Symmetry of the quadratic Zeeman effect for hydrogen

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The $O(4)$ symmetry of the hydrogen-atom degeneracy is exploited to obtain an exact separation of the quadratic Zeeman interaction on the Fock hypersphere in momentum space, and hence a complete classification of levels in the weak-field limit. The separation constant includes a double-minimum potential, and levels below the top of the barrier have an approximate $O(2)\times O(2)$ symmetry and vibrational structure. Levels above the top of the barrier have an approximate $O(3)$ symmetry, and a structure similar to that of an oblate symmetric top. The crossover between the two types of levels becomes sharper at high n, and is related to two different types of collective coupling of angular momentum and the Runge-Lenz vector.

Although the Schrödinger equation for hydrogen in a uniform magnetic field is nonseparable on account of the quadratic Zeeman interaction $H_Q=\frac{1}{8}\alpha^2B^2(x^2+y^2)$, recent empirical discoveries of near crossings,[1] degeneracies,[2] and l-mixing symmetry[3] at low fields offer compelling evidence for some kind of approximate separation. We investigate this idea in the present paper by analyzing the structure of H_Q in the weak-field limit $B\to 0$, where there is an exact $O(4)$ symmetry for constant energy $E_0=-1/2n^2$ (a.u.). The key point is that H_Q is an algebraic quadratic invariant for a subgroup chain $O(4)\supset D_{\infty h}\supset O(2)$ which breaks the hydrogen degeneracy, and this is linked to an exact separation on the four-dimensional Fock hypersphere in momentum space. The approximate symmetries of Refs. 2 and 3 are found as special limiting cases of the general separability, in which perturbation formulas for the energy suggest rotations and vibrations on different regions of the $O(4)$ sphere.

The hydrogen $O(4)$ algebra is generated by $\vec{L}=\vec{r}\times\vec{p}$ and the Runge-Lenz vector

$$\vec{A}=[\tfrac{1}{2}(\vec{L}\times\vec{p}-\vec{p}\times\vec{L})+\hat{r}]/p_0 ,$$

with $p_0=(-2E_0)^{1/2}$, with quadratic invariants $\vec{L}^2+\vec{A}^2=n^2-1$ and $\vec{L}\cdot\vec{A}=0$. The momentum-space wave function is

$$\psi(\vec{p})=(p_0^2+p^2)^{-2}\Phi(\vec{\xi},\xi_4) ,$$

where Φ is expressed in terms of the Fock coordinates $\vec{\xi}=2p_0\vec{p}/(p_0^2+p^2)$ and $\xi_4=(p_0^2-p^2)/(p_0^2+p^2)$ which satisfy $\xi_x^2+\xi_y^2+\xi_z^2+\xi_4^2=1$ for a unit sphere in four dimensions.[4-6] We classify the wave function Φ with $\pm$ symmetry labels for three types of parity on the $O(4)$ sphere: the usual inversion operation $\Pi(\vec{\xi}\to-\vec{\xi})$, and two reflections $\Pi_z(\xi_z\to-\xi_z)$ and $\Pi_4(\xi_4\to-\xi_4$, or $p\to p_0^2/p)$. Any *one* of the parities suffices to determine the other two, because of the relationships $\Pi_4=\Pi(-1)^{n-1}$ and $\Pi_z=\Pi(-1)^m$. Here m is the eigenvalue of L_z, which commutes with H_Q. The usual spherical basis for the subgroup chain $O(4)\supset O(3)\supset O(2)$ with $\vec{L}^2=l(l+1)$, for example, has

$$\begin{aligned}\xi_4&=\cos\chi,\quad (0\le\chi\le\pi)\\ \xi_z&=\sin\chi\cos\theta ,\\ \xi_y&=\sin\chi\sin\theta\sin\phi ,\\ \xi_x&=\sin\chi\sin\theta\cos\phi ,\end{aligned}\tag{1}$$

and the separated wave function (unnormalized) is

$$\Phi_{nlm}=(\sin\chi)^l C_{n-l-1}^{l+1}(\cos\chi)Y_{lm}(\theta,\phi) ,\tag{2}$$

where $C_b^a(t)$ is a Gegenbauer polynomial. The parities are $\Pi=(-1)^l$, $\Pi_z=(-1)^{l-m}$, and $\Pi_4=(-1)^{n-l-1}$.

