# The perturbed hydrogen atom: some new algebraic results

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**Abstract.** We have employed algebraic methods to calculate the bound-state spectra of a non-relativistic hydrogen atom subjected to a wide class of perturbations. Our procedure exploits the linearity of the complete (perturbed) Hamiltonian in the generators of the SO(2, 2) Lie algebra which follows naturally from the separation of variables in Schrödinger's equation in parabolic coordinates. Appropriate transformations then allow the Hamiltonian to be expressed as a linear combination of the compact generators of the two underlying SO(2, 1) algebras. We give some examples for which the bound-state spectra can be obtained completely analytically.

## 1. Introduction

It is well known that the Schrödinger theory for the Kepler problem can be treated algebraically by using irreducible unitary representations of the dynamical symmetry group SO(4, 2) (see, for example, Englefield 1972). Thus the bound states of the unperturbed non-relativistic hydrogenic Hamiltonian are described most conveniently in terms of two independent angular momentum vectors $F$ and $G$ (say) or, more precisely, of their sum and difference. Then, the orbital angular momentum given by $L = F + G$, and the Runge-Lenz vector which is proportional to $A = F - G$, both commute with the system Hamiltonian, while each of the vectors $F$, $G$ separately generates SO(4) symmetry. The corresponding treatment of some modified Coulomb potentials was given by Bednar (1973), who also employed algebraic methods to obtain approximate solutions to perturbation problems.

Recently, there has been considerable renewed interest in algebraic solutions of problems involving perturbed hydrogenic ions. Thus, many authors have treated the hydrogen atom in a strong magnetic field (see, for example, the work of Delande and Gay (1984, 1986), who include many of the earlier references), while Alhassid *et al* (1987) have, in addition, considered the van der Waals interaction.

In the present paper, we use the non-invariance Lie algebra SO(2, 2) in order to obtain the bound-state spectra of a hydrogen atom subjected to each of the following perturbations:

(i) $V = p_z$, the z component of the linear momentum;
(ii) $V = (r^2 - z^2)^{-1}$, where $r^2 = x^2 + y^2 + z^2$; and
(iii) $V = z/r$.

These are all examples of operators which may ultimately be expressed as *linear* functions of the generators of SO(2, 1) Lie algebras when the complete Schrödinger equation is expressed in parabolic coordinates. Our procedure then exploits the

possibility of performing transformations, or rotations, through appropriately chosen tilting angles, so as to diagonalise the compact generator $\Gamma_3$ of SO(2, 1) (cf Wybourne 1974). A similar procedure was followed by Benjamin and Levine (1986) in their treatment of resonances in a simple model of e-H$^-$ scattering.

## 2. Choice of the tilting angles

For simplicity, we suppose that the complete system Hamiltonian (*including* perturbations) may be expressed as a direct sum

$$H = H^{(1)} + H^{(2)}. \tag{1}$$

Here, each of the non-interacting $H^{(k)}$ ($k = 1, 2$) is of the form

$$H^{(k)} = a^{(k)}\Gamma_1^{(k)} + b^{(k)}\Gamma_2^{(k)} + c^{(k)}\Gamma_3^{(k)} \qquad k = 1, 2 \tag{2}$$

where the coefficients $\{a^{(k)}\}$ are scalars, and the two sets of generators $\Gamma_i^{(k)}$ ($i = 1, 2, 3$; $k = 1, 2$) each separately satisfies the usual SO(2, 1) commutation relations (for simplicity of presentation, we suppress the superscript $k$):

$$[\Gamma_1, \Gamma_2] = -i\Gamma_3 \qquad [\Gamma_2, \Gamma_3] = i\Gamma_1 \qquad [\Gamma_3, \Gamma_1] = i\Gamma_2. \tag{3}$$

We now employ the well known Campbell-Hausdorff formula:

$$e^{-A}B\,e^{A} = B + [B, A] + \frac{1}{2!}[[B, A], A] + \ldots \tag{4}$$

to obtain

$$e^{-i\theta\Gamma_2}\Gamma_1\,e^{i\theta\Gamma_2} = \Gamma_1 \cosh \theta + \Gamma_3 \sinh \theta \tag{5}$$

and

$$e^{-i\theta\Gamma_2}\Gamma_3\,e^{i\theta\Gamma_2} = \Gamma_1 \sinh \theta + \Gamma_3 \cosh \theta. \tag{6}$$

