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LETTER TO THE EDITOR

Diamagnetism of the hydrogen atom—an elementary derivation of the adiabatic invariant

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Abstract. The understanding of the magnetism of the atom, in the low-field limit, has recently been greatly improved through the discovery of an adiabatic invariant associated with the diamagnetic interaction. This was achieved using either classical perturbation theory or group theoretical methods on the Fock hypersphere. We present here a new and simple way of establishing its expression based on symmetry considerations and only involving elementary calculations. The result looks like a generalised vectorial model for the diamagnetic interaction. Indeed, the success of the present approach lies in its close connection with the non-invariance algebra of the Coulomb problem thereby supplying us with an interesting starting point for tackling the complete problem.

A complete understanding of the magnetism of the atom implies that the role of the diamagnetic interaction is fully taken into account. This is presently far from being achieved (for example Gay 1983). Recently, two important contributions appeared that gave the first complete description of the phenomenon in the low-field limit, through the discovery of an adiabatic invariant associated with the diamagnetic interaction. A derivation was first given by Solovev (1981) who used classical perturbation theory on the unperturbed set of Kepler ellipses. He showed that $\rho^2 = x^2 + y^2$ can be expressed in a given energy shell with principal quantum number n as a linear function of $4A^2 - 5A_z^2$, where $\boldsymbol{A}$ is the Lenz vector. Herrick (1982) derived a similar expression using the momentum representation of the Coulomb problem on the Fock hypersphere of $R(4)$. The latter approach is more general and based on earlier work (Kalnins *et al* 1976). Although these derivations solve the problem perfectly in the low-field limit, they involve quite long and tedious calculations. Indeed this hinders the very basic physical meaning of the result which provides us with the first correct expression of the so-called Larmor theorem (Delande and Gay 1983). In addition, they do not seem convenient for a further generalisation and analysis of the whole problem.

Our purpose here is to present a completely different analysis based on symmetry considerations. Although we will limit ourselves here to simple arguments which allow us to establish a generalised vectorial model of the diamagnetic interaction, the method turns out to be extremely promising because of close connections with the non-invariance algebra of the Coulomb problem.

The supersymmetry of the Coulomb problem has been recognised for a long time (for example Bander and Itzykson 1966). Besides the angular momentum $\boldsymbol{L}$, there is

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another conservative vectorial operator which is the Runge–Lenz vector $\boldsymbol{A}$:

$$\boldsymbol{A}=[\tfrac{1}{2}(\boldsymbol{p}\times\boldsymbol{L}-\boldsymbol{L}\times\boldsymbol{p})-me^2\boldsymbol{r}/r].$$

In classical terms, $(\boldsymbol{L},\boldsymbol{A})$ completely define a closed Kepler ellipse. Introducing a scaled version of the $\boldsymbol{A}$ vector i.e. $\boldsymbol{a}=(-2mE)^{-1/2}\boldsymbol{A}$, the basic quantum relations are then (we adopt atomic units):

$$\begin{aligned}&\boldsymbol{a}\cdot\boldsymbol{L}=0\\&a^2+L^2+1=-1/2E\end{aligned}\tag{1}$$

where E is the energy ($E=-1/2n^2$).

At this stage, it is worthwhile introducing the generalised angular momenta such that (Bander and Itzykson 1966):

$$\boldsymbol{j}_{\frac{1}{2}}=(\boldsymbol{L}\pm\boldsymbol{a})/2\tag{2}$$

which satisfy the relations

$$j_1^2=j_2^2=j(j+1)=(n^2-1)/4.\tag{3}$$

This leads to a fully symmetric description of the degeneracy in a given shell with principal quantum number n, in terms of the two independent angular momenta $\boldsymbol{j}_1$ and $\boldsymbol{j}_2$.

When applying an external magnetic field on the Coulombic system, it may drastically change all the properties of the atom. At low field strengths, the main role of the magnetic interactions is the breaking of the Coulomb supersymmetry in a definite way. The Hamiltonian is then

$$H=\frac{p^2}{2}-\frac{1}{r}+\frac{\gamma}{2}L_z+\frac{\gamma^2}{8}(x^2+y^2)\tag{4}$$

where $\gamma=\hbar\omega_c/2R$ is the ratio of the cyclotron frequency ($\omega_c=qB/m$) to the Rydberg constant. The treatment of the paramagnetic term responsible for the Zeeman effect is straightforward as L_z is a constant of motion. It is equivalent to performing a rotation to Larmor's frame. One gets:

$$L_z=j_{1z}+j_{2z}=m.\tag{5}$$

The treatment of the diamagnetic interaction is much more difficult as the Hamiltonian (4) does not separate. Under low-field conditions ($2R/n^3\gg\hbar\omega_c$), this can be done in the framework of degenerate perturbation theory or equivalently by deducing an adiabatic invariant proportional to $\rho^2=x^2+y^2$, in a given energy shell with principal quantum number n. This is done below using a two-step analysis, in terms of the $(\boldsymbol{j}_1,\boldsymbol{j}_2)$ operators.