General considerations of quadratic invariants show that altogether there are six separable bases on the $O(4)$ sphere, whereas there are only four in position space.[7] Our investigation shows the Zeeman wave function has a separable representation

$$\Phi=A(\alpha)B(\beta)\exp(im\phi)$$

in elliptic cylindrical coordinates (type I) defined as

$$\begin{aligned}\xi_4&=\mathrm{cn}\alpha\,\mathrm{cn}\beta ,\\ \xi_z&=\mathrm{dn}\alpha\,\mathrm{sn}\beta ,\\ \xi_y&=\mathrm{sn}\alpha\,\mathrm{dn}\beta\sin\phi ,\\ \xi_x&=\mathrm{sn}\alpha\,\mathrm{dn}\beta\cos\phi ,\end{aligned}\tag{3}$$

with arguments $0\le\alpha\le 2K$ for Jacobian elliptic functions of modulus q $(0\le q^2\le 1)$, and $-K'\le\beta\le K'$ for complementary modulus $q'=(1-q^2)^{1/2}$. The separated equations for $A(\alpha)$ and $B(\beta)$ are

$$\frac{1}{\mathrm{sn}\alpha}\frac{d}{d\alpha}\left[\mathrm{sn}\alpha\frac{dA}{d\alpha}\right] - \left[\frac{m^2}{\mathrm{sn}^2\alpha}+q^2(n^2-1)\mathrm{sn}^2\alpha-b\right]A=0\,, \quad (4)$$

$$\frac{1}{\mathrm{dn}\beta}\frac{d}{d\beta}\left[\mathrm{dn}\beta\frac{dB}{d\beta}\right] + \left[\frac{q^2m^2}{\mathrm{dn}^2\beta}+(n^2-1)\mathrm{dn}^2\beta-b\right]B=0\,, \quad (5)$$

where b is an eigenvalue of the operator[8]

$$\hat{b}=n^2-1+L_z^2-A_z^2-(1-q^2)\vec{\mathrm{L}}^2\,.$$

A complete classification of the spectrum is obtained by solving for either A or B, since the two equations are related by the transformation $\alpha\to K+iK'+i\beta$ which takes $\mathrm{sn}\alpha\to dn\beta/q$. Parities are determined from either the symmetry of A under

$$\Pi_4(\alpha\to 2K-\alpha)$$

and

$$\Pi_z(\alpha\to 2K+2iK'-\alpha)\,,$$

or the symmetry of B under $\Pi_4(\beta\to 2K'-\beta)$ and $\Pi_z(\beta\to-\beta)$. Although we shall be concerned with the general form of the solutions for all values of q^2 that could be related to approximate symmetries, there is only one value which separates H_Q on the $O(4)$ sphere. This is found from matrix elements of the operator $x^2+y^2\to\hat{\epsilon}$ for constant n. Similar $O(4)$ operator replacements for constant n are

$$\vec{r}\to\tfrac{3}{2}n\vec{\mathrm{A}}\,,$$

$$\hat{r}\to\vec{\mathrm{A}}/n\,,$$

and

$$r^2\to\tfrac{1}{2}n^2(5n^2+1-3\vec{\mathrm{L}}^2)\,,$$

from which it may be seen that

$$\hat{\epsilon}=\tfrac{1}{2}n^2(5\hat{b}+4-4L_z^2)\,, \quad (6)$$

with the parameter $q^2=\frac{1}{5}$.