Then

$$\tilde{H} = e^{-i\theta_1\Gamma_2}H\,e^{i\theta_1\Gamma_2}$$

$$= (a \cosh \theta_1 + c \sinh \theta_1)\Gamma_1 + b\Gamma_2 + (a \sinh \theta_1 + c \cosh \theta_1)\Gamma_3 \tag{7}$$

and provided that $a^2 \neq c^2$ we may choose the tilting angle $\theta_1$ so that

$$\tanh \theta_1 = -a/c \tag{8}$$

with the result that

$$\tilde{H} = b\Gamma_2 + (c^2 - a^2)^{1/2}\Gamma_3. \tag{9}$$

A further rotation through a tilting angle $\theta_2$ chosen so that

$$\tanh \theta_2 = b/(c^2 - a^2)^{1/2} \tag{10}$$

(again, provided that $b^2 \neq c^2 - a^2$) yields

$$\tilde{\tilde{H}} = e^{-i\theta_2\Gamma_1}\tilde{H}\,e^{i\theta_2\Gamma_1} = (c^2 - a^2 - b^2)^{1/2}\Gamma_3. \tag{11}$$

Thus, the bound-state spectrum of $H$ may be obtained by diagonalising the *compact* generator $\Gamma_3$ of SO(2, 1).

If an eigenfunction of $\Gamma_3$ is denoted by $\psi$, the corresponding eigenfunction of $H$ is given simply by $e^{-i\theta_2\Gamma_1}e^{-i\theta_1\Gamma_2}\psi$. The order of these rotations may be reversed, even though $\Gamma_1$ and $\Gamma_2$ do not commute; the functions $e^{-i\theta_1\Gamma_2}e^{-i\theta_2\Gamma_1}\psi$ and $e^{-i\theta_2\Gamma_1}e^{-i\theta_1\Gamma_2}\psi$ differ only in a *phase* factor since, from (3), $[\Gamma_1, \Gamma_2] = -i\Gamma_3$ and $\psi$ is an eigenfunction of $\Gamma_3$. Note that, if either $a$ or $b$ vanishes, a single rotation suffices.

In order to exploit this result, it is necessary to express Schrödinger's equation in such a way that it becomes linear in the SO(2, 1) generators. This is achieved most conveniently by employing parabolic coordinates, and in the following section we give a brief treatment of the *unperturbed* hydrogen atom in order to establish notation. The various perturbation problems are then solved individually in a later section.

## 3. The unperturbed hydrogen atom

As is well known, Schrödinger's equation for a non-relativistic electron in a Coulomb field may be separated in parabolic coordinates (see, for example, Bethe and Salpeter 1957). By definition, we have

$$x = (\xi\eta)^{1/2}\cos\phi \qquad z = \tfrac{1}{2}(\xi - \eta) \qquad y = (\xi\eta)^{1/2}\sin\phi \qquad r = \tfrac{1}{2}(\xi + \eta) \qquad (12)$$

and if an eigenfunction is written

$$\Psi(x, y, z) = e^{\pm im\phi}\psi(\xi, \eta) \qquad (13)$$

and we employ the usual Hartree atomic units ($e = m = \hbar = 1$), Schrödinger's equation becomes, after multiplication by a factor $(\xi + \eta)$,

$$\left\{\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right) + \frac{\partial}{\partial\eta}\left(\eta\frac{\partial}{\partial\eta}\right) - \frac{m^2}{4}\left(\frac{1}{\xi} + \frac{1}{\eta}\right) + 1 + \tfrac{1}{2}E(\xi + \eta)\right\}\psi(\xi, \eta) = 0. \quad (14)$$

For *bound* states, the energy $E$ is real and negative, and it is convenient to change the *scale* of the variables $(\xi, \eta)$ according to

$$\xi \to \alpha\xi \qquad \eta \to \alpha\eta \qquad \alpha^2 = -2/E \qquad (15)$$

so that (14) becomes

$$\left\{\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right) + \frac{\partial}{\partial\eta}\left(\eta\frac{\partial}{\partial\eta}\right) - \frac{m^2}{4}\left(\frac{1}{\xi} + \frac{1}{\eta}\right) - (\xi + \eta) + \alpha\right\}\psi(\xi, \eta) = 0. \quad (16)$$

We now introduce the following realisation of the generators $S_i$ ($i = 1, 2, 3$) of SO(2, 1):

$$S_1 = \frac{1}{2}\left\{\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right) - \frac{m^2}{4\xi} + \xi\right\}$$

$$S_2 = i\left\{\xi\frac{\partial}{\partial\xi} + \frac{1}{2}\right\} \qquad (17)$$

$$S_3 = -\frac{1}{2}\left\{\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right) - \frac{m^2}{4\xi} - \xi\right\}.$$