Firstly, the expression Λ of the invariant must comply with the symmetries of the diamagnetic interaction. It is invariant under a large number of spatial transformations: spatial parity, reflections in the $(x0y)$ plane perpendicular to the field, reflections in the $(z0x)(z0y)$ planes parallel to the field and reflections in the first bisector plane due to the (x, y) symmetry in ρ^2. Indeed $\rho^2=x^2+y^2$ can be expressed as the sum of a rank 0 and rank 2 irreducible tensor operators on the orbital variables and then exhibits all the geometrical symmetry properties of these operators.

In order to derive the transformations of $(\boldsymbol{j}_1,\boldsymbol{j}_2)$ under such operations, one should remark that $\boldsymbol{L}$ is an axial vector while $\boldsymbol{a}$ is a polar one. The result of the operations on the $(\boldsymbol{j})$ are given in table 1, where the notation $(x \rightleftarrows y)$ indicates the exchange of the x and y components of j_1 and j_2, $(1,2)$ the exchange of $\boldsymbol{j}_1$ and $\boldsymbol{j}_2$ and $(-)$ a change of sign.

Table 1. Transformations under spatial operations of the components of the $(\boldsymbol{j})$ operators. $(1,2)$ indicates the interchange of 1 and 2. $(-)$ the change of sign. $(x \rightleftarrows y)$ the interchange of the x and y components. The $\boldsymbol{B}$ field is along the z axis.

Spatial parity	$(1,2)$	
Plane reflection—first bisector	$(1,2)\ (x \rightleftarrows y)$	$(-)$
Plane reflection $(x0y)$	$(1,2)\ (-)$	(x, y)
	$(1,2)$	(z)
Plane reflection $(x0z)$	$(1,2)\ (-)$	(x)
	$(1,2)$	(y)
	$(1,2)\ (-)$	(z)
Plane reflection $(y0z)$	$(1,2)$	(x)
	$(1,2)\ (-)$	(y)
	$(1,2)\ (-)$	(z)

From this analysis, one derives the expression of Λ complying with the symmetries of ρ^2. Λ certainly does not contain any term linear in the components of the $\boldsymbol{j}$, and this can be directly verified from table 1. Thus Λ should be a quadratic function of the components of the $\boldsymbol{j}$. From the invariance under parity operation, it is a symmetrical function in $(1,2)$. The invariance under reflection in the bisector plane implies a symmetrical dependence in the j_{ix} and j_{ky} components.

Then, making use of the two additional relations from the invariance under $(x0z)$ and $(y0z)$ plane reflections, one deduces that terms like $j_{ix} \cdot j_{ky}$ and $j_{i\alpha} \cdot j_{kz}$ $(\alpha = x, y)$ are necessarily 0.

The more general form of the invariant $\Lambda = \rho^2$ is then:

$$\Lambda = A(j_1^2 + j_2^2) + B(j_{1z}^2 + j_{2z}^2) + C(\boldsymbol{j}_1 \cdot \boldsymbol{j}_2) + D j_{1z} \cdot j_{2z} \tag{6}$$

or in terms of $(\boldsymbol{L}, \boldsymbol{a})$:

$$\Lambda = \alpha L^2 + \beta a^2 + \delta L_z^2 + \xi a_z^2. \tag{7}$$

Making use of equations (3) and (5), one gets:

$$\Lambda = \rho^2 = \Lambda_0 + A'(j_{1z} j_{2z} + B' \boldsymbol{j}_1 \cdot \boldsymbol{j}_2). \tag{8}$$

The second step is obtaining the values of the coefficients in the expansions, in order that Λ really represents ρ^2. The analysis is obviously very similar to that used for applying Wigner–Eckart theorem. From (6) or (8), which have been derived in a more general manner, one can evaluate the quantum expression of the coefficients using simple situations and the parabolic basis states associated with the $\{j_1^2 j_2^2 j_{1z} j_{2z}\}$ representation. Another way is to remark that (6) is the expression of ρ^2 in terms of the irreducible tensor operators $|jj^+kq\rangle\rangle = {}^{jj}T_q^k$ built on $\boldsymbol{j}_1$ and $\boldsymbol{j}_2$. The expression of ρ^2 in terms of the orbital irreducible basis is well known and involves ${}^{LL'}T_0^K$ $(K=0, K=2)$ tensor operators with coupling schemes of the $\{(\boldsymbol{j}_1, \boldsymbol{j}_2)\boldsymbol{L}\}$ types. The transformation from one representation to the other is made by using $\{9j\}$ coefficients. This would allow it to be shown that (8) holds exactly.

