potential

Consider the hamiltonian for a fully attractive potential, characterized by

$$\mathcal{H}=-\frac{d^2}{dx^2}-\lambda(\lambda+1)k^2\operatorname{sech}^2(kx). \tag{43}$$

The transformation $kx=-\tanh^{-1}(\cos\theta)$ compresses the entire range of the independent variable x to the $[0, \pi]$-interval in an angular variable θ. Applying this transformation to the above hamiltonian, the wave equation values the following form:

$$\left(-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\frac{d}{d\theta}\right)-\lambda(\lambda+1)-\frac{E}{k^2\sin^2\theta}\right)|\Phi\rangle=0. \tag{44}$$

Substituting $E=-k^2m_\lambda^2$ in Eq. (44), and assuming that λ and m_λ are integers, the transformed equation is readily recognized as the associated Legendre equation, describing the $\Theta_{\lambda|m_\lambda|}$ part of the spherical harmonics.

In this transformed space the constant λ of the Pöschl–Teller equation adopts the role of angular quantum number. The energies represent the azimuthal quantizations.

In a $|\lambda m_\lambda\rangle$ notation, the ground state thus must be written $|\lambda\lambda\rangle$. The total number of bound states equals $(\lambda+1)$, including the $|\lambda 0\rangle$ state with zero energy. The capacity of this potential hole to contain bounded states is thus a finite number. Interestingly the original loop equation yielded $\lambda=2$ (Eq. (37)). In this case only three states are to be found. The potential itself is the $|d2\rangle$ state. The first excited state corresponds to $|d1\rangle$. This is an "ungerade" state in x-space, corresponding to change of sign upon reflection through a horizontal plane of symmetry in θ-space. Finally the zero energy state is describable as $|d_z2\rangle$. As noticed earlier, no other bound gerade modes can be present in this case, since that would violate the orthogonality condition in Eq. (30). Solutions can now be expressed in terms of associated Legendre functions, and normalized in θ-space

$$|\lambda m_\lambda\rangle=(-1)^{m_\lambda}\left[\frac{2\lambda+1}{2}\,\frac{\lambda-m_\lambda}{\lambda+m_\lambda}\right]^{1/2}P_\lambda^{m_\lambda}(-\tanh(kx))$$

with:

$$P_\lambda^{m_\lambda}(-\tanh(kx))=\frac{(-1)^\lambda}{2^\lambda\lambda!}\operatorname{sech}^{m_\lambda}(kx)\left[\frac{d}{d\tanh(kx)}\right]^{\lambda+m_\lambda}(\tanh^2(kx)-1)^\lambda. \tag{45}$$

These equations are conformal to Condon & Shortley phase conventions [21] $(m_\lambda\geq 0)$.

Similarly, the angular ladder operators can be defined

$$\mathscr{L}^+ = -\cosh(kx)\frac{d}{d(kx)} - m_\lambda \sinh(kx)$$

$$\mathscr{L}^- = \cosh(kx)\frac{d}{d(kx)} - m_\lambda \sinh(kx). \tag{46}$$

The operators act as usual shift operators on the $|\lambda m_\lambda\rangle$ functions as defined in Eq. (45). These functions are normalized in θ-space. The volume element in this space is transformed in an interesting way:

$$d(\cos\theta) = -d(\tanh(kx)) = -\operatorname{sech}^2(kx)\,d(kx). \tag{47}$$

Hence the volume element of the angular space incorporates the potential of the anharmonic oscillator. The potential thus really holds the metric of the x-space. As a consequence, functions that are normalized in θ are characterized by the same (un-normalized) expectation value $\langle\Phi|V|\Phi\rangle$ in x-space.