It is easily verified that these satisfy the commutation relations (3). The Casimir operator of SO(2, 1) is given by

$$S^2 = S_1^2 + S_2^2 - S_3^2 = \tfrac{1}{4}(1 - m^2) \qquad (18)$$

and the basis states which simultaneously diagonalise $S^2$ and the *compact* generator $S_3$ are written conventionally $|n, k\rangle$ where $n$ is a non-negative integer and $k = \frac{1}{2}(|m|+1)$. Then (see, for example, Wybourne 1974)

$$S^2|n, k\rangle = \frac{1}{4}(1-m^2)|n, k\rangle = k(1-k)|n, k\rangle$$

$$S_3|n, k\rangle = (n+k)|n, k\rangle$$

$$S^+|n, k\rangle = [(n+1)(n+2k)]^{1/2}|n+1, k\rangle \tag{19}$$

$$S^-|n, k\rangle = [n(n+2k-1)]^{1/2}|n-1, k\rangle$$

where, as usual,

$$S^{\pm} = S_1 \pm iS_2. \tag{20}$$

If we define a similar set of generators $T_i$ ($i = 1, 2, 3$) in terms of the coordinate $\eta$, (16) may evidently be written

$$(S_3 + T_3 - \tfrac{1}{2}\alpha)\psi = 0 \tag{21}$$

and the two sets of generators $\{S_i\}$, $\{T_i\}$ together generate the SO(2, 2) Lie algebra as a direct sum of the underlying SO(2, 1) algebras. The direct product basis $|n_1, k\rangle \otimes |n_2, k\rangle$ now diagonalises the operators $(S^2, S_3, T^2, T_3)$ so that (21) yields

$$\tfrac{1}{2}\alpha = (n_1 + k) + (n_2 + k) = n_1 + n_2 + |m| + 1 = n \tag{22}$$

say, and, in view of (15), we obtain the hydrogenic spectrum:

$$E_n = -1/2n^2 \qquad n = 1, 2, 3, \ldots. \tag{23}$$

As may be easily verified, the degeneracy of the $n$th eigenvalue is $n^2$ and $n_1$, $n_2$ correspond to the conventional parabolic quantum numbers (Bethe and Salpeter 1957).


## 4. The hydrogen atom with perturbations

### 4.1. The perturbation $p_z$

In parabolic coordinates, we have

$$\lambda p_z = \frac{2\lambda}{\xi + \eta}\left(\xi\frac{\partial}{\partial\xi} - \eta\frac{\partial}{\partial\eta}\right) \tag{24}$$

where $\lambda$ measures the strength of the perturbation. Thus, the perturbed Schrödinger equation becomes

$$[(S_3 + T_3) + \beta(S_2 - T_2) - \tfrac{1}{2}\alpha]\psi = 0 \tag{25}$$

where we have written

$$\beta = \tfrac{1}{2}i\lambda\alpha \qquad \alpha^2 = -2/E. \tag{26}$$

After rotations involving $e^{-i\theta_1 S_1}$ and $e^{-i\theta_2 T_1}$ (which commute in this case, since the coordinates $\xi$, $\eta$ are independent), we obtain as in (11)

$$[(1-\beta^2)^{1/2}(S_3 + T_3) - \tfrac{1}{2}\alpha]\exp[-i(\theta_1 S_1 + \theta_2 T_1)]\psi = 0 \tag{27}$$

so that

$$\tfrac{1}{2}\alpha = (1-\beta^2)^{1/2}(n_1 + n_2 + 2k) = (1-\beta^2)^{1/2}n \tag{28}$$

say (cf (22) above), yielding

$$E = -\frac{1}{2n^2} + \tfrac{1}{2}\lambda^2. \tag{29}$$

Thus, the energy shift is *independent* of the particular state $|n, k\rangle$ and is given *exactly* by second-order perturbation theory. This result may be understood as follows: the perturbation $\lambda p_z = \lambda\, \partial/\partial z$ corresponds to a simple change of the zero of energy, since we have

$$e^{-\lambda z} \begin{bmatrix} x \\ y \\ z \end{bmatrix} e^{\lambda z} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} \qquad e^{-\lambda z} \begin{bmatrix} \partial/\partial x \\ \partial/\partial y \\ \partial/\partial z \end{bmatrix} e^{\lambda z} = \begin{bmatrix} \partial/\partial x \\ \partial/\partial y \\ \partial/\partial z + \lambda \end{bmatrix}. \tag{30}$$