Reference 7 outlines a procedure for constructing four distinct types of solutions which correspond in our notation to pairs of parity symmetries $\Pi_4\Pi_z=++,\,-+,\,+-$, and $--$. Here we give a similar method which leads to a more compact representation of the exact solutions of $A(\alpha)$, based on a series expansion

$$A(\alpha)=\mathrm{dn}^t\alpha\,\mathrm{sn}^m\alpha\sum_{r\ge 0}A_r\mathrm{cn}^r\alpha\,, \quad (7)$$

with $m\ge 0$, and $t=0$ or 1 for states with parity $\Pi_z=(-1)^t$, $\Pi_4=(-1)^{n-1-m-t}$, and $\Pi=(-1)^{m+t}$. The coefficients A_r for *even* $(\Pi_4=+1)$ or *odd* $(\Pi_4=-1)$ values of r satisfy the recurrence relation

$$(1-q^2)(r+1)(r+2)A_{r+2}+\{b-q^2[n^2-1-(r+t)^2+m^2]-(1-q^2)(m+r)(m+r+1)\}A_r + q^2[n^2-(m+r+t-1)^2]A_{r-2}=0\,, \quad (8)$$

with $A_{-2}=A_{-1}=0$. When $0<q^2<1$ the series terminates if $A_{n-m-t+1}=0$. The eigenvalues b are roots of the corresponding secular equation, which leads to the condition $\Delta_{n-1-m-t}=0$ in the recurrence relation

$$\Delta_r=\{q^2[n^2-1-(r+t)^2+m^2]+(1-q^2)(m+r)(m+r+1)-b\}\Delta_{r-2} - q^2(1-q^2)r(r-1)[n^2-(m+r+t-1)^2]\Delta_{r-4}\,, \quad (9)$$

with $\Delta_{-2}=\Delta_{-1}=0$ and $\Delta_0=\Delta_1=1$. The roots for each value of m may be labeled b_i, where i is the number of nodes in the wave function $A(\alpha)$. There are $n-m$ values with $b_0<b_1<\cdots<b_{n-1-m}$ and parities $\Pi_4=(-1)^i$, $\Pi=(-1)^{n-1-i}$, and $\Pi_z=(-1)^{n-1-m-i}$.

The Zeeman levels have two approximate-symmetry classifications, related to the correlation of eigenvalues of $\hat{b}$ between two exact symmetry limits $O(4)\supset O(3)\supset O(2)$ at $q^2=0$ and $O(4)\supset O(2)\times O(2)$ at $q^2=1$. These correspond, respectively, to the approximate-symmetry bases for Zeeman levels investigated in Refs. 3 and 2. Here the $O(3)$ symmetry at $q^2=0$ is related to the diagonal operator $\hat{b}\to\vec{\Lambda}^2=\lambda(\lambda+1)$, with the angular momentum vector $\vec{\Lambda}=(A_x,A_y,L_z)$ and $|m|\le\lambda\le n-1$. Rotations for the group $O(3)_\lambda$ leave $\xi_x^2+\xi_y^2+\xi_4^2$ invariant in Fock space, whereas the usual spatial rotations for the group $O(3)_l$ leave $\xi_x^2+\xi_y^2+\xi_z^2$ invariant. The transformation between

the two $O(3)$ bases is therefore related to exchange of the two coordinates ξ_z and ξ_4. This is seen in elliptic cylindrical coordinates by taking the appropriate limits

$$\mathrm{cn}\alpha \rightarrow \cos\alpha (0 \leq \alpha \leq \pi)$$

and

$$\mathrm{sn}\beta \rightarrow \tanh\beta \equiv \cos\gamma (0 \leq \gamma \leq \pi) ,$$

which leads to

$$\begin{aligned} \xi_z &= \cos\gamma , \\ \xi_4 &= \sin\gamma \cos\alpha , \\ \xi_y &= \sin\gamma \sin\alpha \sin\phi , \\ \xi_x &= \sin\gamma \sin\alpha \cos\phi , \end{aligned} \tag{10}$$

and the wave function (unnormalized)

$$\Phi_{n\lambda m} = (\sin\gamma)^{\lambda} C^{\lambda+1}_{n-\lambda-1}(\cos\gamma) Y_{\lambda m}(\alpha,\phi) , \tag{11}$$

with $\Pi_4 = (-1)^{\lambda-m}$, $\Pi = (-1)^{n-1-\lambda+m}$, and $\Pi_z = (-1)^{n-1-\lambda}$. The leading-order perturbation expansion of $\hat{b} = \vec{\Lambda}^2 + q^2(L_x^2 + L_y^2)$ for $q^2 \simeq 0$ is

$$b \simeq \lambda(\lambda+1) + q^2 \left[\frac{[2n^2 - 2\lambda(\lambda+1)+1][\lambda(\lambda+1)-1+m^2]}{4\lambda(\lambda+1)-3} - 1 \right] . \tag{12}$$

