Case of broken symmetry in the quadratic Zeeman effect

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A particularly simple instance of broken symmetry arises in the problem of a hydrogen atom in a uniform magnetic field. In a limited sense, the magnetic Hamiltonian nearly commutes with the unit projection of the Runge-Lenz vector upon the field direction.

Zimmerman, Kash, and Kleppner have recently[1] given evidence for an approximate constant of the motion of a hydrogen atom in a uniform magnetic field; Ken Taylor and I have reported[2] similar findings, though with a different emphasis on their interpretation. The purpose of this communication is to identify an approximate constant of the motion visible at the level of perturbation theory; but one which, since it gives a connection between states of different parity, is not obviously related to the "experimental" data of the first two references.

Consider the Hamiltonian for a hydrogen atom (without spins or center of mass motion) in a uniform magnetic field $\vec{B}=B\hat{z}$, with the magnetic vector potential taken to be $\vec{A}=-\frac{1}{2}\vec{r}\times\vec{B}$:

$$H=\tfrac{1}{2}p^2-1/r+\beta l_z+\tfrac{1}{2}\beta^2 r^2\sin^2\theta \tag{1}$$

in atomic units. The parameter β is one half the magnetic cyclotron frequency, $2\beta=\omega_c=eB/mc$. Clearly l_z is a constant of the motion, so its associated linear Zeeman shift may simply be incorporated in the energy eigenvalue. Then

$$H'=H^C+\tfrac{1}{2}\beta^2H^M=H-\beta l_z\,, \tag{2}$$

where H^C is the ordinary Coulomb Hamiltonian and $H^M=r^2\sin^2\theta$. For terrestial laboratory fields β is small, e.g., $\beta=10^{-5}$ when $B=47$ kG, so for states with not too high principal quantum number n it is appropriate to treat the second term of (2) by degenerate perturbation theory (for 47 kG this is satisfactory for $n\lesssim 20$). In short, the lower part of the spectrum of (2) is generated to a good approximation by diagonalizing H^M within each manifold of hydrogenic states of constant principal quantum number n, with n running from one up to some maximum value.

Since H^M is invariant under inversion of all space coordinates, the standard method of carrying out the calculation has been to treat separately the states of even and odd parity. In the usual basis of states $|nlm\rangle$ with definite principal quantum number n, angular momentum l and projection $m=l_z$, the matrix elements $\langle nlm|H^M|nl'm\rangle$ vanish unless $|l-l'|\leq 2$. Thus in this form the problem reduces for each n to the diagonalization of two separate tridiagonal matrices. The matrix elements involved are simple algebraic functions of n, l, and m.[3]

I shall, however, consider the problem as it appears in the parabolic coordinate system. As is well known, the Schrödinger equation for H^C separates in the system of coordinates $\xi=r+z$, $\eta=r-z$. Its normalized eigensolutions are

$$|n_1n_2m\rangle=\frac{e^{im\phi}}{(2\pi)^{1/2}}u_{n_1}(\xi)u_{n_2}(\eta)\,, \tag{3}$$

where

$$u_{n_i}(x)=\frac{2^{1/4}}{n^{1+|m|/2}}\left(\frac{n_i!}{(n_i+|m|)!}\right)^{1/2}e^{-x/2n}x^{|m|/2}L_{n_i}^{|m|}(x/n)\,. \tag{4}$$

The $L_n^{|m|}$ are the associated Laguerre functions as defined by Szego.[4] The principal quantum number $n=n_1+n_2+|m|+1$, and n_1,n_2 are non-negative integers which for given n assume all values consistent with this equality. The solutions (3) are not eigenfunctions of the parity operator P; clearly, since P interchanges ξ and η,

$$P|n_1n_2m\rangle=(-1)^m|n_2n_1m\rangle\,. \tag{5}$$

In this coordinate system H^M takes the form

$$H^M=r^2\sin^2\theta=\xi\eta\,, \tag{6}$$

so that in contrast to the spherical polar system it is linear, rather than quadratic, in the separate orthogonal coordinates, and also symmetric in those coordinates. An obvious consequence of the second fact is that $\langle n_1n_2m|H^M|n_1'n_2'm\rangle=\langle n_2n_1m|H^M|n_2'n_1'm\rangle$. As regards the linear dependence, a short calculation shows that within a given n manifold, for which always $n_1'=n_1+j$ and $n_2'=n_2-j$, the matrix element $\langle n_1n_2m|H^M|n_1+jn_2-jm\rangle$ vanishes except when $j=0,\pm1$. For completeness I give the correct expressions for these matrix elements, though the remaining part of the argument does not really depend upon them:

$$\langle n_1 n_2 m | H^M | n_1 n_2 m \rangle = (2n_1 + |m|+1)(2n_2 + |m|+1)n^2 + \frac{n(2n_1 + |m|+1)}{2} [n_2(n_2 + |m|) + (n_2+1)(n_2+1+|m|)] + \frac{n(2n_2 + |m|+1)}{2} [n_1(n_1 + |m|) + (n_1+1)(n_1+1+|m|)], \quad (7)$$

$$\langle n_1 n_2 m | H^M | n_1+1\ n_2-1\ m \rangle = 2n^2[(n_1+1)(n_1+1+|m|)n_2(n_2+|m|)]^{1/2}. \quad (8)$$

Therefore, if the states $|n_1 n_2 m\rangle$ are ordered according to increasing value of n_1, the $n-m$ dimensional matrix of H^M is tridiagonal. Henceforth I shall discuss only the cases for which this dimensionality is an even number, the numbers of even parity and of odd parity states being then identical. When $n-m$ is odd the qualitative conclusions turn out very little different from those drawn below, and they can easily be developed along the same line of argument.