Other interesting generalizations are possible as well. Associated Legendre orbitals are characterized by the following recurrence relations [22] in λ

$$\left(z^2-1\right)\frac{dP_\lambda^{m_\lambda}(z)}{dz} = \lambda z P_\lambda^{m_\lambda}(z) - (\lambda + m_\lambda)P_{\lambda-1}^{m_\lambda}(z)$$

$$(z^2-1)\frac{dP_{\lambda-1}^{m_\lambda}(z)}{dz} = (\lambda - m_\lambda)P_\lambda^{m_\lambda}(z) - \lambda z P_{\lambda-1}^{m_\lambda}(z). \tag{48}$$

With $z = -\tanh(kx)$ these equations supply raising and lowering operators for λ, that leave m_λ constant

$$\mathscr{A}^- = -\frac{d}{d(kx)} - \lambda\tanh(kx) \quad \text{with: } \mathscr{A}^- P_\lambda^{m_\lambda} = (\lambda + m_\lambda)P_{\lambda-1}^{m_\lambda}$$

$$\mathscr{A}^+ = \frac{d}{d(kx)} - \lambda\tanh(kx) \quad \text{with: } \mathscr{A}^+ P_{\lambda-1}^{m_\lambda} = (\lambda - m_\lambda)P_\lambda^{m_\lambda}. \tag{49}$$

These operators factorize the hamiltonian as follows:

$$\mathscr{H}(kx) = \mathscr{A}^+ \cdot \mathscr{A}^- - \lambda^2. \tag{50}$$

Fig. 6 summarizes these results. It can be seen that the whole manifold of angular momentum space can be transferred to anharmonic oscillators. It is known that

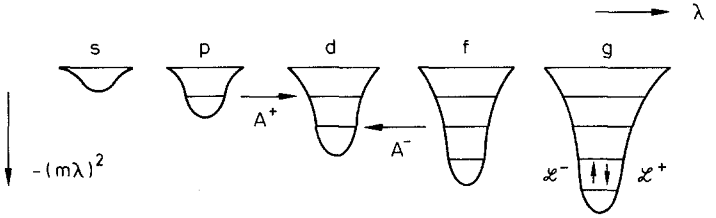

Fig. 6. Effects of raising and lowering operators for the attraction P.T.-potential

the group $U(3)$ allows lowering of λ beyond zero. Then states correspond to waves that are unbound at the origin, and are therefore rejected from the solutions of the wave equation [20]. In our opinion the repulsive states explore this extended space.

6.3. The Repulsive States

The repulsive part of the P.T.-Hamiltonian will be written in a form that underlines the angular momentum origin of κ

$$H=-\frac{d^2}{dx^2}+(-\kappa)(-\kappa+1)k^2\operatorname{cosech}^2(kx). \tag{51}$$

The minus sign (with $\kappa>0$) is used to distinguish the repulsive and attractive states. Repulsive states are thus denoted $|-\kappa m_\kappa\rangle$.

Solutions occurred as auxiliary functions in the study of the group of scattering states for hydrogen [23]. They can be written:

$$\sinh^\kappa(kx)\left[\frac{d}{d\cosh(kx)}\right]^\kappa\cos(m_\kappa(kx)) \tag{52}$$

(see also Ref. [24]).

Since these are continuum states m_κ is not quantized. At infinity these functions have an oscillatory behaviour, due to the periodic cosine. As such these states cannot be combined with $|\lambda m_\lambda\rangle$ states to form eigenstates of the full P.T.-potential. However, they can be prepared in view of such a coupling. This requires the adhesion of the imaginary to m_κ. Hence:

$$\cos(im_\kappa(kx))=\cosh(m_\kappa(kx)). \tag{53}$$

By introducing hypergeometric functions [22], we have

$$\cosh(m_\kappa(kx))={}_2F_1(-m_\kappa/2,\,m_\kappa/2;\,1/2;\,-\sinh^2(kx)). \tag{54}$$

Using known quadratures, Eq. (52) can finally be transformed to

$$|-\kappa m_\kappa\rangle\sim\sinh^\kappa(kx)\,{}_2F_1((\kappa-m_\kappa)/2,\,(\kappa+m_\kappa)/2;\,\kappa+1/2;\,-\sinh^2(kx)). \tag{55}$$

For $m_\kappa=\kappa$ the ${}_2F_1$-function equals 1 and hence:

$$|-\kappa\kappa\rangle\sim\sinh^\kappa(kx). \tag{56}$$

If m_κ is allowed to *increase* with even increments, the ${}_2F_1$-function takes the form of a finite power series in $\sinh^2(kx)$, that is multiplied with the $|-\kappa\kappa\rangle$ fundamental.