At $q^2 = 1$ the operator $\hat{b} \rightarrow n^2 - 1 + L_z^2 - A_z^2$ is related to a reduction of the elliptic cylindrical coordinates to ordinary cylindrical coordinates[7] for the $O(2)\times O(2)$ symmetry of the linear Stark effect, which separates in parabolic coordinates in position space. Diagonal operators for states of definite parity are $L_z = m$ and $A_z^2 = k^2$, with $k = n - |m| - 1, n - |m| - 3, \ldots, 0$ or 1. There is a twofold degeneracy of states of opposite parity for each value of m when $k > 0$, and one state with $\Pi_4 = \Pi_z = +1$, $\Pi = (-1)^{n-1}$ when $k = 0$. The leading-order perturbation formula when $q^2 \simeq 1$ is

$$b \simeq \tfrac{1}{2}(1+q^2)(n^2 - 1 + m^2 - k^2) . \tag{13}$$

The Stark quantization of $\hat{b}$ is very similar to that of two independent two-dimensional oscillators, if we interpret $v \equiv n - 1 - k$ as a quantum number for vibrations. The complete hiearchy of quantum numbers in this classification is

$$\begin{aligned} v &= 0,1,2,\ldots,n-1, \quad \Pi = (-1)^{n-1} \\ &= 0,1,2,\ldots,n-2, \quad \Pi = (-1)^{n} \\ |m| &= v, v-2, \ldots, 1 \text{ or } 0 . \end{aligned} \tag{14}$$

Figure 1 depicts the correlation of λ and v for arbitrary m.

The degree of $O(3)$ or $O(2)\times O(2)$ symmetry in actual wave functions depends on the value of q^2. On account of the relatively small value $q^2 = \frac{1}{5}$ for the Zeeman effect, the $O(3)_\lambda$ symmetry is strong for most levels. We find this "rotational" symmetry breaks down for the lower levels (low m and λ) in each shell at high n (> 10), however, on account of an approximate vibrational symmetry that is more closely related to the degeneracy in the $O(2)\times O(2)$ classification. This is illustrated in Fig. 2 for $n = 20$, $m = 0$. Note, in particular, the crease of avoided crossings along the critical line $b^* = q^2(n^2-1)$. Levels with $b > b^*$ tend to have the structure of the $O(3)$ symmetry classification at $q^2 = 0$, while the level structure for $b < b^*$ includes twofold accidental degeneracies more typical of the $O(2)\times O(2)$ symmetry at $q^2 = 1$. This division of levels into two different types of symmetry structure becomes even more evident at higher n, as shown in Fig. 3. In the case of the Zeeman effect the calculations suggest b^* corresponds approximately to the quantum numbers $v^* \simeq \lambda^* \simeq \frac{1}{4}n$.

We interpret the critical value $b^* = q^2(n^2-1)$ as the value of b at the top of the potential barrier $q^2(n^2-1)\mathrm{sn}^2\alpha$ in the wave equation (4) for $A(\alpha)$.

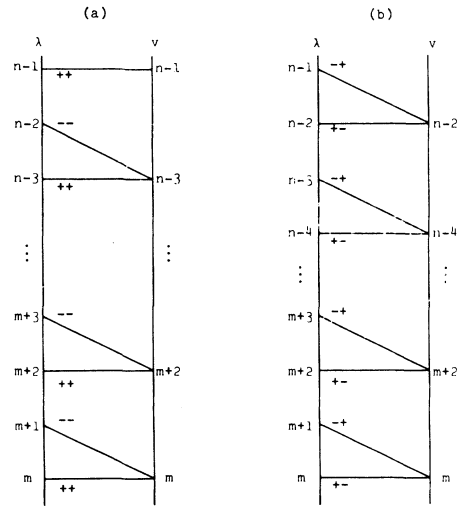

FIG. 1. Correlation of $O(4)$ quantum numbers $\lambda(q^2=0)$ and $v(q^2=1)$, with $m \geq 0$ and (a) $n-m-1 = even$; (b) $n-m-1 = odd$. Parity labels are $\Pi_4\Pi_z$.