So, let $n-m=2\mu$, and consider the matrix of H^M in the standard basis defined above: the first state $|1\rangle$ being $|0\ 2\mu-1\ m\rangle$, the second $|2\rangle = |1\ 2\mu-2\ m\rangle$, and so on. The symmetry of the magnetic Hamiltonian under interchange of n_1, n_2 then gives $H^M_{ij} = H^M_{2\mu+1-i\ 2\mu+1-j}$. Now recombine the parabolic functions to form a new basis of functions with definite parity, as follows:

$$|1'\rangle = 2^{-1/2}(|1\rangle + |2\mu\rangle) = 2^{-1/2}(|0\ 2\mu-1\ m\rangle + |2\mu-1\ 0\ m\rangle),$$

$$|2'\rangle = 2^{-1/2}(|2\rangle + |2\mu-1\rangle),$$

$$\vdots$$

$$|\mu'\rangle = 2^{-1/2}(|\mu\rangle + |\mu+1\rangle),$$

$$|(\mu+1)'\rangle = 2^{-1/2}(|1\rangle - |2\mu\rangle),$$

$$|(\mu+2)'\rangle = 2^{-1/2}(|2\rangle - |2\mu-1\rangle),$$

$$\vdots$$

$$|(2\mu)'\rangle = 2^{-1/2}(|\mu\rangle - |\mu+1\rangle).$$

An elementary manipulation then shows that the matrix of H^M in this new basis takes the form

$$(H^M)' = \begin{pmatrix} H^1 & 0 \\ 0 & H^2 \end{pmatrix}, \quad (9)$$

where H^1 and H^2 are both tridiagonal, and refer, respectively, to states with inversion parity $(-1)^m$ and $(-1)^{m+1}$. Moreover, H^1 and H^2 are *identical* except for their last diagonal elements: that is,

$$H^1_{ij} = H^2_{ij}, \quad (10)$$

unless $i=j=\mu$. A simple mechanical analogy for this problem is thus suggested. The eigenvalue spectrum of H^1 is equivalent to the set of frequencies of normal modes of oscillation of a system of μ collinear point mass particles, each connected to its nearest neighbors by springs, and with the two end particles attached with springs to fixed walls. The masses of the particles and the force constants of the springs are generally not all equal. The spectrum of H^2 is represented by a similar mechanical system, which is in fact identical to that for H^1 except for the spring which connects one of the end particles to the wall. This end spring is, moreover, the stiffest in both systems. One then expects that those modes of oscillation which occasion only small displacements of this stiffest spring, will be very nearly equal in frequency and relative amplitude for the two systems. Calculation readily confirms this. For $n=40$, $m=0$, as an example, the three lowest eigenvalues of H^1 and H^2 coincide to thirteen, eleven, and seven decimal figures, respectively. It is also worth noting that $H^1_{\mu\mu} - H^2_{\mu\mu} = n^2(n^2-m^2)$. Thus the average shift of levels with parity $(-1)^m$—which is determined from the trace of H^1—is greater than the average shift of levels with the opposite parity. This is in accordance with our expectations, as states with parity $(-1)^m$ have finite amplitude in the plane $\theta=\pi/2$ where H^M obtains its maximum.

To recapitulate, the matrices for even and odd states are nearly identical; or in other words, the exchange of each even state with its odd partner yields only a minor change in the Hamiltonian matrix. So it is possible to state in a well-defined sense that the Hamiltonian H^M *nearly commutes* with the operator which affects this exchange: the commutator being representable as a matrix consisting extirely of zeros but for the last diagonal element. This is about as elementary an example of symmetry breaking as I can envisage.

Now there is a familiar dynamical operator which does exchange even states with odd in the right way. The parabolic basis functions $|n_1 n_2 m\rangle$ are simultaneously eigenfunctions of the energy, the z component of the angular momentum, and the z component of the Runge-Lenz vector $\vec{A}$ (not to be confused with the vector potential):

$$\vec{A} = \tfrac{1}{2}(\vec{p} \times \vec{l} - \vec{l} \times \vec{p}) - \vec{r}/r. \tag{11}$$

The classical analog of this operator is a vector pointing along the major axis of a Kepler orbit from its focus to its perihelion, and the magnitude of the vector gives the eccentricity of the orbit. The uncertainty principle prevents one from specifying more than one component of $\vec{A}$ simultaneously. The eigenvalues of A_z in the parabolic basis are given by[5]:

$$A_z \,|n_1 n_2 m\rangle = n^{-1}(n_2 - n_1)\,|n_1 n_2 m\rangle. \tag{12}$$

Thus the sign Σ of A_z is well defined in this basis as the operator

$$\Sigma = (A_z^2)^{-1/2} A_z, \tag{13}$$

and it is clear that Σ effects the required change of even to odd states. So, the *direction* of the Runge-Lenz vector is, in this sense, nearly a constant of the motion of the perturbed Hamiltonian. (Though one cannot define the components of A perpendicular to the field as well in quantum mechanics, in the classical picture one would get a precession of A about the field direction induced by the linear Zeeman term.)

Whether this observation remains relevant beyond the realm of perturbation theory I shall leave as an open question. Ken Taylor and I have indeed observed, in much more elaborate calculations, some remarkable near degeneracies of even and odd levels in the Balmer emission lines, though these are characterized by different values of l_z as well.[6] Nevertheless, it may aid the successful placing of some small pieces in what remains a very large and complicated puzzle.

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[5]L. Landau and E. M. Lifshitz, *Quantum Mechanics: Non Relativistic Theory*, 2nd ed. (Pergamon, Oxford, 1965).

[6]C. W. Clark and K. T. Taylor, Abstracts of the First European Conference on Atomic Physics (1981).