This is entirely analogous to the even attractive states. Their ground state is written

$$|\lambda\lambda\rangle\sim\operatorname{sech}^\lambda(kx). \tag{57}$$

Now *decreasing* m_λ with even numbers generates all other gerade modes, which can be written:

$$\operatorname{sech}^\lambda(kx)\,{}_2F_1((m_l-\lambda)/2, -(m_\lambda+\lambda)/2; 1/2; -\sinh^2(kx)). \tag{58}$$

The repulsive states are unacceptable as such since they are divergent at infinity. In order to obtain net attractive states, they have to be coupled with appropriate attractive states, so that a convergent result is obtained.

6.4. The Descent in Radial Symmetry

A spherically symmetric potential divides three-dimensional space into two subspaces of radial and angular coordinates. These are complementary and the nodal pattern in the combined space is a unique characteristic of each individual eigenfunction.

Symmetry in angular space has a clear geometric meaning: the infinitesimal operators that characterize the angular symmetry represent infinitesimal rotations on a sphere. Radial symmetry cannot possibly be characterized in an analogous sense, since the potential would not allow infinitesimal displacements in radial space, unless it is constant. However, whenever degeneracies between radial and angular nodal patterns are observed, radial symmetry can acquire a geometrical sense in a transformed space, where it is categorized as a generalized angular coordinate. This is the case for the harmonic oscillator in three dimensions where one radial node is equivalent to two angular nodal planes. The $U(3)$ symmetry of this hamiltonian was demonstrated by Baker [16] using the transformed space of the boson-operators. In the hydrogen problem one radial node is equivalent to one angular nodal plane. The symmetry group for this equivalence was established by Fock [24] as the orthogonal group in four dimensions O(4).

Since at present we have been dealing with uni-dimensional problems, which cannot be mapped directly in three dimensions (see Sect. 5.3), recurrence to the above concept of radial symmetry could not be made. However, the symmetry of P.T.-potentials can easily be established by referring to dynamical groups. This involves a mapping of states into components of a single representation of a continuous group. Ladder operators that connected different eigenstates, become symmetry operators in the generalized space. This is the concept of radial symmetry, that we will be referring to.

As shown (Sect. 6.2) attraction potentials, characterized by integer values of λ allowed a straightforward transform to the space of spherical harmonics. All states could be mapped on $|\lambda m_\lambda\rangle$ components of this space. Evidently, the sum of all components for a given potential well transforms as a totally symmetric quantity in the harmonic space. Moreover, we claim that (suitably prepared) repulsive states can also be accommodated in this space.

However a generalized P.T.-potential will involve the coupling of several attractive and repulsive potentials and thus break the symmetry of this angular space.

A more elaborate treatment of this coupling and the descent in symmetry it represents, shall be presented in further studies.

7. Conclusions

A single particle representation of vibrational states has been described. The assignments of spurious centre-of-mass motions in such a scheme, leads to the removal of the mass-dipole. Molecular normal modes can be described in this representation. So far [1] only angular quantum numbers have been used. The introduction of radial information might provide a useful extension of the subduction process, especially in cluster compounds, such as boron hydrides, where more than one coordination shell is present. Vibronic coupling implies a product of the vibrational representations with the momentum representation of electronic motions.

We observed that conservation conditions impose very strict boundary conditions on potential walls of finite square box models. An attempt was made to examine continuous potentials that would incorporate these boundary conditions. The resulting loop equations in general describe a dissipation from a finite source under limiting conditions, and have their analogs in kinetics and stellar physics. We suggest that they might offer valuable potential shapes for anharmonic oscillators. The presently investigated P.T.-potentials are especially defective in the long-range region. Probably, consideration of the $\mathscr{C}_1(1)$-loop equation might suggest an improved description of this region.

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