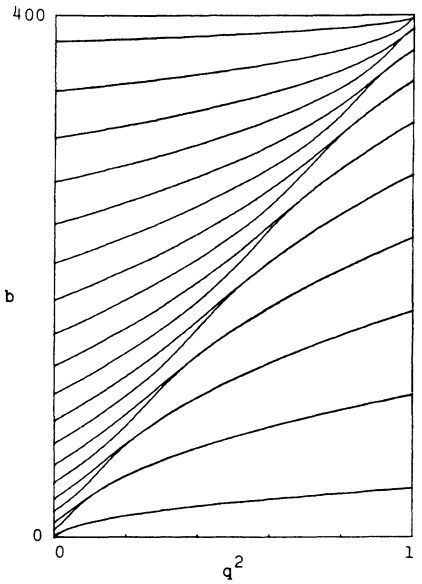

FIG. 2. Curves show eigenvalues of $\hat{b}$ as continuous functions of q^2 for $n=20$, $m=0$.

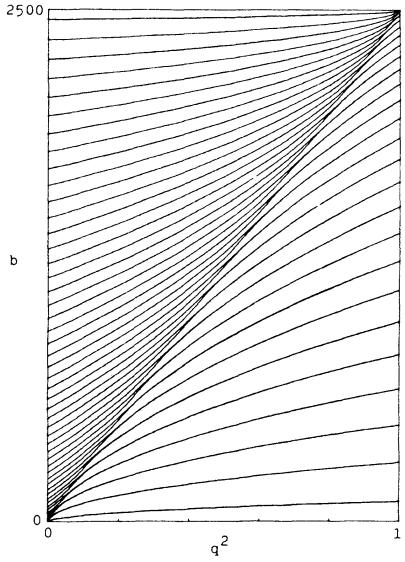

FIG. 3. Curves show eigenvalues of $\hat{b}$ as continuous functions of q^2 for $n=50$, $m=0$.

This maximum occurs when $\alpha=K$, and hence $p_z^2=0$ and $\xi_x^2+\xi_y^2+\xi_4^2=1$. Wave functions $A(\alpha)$ with $b\gg b^*$ tend to have the largest amplitudes in this region, and hence the highest degree of $O(3)_\lambda$ symmetry. Wave functions of levels with $b\ll b^*$, on the other hand, tend to be localized near a minimum in the potential. There are two minima at $\alpha=0$ and $\alpha=2K$, where $p_x^2+p_y^2=0$ and $\xi_z^2+\xi_4^2=1$. When barrier penetration is weak, for example, at very high n, the two wells support identical sets of levels and therefore account for the accidental twofold degeneracy of states when $b<b^*$. Interaction of the states, and hence splitting of the degeneracy, tends to increase as b approaches the top of the barrier. The splitting leads to states of definite parity Π_4, with the lower (higher) level in each pair having $\Pi_4=+1(-1)$. A similar investigation of the level structure of $\hat{b}$ with $m>0$ shows the crease of avoided crossings is described by $b^*=m^2+q^2(n^2-1)$, which corresponds to a maximum in the potential

$$m^2/\mathrm{sn}^2\alpha+q^2(n^2-1)\mathrm{sn}^2\alpha$$

in (4).