## 4.2. The perturbation $(r^2 - z^2)^{-1}$

In this case, we have

$$\frac{\lambda}{r^2 - z^2} = \frac{\lambda}{\xi + \eta}\left(\frac{1}{\xi} + \frac{1}{\eta}\right) \tag{31}$$

and the perturbed Schrödinger equation becomes

$$(\bar{S}_3 + \bar{T}_3 - \tfrac{1}{2}\alpha)\psi = 0 \tag{32}$$

provided that we modify the generators $S_i$ of (17) to $\bar{S}_i$ (and similarly for the $\bar{T}_i$) simply by writing $\gamma^2$ in place of $m^2$, where

$$\gamma^2 = m^2 + 2\lambda. \tag{33}$$

In this case, no rotation is necessary and the spectrum is given by

$$\tfrac{1}{2}\alpha = n_1 + n_2 + 2k \tag{34}$$

which is identical in form to (22). However, we now have $k = \tfrac{1}{2}(|\gamma| + 1)$ in place of $\tfrac{1}{2}(|m| + 1)$, so that the energy spectrum is given explicitly by

$$E = -\frac{1}{2(n_1 + n_2 + |\gamma| + 1)^2}. \tag{35}$$

This result may also be derived by noting that, in spherical polar coordinates, the Laplacian operator contains a term $-\tfrac{1}{2}(r^2 - z^2)^{-1}\, \partial^2/\partial\phi^2$. The effect of the perturbation $\lambda(r^2 - z^2)^{-1}$ is to modify this operator to $-\tfrac{1}{2}(r^2 - z^2)^{-1}(\partial^2/\partial\phi^2 - 2\lambda)$, with a consequential change in the spectrum as seen in the appearance of a new effective azimuthal quantum number $|\gamma|$.

## 4.3. The perturbation $z/r$

This operator, which may be viewed as a *component* of the classical Runge–Lenz vector, also has some features similar to the dipole operator $z$ which is responsible for optical transitions and the Stark effect. In this case

$$\lambda\frac{z}{r} = \lambda\frac{\xi - \eta}{\xi + \eta} \tag{36}$$

and the perturbed Schrödinger equation takes the form

$$\{[(1+\mu)S_3+\mu S_1]+[(1-\mu)T_3-\mu T_1]-\tfrac{1}{2}\alpha\}\psi=0 \tag{37}$$

where we have written

$$\mu=\tfrac{1}{4}\lambda\alpha^2 \qquad \alpha^2=-2/E. \tag{38}$$

After rotation, we have (cf. (11))

$$\{(1+2\mu)^{1/2}S_3+(1-2\mu)^{1/2}T_3-\tfrac{1}{2}\alpha\}\exp[-i(\theta_1S_2+\theta_2T_2)]\psi=0 \tag{39}$$

so that

$$\tfrac{1}{2}\alpha=(1+2\mu)^{1/2}p_1+(1-2\mu)^{1/2}p_2 \tag{40}$$

where

$$p_i=n_i+\tfrac{1}{2}(|m|+1) \qquad i=1,2. \tag{41}$$

Now, if $p_1=p_2$ ($=\tfrac{1}{2}n$, say), we obtain for the exact perturbed energy

$$E_n=-\frac{1}{2n^2}-\tfrac{1}{2}n^2\lambda^2 \tag{42}$$

so that only the second-order correction to the energy is non-vanishing in this case. However, if $p_1\neq p_2$, we have

$$E(p_1,p_2)=-\frac{1}{2}\frac{(p_1^2+p_2^2)^2[1+2\lambda(p_2^2-p_1^2)]-2p_1p_2[1+4\lambda(p_2^2-p_1^2)]^{1/2}}{(p_2^2-p_1^2)^2} \tag{43}$$

or, if we employ the principal quantum number $n$ ($=p_1+p_2$) together with the parabolic quantum numbers $n_1$, $n_2$, we may write

$$E(n,n_1,n_2)=-\frac{1}{4n^2}\{[1+2\lambda n(n_2-n_1)]+[1+4\lambda n(n_2-n_1)]^{1/2}\}$$

$$-\frac{1}{4(n_2-n_1)^2}\{[1+2\lambda n(n_2-n_1)]-[1+4\lambda n(n_2-n_1)]^{1/2}\}. \tag{44}$$

(This reproduces (42) when $n_2=n_1$, as it should.)

From (44), we see that a perturbation expansion of the energy in ascending powers of $\lambda$ cannot converge unless

$$\lambda\leqslant\frac{1}{4n(n_2-n_1)} \tag{45}$$

which is clearly state dependent. Furthermore, the energy is *complex* whenever

$$\lambda\geqslant\frac{1}{4n(n_1-n_2)}.$$

This latter result can perhaps be best understood by noting that the complete potential for this problem

$$V=-\frac{1}{r}+\lambda\frac{z}{r} \tag{46}$$

will possess a maximum if $\lambda z>1$, leading to a potential barrier with characteristic tunnelling probability and metastable (complex energy) states.

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