Although the concepts are completely clear, these methods are a bit tedious. In addition, a more powerful method based on the non-invariance algebra of the hydrogen atom (Delande *et al* 1983) leads to simple calculations of the quantum form of the invariant. Consequently we will limit ourselves here to the classical calculation of $(\alpha, \beta, \delta, \xi)$ in (8). This is elementary and we only need to consider the average of ρ^2 over four highly degenerate Kepler orbits that is: a straight line along $0x$, a straight line along the $\boldsymbol{B}$ field and two circular trajectories respectively in the $(x0y)$ and $(z0y)$ planes (see figure 1). One gets:

(1) $(x0y)$ circular trajectory $(L_z = L = n)(a_z = a = 0)\langle\rho^2\rangle = n^4 = (\alpha+\delta)n^2$

(2) straight line along $0x$ $(L = L_z = 0)(a_z = 0\ a = n)\langle\rho^2\rangle = \frac{5}{2}n^4 = \beta n^2$

(3) $(z0y)$ circular trajectory $(a = 0)(L = L_x = n)\langle\rho^2\rangle = \langle y^2\rangle = \frac{1}{2}n^4 = \alpha n^2$

(4) straight line along $0z$ $(L = 0)(a = a_z = n)\langle\rho^2\rangle = 0 = (\beta+\xi)n^2$ (keeping in mind that the classical form of (1) is $a^2 + L^2 = n^2$).

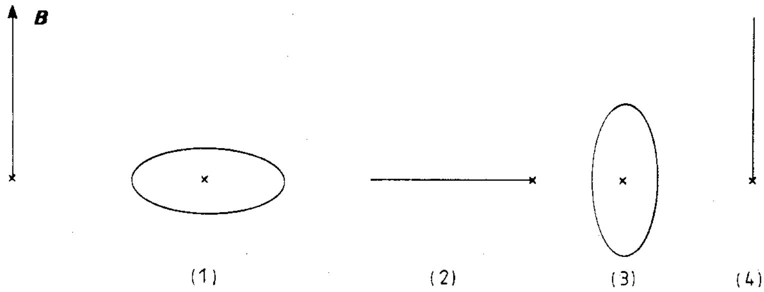

Figure 1. The four Kepler trajectories needed to get the expression of the invariant (two lines, two circles).

Hence, one obtains:

$$\Lambda = \tfrac{1}{2}(n^2L^2 + 5n^2a^2 + n^2L_z^2 - 5n^2a_z^2) \tag{9}$$

and making use of equations (1) in their classical form:

$$\Lambda = \tfrac{1}{2}n^2[n^2 + L_z^2 + (4a^2 - 5a_z^2)] \tag{10}$$

which is equivalent to Solovev's result (Solovev 1981). A further transformation leads to:

$$\Lambda = \tfrac{1}{2}n^2(3n^2 - 4m^2 + 20j_{1z}j_{2z} - 8\boldsymbol{j}_1 \cdot \boldsymbol{j}_2) \tag{11}$$

which is the exact classical result. It differs from the quantum one in that there is a missing (+1) constant term in the right parenthesis (because of the commutation relations). Equations (3), (5) and (11) are the correct expression of the Larmor theorem at low fields (Delande and Gay 1983), for the hydrogen atom.

This is by far the shortest method for deriving the adiabatic invariant in the low-field diamagnetic limit. The method is also powerful in the sense it can apply to a large class of perturbing potentials in the Coulomb problem and is extremely simple to use.

The first attempt using a similar formalism was by Labarthe (1981) who tentatively made use of the Fermi replacement $\boldsymbol{r} \rightarrow \frac{3}{2}n\boldsymbol{A}$. This is indeed incorrect for the present purpose which requires a complete analysis of the symmetry properties of the diamagnetic interaction in a given energy shell.

A proper generalisation of the present method using the non-invariance algebra of the Coulomb problem (Delande *et al* 1983) seems promising. At least, it allows us to understand on more general grounds why some earlier theoretical attempts making use of a Sturmian basis (Clark and Taylor 1980) or semi-parabolic coordinates (Delande 1981, Reinhardt and Farrelly 1982) have been partially successful when tackling the complete problem at arbitrary field strengths.

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