Estimates of the low-lying eigenvalues follow from a harmonic approximation of wave functions at very high n, assuming no interaction between the wells. This is obtained from an expansion of (4) with respect to the parameter $\sigma=[q^2(n^2-1)]^{-1/2}$ after making the substitution $\mathrm{sn}\alpha=\rho\sigma^{1/2}$. The result is an equation $(\hat{b}-b)A=0$, with

$$\begin{aligned}
&\sigma\hat{b}=\hat{b}_0+\sigma\hat{b}_1+\sigma^2\hat{b}_2\ ,\\
&\hat{b}_0=-\frac{d^2}{d\rho^2}-\frac{1}{\rho}\frac{d}{d\rho}+\frac{m^2}{\rho^2}+\rho^2\ ,\\
&\hat{b}_1=(1+q^2)\left[\rho^2\frac{d^2}{d\rho^2}+2\rho\frac{d}{d\rho}\right]\ ,\\
&\hat{b}_2=q^2\left[\rho^4\frac{d^2}{d\rho^2}-3\rho^3\frac{d}{d\rho}\right]\ ,
\end{aligned}\tag{15}$$

and $0\le\rho\le\sigma^{-1/2}$. The operator $\hat{b}_0$ is essentially the radial Hamiltonian for a two-dimensional oscillator, with eigenfunctions

$$A_0=C\rho^m\exp(-\tfrac{1}{2}\rho^2)L_r^m(\rho^2)$$

when $\sigma=0$. Here C is a normalization constant, $m\ge0$, and $r=\frac{1}{2}(v-m)$. Leading-order coefficients in the expansion $\sigma b=b_0+\sigma b_1+\cdots$ are found to be

$$b_0=2(v+1)$$

and

$$b_1=-\tfrac{1}{2}(q^2+1)[(v+1)^2+1-m^2]\ .$$

Neglecting higher-order terms in the expansion leads to the following expression for eigenvalues of the quadratic Zeeman operator $\hat{\epsilon}$:

$$\epsilon(nvm)\simeq\tfrac{1}{2}n^2[2\omega(v+1)-3(v+1)^2+1-m^2]\ ,\tag{16}$$

with $\omega=[5(n^2-1)]^{1/2}$. The level structure in the

lower region of each shell then, is essentially that of a harmonic oscillator with "anharmonic" corrections.

Estimates of Zeeman levels in the $O(3)$ symmetry regime follow from perturbation theory with (6) expressed in the form

$$\hat{\epsilon}=\tfrac{1}{2}n^2(n^2+3+4\vec{\Lambda}^2-3L_z^2-A_z^2) .$$

Nonzero matrix elements, which have the selection rule $\Delta\lambda=0,\pm2$, are

$$\langle n\lambda m\,|\,\hat{\epsilon}\,|\,n\lambda-2m\rangle=-n^2\left[\frac{(n^2-\lambda^2)[n^2-(\lambda-1)^2](m^2-\lambda^2)[m^2-(\lambda-1)^2]}{4(2\lambda-3)(2\lambda+1)(2\lambda-1)^2}\right]^{1/2},$$
$$\langle n\lambda m\,|\,\hat{\epsilon}\,|\,n\lambda m\rangle=n^2\left[\frac{(n^2+9w+5)(w+m^2-1)+4w(1-4m^2)}{4w-3}\right], \tag{17}$$

with $w=\lambda(\lambda+1)$. The off-diagonal coupling weakens with increasing λ and when $\lambda\gg m$ the levels are described approximately by the expression

$$\epsilon(n\lambda m)\simeq\tfrac{1}{4}n^2[n^2+9+9\lambda(\lambda+1)-16m^2] . \tag{18}$$

This is qualitatively similar to the level structure of an oblate symmetric top. Breakdown of the classification at low λ is evident in crossings of diagonal matrix elements in (17). Examples are the crossings of $\lambda=0$ and 2 for $m=0$ near $n=12$, and of $\lambda=2$ and 4 for $m=2$ near $n=15$. This can be lead to *inversions* of λ assignments made from overlaps of wave functions instead of correlations of levels as a function of q^2.

A complete classification of the levels for $n=15$ is shown in Fig. 4. These are labeled with Π and λ (from wave-function overlap) and with v at lower

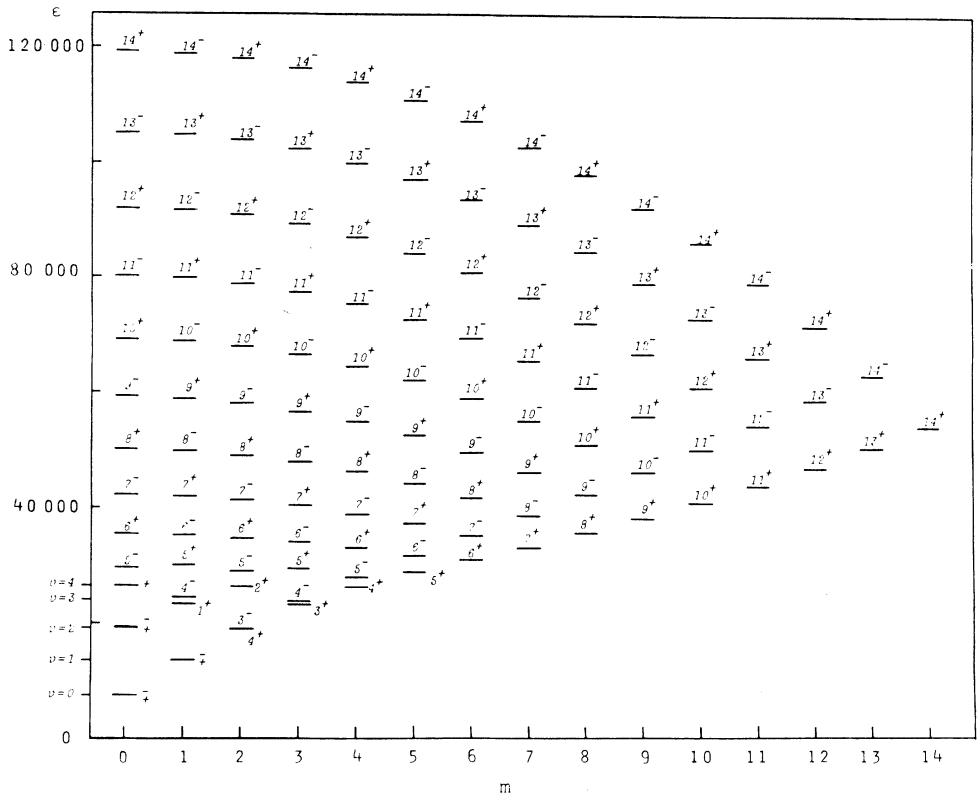

FIG. 4. $O(4)$ classification of quadratic Zeeman eigenvalues for the shell $n=15$. The inverted order for λ in some lower levels is the classification obtained by computing overlaps of wave functions with $O(3)_\lambda$ states, instead of correlating eigenvalues as a function of q^2. The position of the barrier maximum b^* corresponds to $\epsilon^*=\frac{1}{2}n^2(n^2+3+m^2)$, and is seen here in the region $v\simeq4,\lambda\simeq5$.

energies. The crossover from a vibrationlike structure to a rotationlike structure occurs at $v^* \simeq 4$. Low-lying levels for $n=16$ would look very similar, except that the parity Π is reversed. In general, the lowest level for each m has $\Pi_4=+1$, and hence $\Pi(-1)^{n-1}$, with alternating signs for successively higher levels. The highest level for each m always has $\Pi_z=+1$, and hence $\Pi=(-1)^m$. With increasing n the lower levels tend to scale as n^3 [cf. Eq. (16)] and the higher levels as n^4 [cf. Eq. (18)].

Rotational and vibrational level structure is generally found in many-particle systems when there are collective excitations associated with interparticle coupling. There is a similar interpretation of the hydrogen Zeeman levels in terms of two quasiparticles represented by the two commuting angular momentum vectors $\vec{F}=\frac{1}{2}(\vec{L}+\vec{A})$ and $\vec{G}=\frac{1}{2}(\vec{L}-\vec{A})$ which satisfy $\vec{F}^2=\vec{G}^2=a(a+1)$, with $a=\frac{1}{2}(n-1)$. The quasiparticle representation of the elliptic cylindrical constant of motion is

$$\hat{b}=2(1+q^2)a(a+1) +4F_zG_z-2(1-q^2)\vec{F}\cdot\vec{G}\ , \tag{19}$$

with the independent-particle limit corresponding to diagonalization of F_z and G_z in the Stark basis when $q^2=1$. The basis for $O(3)_l$ is associated with the coupling scheme $\vec{L}=\vec{F}+\vec{G}$ for diagonalization of $\hat{b}$ when $q^2\to\infty$. The basis for $O(3)_\lambda$ is associated with the nonstandard coupling

$$\vec{\Lambda}=(F_x-G_x,F_y-G_y,F_z+G_z)$$

for diagonalization of $\hat{b}$ when $q^2=0$. It is very interesting to note that the same type of coupling has been discovered in the problem of electron correlation in simple atoms and molecules[9–11] where there are also collective excitation spectra. The transformation between the two $O(3)$ bases is found by working through the Stark basis, with the result

$$|n\lambda m\rangle=\sum_l |nlm\rangle C^l_{n\lambda m}\ ,$$

$$C^l_{n\lambda m}=\sum_{\alpha,\beta}\langle a\alpha,a\beta\,|\,lm\rangle\langle a\alpha,a\beta\,|\,\lambda m\rangle(-1)^{a-\beta}\ , \tag{20}$$

in terms of the usual Clebsch-Gordan coupling coefficients. A similar transformation was found in Ref. 3. In position space the definition of $O(3)_\lambda$ states in (20) is consistent with a radial basis $R_{nl}(r)$ in which functions with the same n have the same phase at large r. It is not known at present whether there is another set of coordinates which could be used to represent the states more efficiently in position space.

There is another connection between the two $O(3)$ bases which suggests the transformation could be carried out by application of an electric field. This is related to the fact that the interconversion corresponds to an exchange of ξ_z and ξ_4 in Fock space. Except for a phase factor, this can be accomplished by rotating the wave function by 90° in the $\xi_z\xi_4$ plane. In ordinary three-dimensional coordinates the rotation is effected with the unitary operator $R=\exp(ivA_z)$ when $v=\pm\pi/2$. If ψ_{nlm} is an eigenfunction of the $O(3)_l$ operator $\vec{L}^2$, then $R\psi_{nlm}\equiv\psi'_{n\lambda m}$ is an eigenfunction of the $O(3)_l$ operator $\vec{\Lambda}^2$ with $\lambda=l$. The inverse transformation is $\psi_{nlm}=R^{-1}\psi'_{n\lambda m}$ with $l=\lambda$. The key point of interest is that R represents a special case of the time-evolution operator for the linear Stark effect if we neglect n-changing transitions. For constant n the time-dependent Stark field $V=-F(t)z$ is represented by $V\to-\frac{3}{2}nF(t)A_z$, which leads to the evolution operator[12]

$$U(t)=\exp(i\omega A_z)\ ,\quad \omega=\int_0^t \tfrac{3}{2}nF(t)dt\ . \tag{21}$$

In particular, $U(t)=R$ when $\omega=\pi/2(\mathrm{mod}\pi)$. Selective radiative excitation of a high-λ Zeeman level followed by an appropriate electric field pulse would lead to a high-l state, with $l=\lambda$, for example.

Finally, we should like to point out that during preparation of this manuscript we have learned of another investigation of Zeeman levels for constant energy by Goebel and co-workers at Wisconsin. Using classical mechanics, they have found a constant of motion $A_x^2+A_y^2+\frac{1}{5}(L_x^2+L_y^2)$ that is essentially the same as our operator $\hat{b}$ at $q^2=\frac{1}{5}$.

Note added in proof. We have recently learned of a second semiclassical investigation of the approximate symmetry at high n [E. A. Soloviev, Zh. Eksp. Teor. Fiz. Lett. 34, 278 (1981)] from an English translation of the original work provided by Dr. C. W. Clark. Our present work is more general in the sense of providing in (6) the exact quantum representation of the Zeeman operator for all values of n, and an unambiguous classification of levels via the Sturm sequence associated with (9).

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