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Bound states of the hydrogen atom in parabolic coordinates

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The spectrum and separable eigenfunctions in parabolic coordinates for the bound states of the hydrogen atom, as well as their relation with the separable eigenfunctions in spherical coordinates, are obtained making use of the elementary theory of angular momentum.

Keywords: Hydrogen atom; parabolic coordinates; angular momentum.

Se obtiene el espectro y las eigenfunciones separables en coordenadas parabólicas para los estados ligados del átomo de hidrógeno, así como su relación con las eigenfunciones separables en coordenadas esféricas, haciendo uso de la teoría elemental del momento angular.

Descriptores: Átomo de hidrógeno; coordenadas parabólicas; momento angular.

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1. Introduction

In the usual treatment of the problem of the hydrogen atom in quantum mechanics, the Schrödinger equation is solved employing spherical coordinates. This choice seems natural owing to the spherical symmetry of the Coulomb potential. However, as is well known, the Schrödinger equation for the Coulomb potential can also be solved by separation of variables in parabolic coordinates (see, *e.g.*, Refs. 1 and 2) as a consequence of the existence of a symmetry group containing the rotation group. This larger symmetry group is associated with the conservation of the angular momentum and of the Runge–Lenz vector (see, *e.g.*, Refs. 3, 1, and 2) and to the accidental degeneracy of the energy spectrum. Already in 1926, Pauli [4] obtained the energy of the bound states of the hydrogen atom algebraically, making use of the Lie algebra generated by these conserved quantities (see also Refs. 3, 1, and 2). In the case of the bound states, the symmetry group generated by the angular momentum and the Runge–Lenz vector is isomorphic to SO(4).

Whereas the spherical coordinates are naturally adapted to the SO(3) symmetry of the Coulomb potential, the SO(4) symmetry can be more easily exhibited by considering the separable solutions of the Schrödinger equation for the hydrogen atom in parabolic coordinates. In fact, as we shall show below, a basis for the eigenstates of the Hamiltonian can be obtained algebraically, in the same form as the eigenstates of L^2 and L_3 are constructed in elementary quantum mechanics with the aid of ladder operators (see also Ref. 5). The key to finding the eigenvalues and eigenstates of the Hamiltonian of the hydrogen atom is to combine the components of the angular momentum and of the Runge–Lenz vector so as to obtain generators of two SU(2) groups.

A similar procedure has been applied in the case of the hydrogen atom in two dimensions, where the two components of the Runge–Lenz vector and the angular momentum generate a Lie algebra isomorphic to that of SO(3) [6].

In Sec. 2, following Refs. 4, 3, 1, and 2, the Lie algebra generated by the Cartesian components of the angular momentum and the Runge–Lenz vector is employed to find the energy eigenvalues for the bound states of the hydrogen atom, and to identify two sets of raising and lowering operators that enable us to find explicitly the wavefunctions of the bound states. In Sec. 3, we make use of the fact that the separable solutions in parabolic coordinates of the Schrödinger equation for the hydrogen atom are eigenfunctions of L_3 and A_3 (the z-component of the Runge–Lenz vector) and of the results of Sec. 2 to find the relation between these separable solutions and the separable solutions of the Schrödinger equation in spherical coordinates (*cf.* also Refs. 3 and 5 and the references cited therein).

2. The SO(4) symmetry of the Hamiltonian

The Hamiltonian operator for the hydrogen atom (neglecting spin) in non-relativistic quantum mechanics is taken as

$$H = \frac{\mathbf{p}^2}{2M} - \frac{e^2}{r}, \tag{1}$$

where M is the reduced mass of the atom and e is the electric charge of the electron. The rotational symmetry of H is equivalent to the vanishing of the commutator of H with each Cartesian component of the angular momentum,

$$[H, L_i] = 0,$$

$$i, j, \ldots = 1, 2, 3,$$

where

$$\mathbf{L} = \mathbf{r} \times \mathbf{p},$$

and one can verify that each Cartesian component of the Runge–Lenz vector

$$\mathbf{A} = \frac{1}{2}(\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p}) - \frac{Me^2\mathbf{r}}{r} \tag{2}$$

also commutes with H [1-4].

From the foregoing expressions one can show that

$$\mathbf{L} \cdot \mathbf{A} = 0,$$

and that

$$\mathbf{A}^2 = 2MH(\mathbf{L}^2 + \hbar^2) + M^2e^4. \tag{3}$$

The components of the angular momentum satisfy the well-known commutation relations

$$[L_i, L_j] = \mathrm{i}\hbar\varepsilon_{ijk}L_k, \tag{4}$$

with summation over repeated indices ($i, j, k, \ldots$=$1, 2, 3$). A straightforward computation shows that

$$[L_i, A_j] = \mathrm{i}\hbar\varepsilon_{ijk}A_k, \tag{5}$$

as required for a vector operator, and

$$[A_i, A_j] = \mathrm{i}\hbar\varepsilon_{ijk}(-2MH)L_k. \tag{6}$$

Hence, on the subspace formed by the eigenvectors of H with eigenvalue E, the operator H appearing on the right-hand side of Eq. (6) can be replaced by the real number E. Since we are interested in the bound states of the hydrogen atom, we shall consider negative values of E only and, defining

$$p_0 \equiv \sqrt{-2ME}, \tag{7}$$

from Eq. (6) we have

$$[A_i/p_0, A_j/p_0] = \mathrm{i}\hbar\varepsilon_{ijk}L_k, \tag{8}$$

which means that, on the subspace H=E, the set formed by the operators L_i and A_i/p_0 is a basis of a Lie algebra. The group generated by this algebra is isomorphic to SO(4), the group of rotations in $\mathbb{R}^4$ [3,1,7], though this fact is not essential in what follows. What is very useful is that this Lie algebra is the direct sum of two Lie algebras isomorphic to that of SU(2). Specifically, letting

$$\mathbf{I} \equiv \frac{1}{2}(\mathbf{L} + \mathbf{A}/p_0), \qquad \mathbf{K} \equiv \frac{1}{2}(\mathbf{L} - \mathbf{A}/p_0), \tag{9}$$

from Eqs. (4), (5), and (8), one readily finds that

$$[I_i, I_j] = \mathrm{i}\hbar\varepsilon_{ijk}I_k, \quad [I_i, K_j] = 0, \quad [K_i, K_j] = \mathrm{i}\hbar\varepsilon_{ijk}K_k. \tag{10}$$

According to the elementary theory of angular momentum, from Eqs. (10) it follows that the eigenvalues of $\mathbf{I}^2$, for instance, are of the form

$$j(j+1)\hbar^2, \tag{11}$$

where j can take the values $0, 1/2, 1, 3/2, \ldots$. On the other hand, since $\mathbf{L} \cdot \mathbf{A}$=$0$, from Eqs. (9) we see that

$$\mathbf{I}^2 = \mathbf{K}^2 = \frac{1}{4}\left(\mathbf{L}^2 + \mathbf{A}^2/{p_0}^2\right)$$

or, taking into account Eq. (3), we find that, on the subspace H=E=$-{p_0}^2/2M$,

$$\mathbf{I}^2 = \mathbf{K}^2 = \frac{1}{4}\left(\frac{M^2e^4}{{p_0}^2} - \hbar^2\right),$$

which implies that the values of E are of the form

$$E = -\frac{Me^4}{2\hbar^2(2j+1)^2}, \tag{12}$$

which is the well-known expression for the energies of the bound states of the hydrogen atom, identifying $2j+1$ with the principal quantum number, usually denoted by n [1–4].

If the eigenvalue of $\mathbf{I}^2$ (and, hence, of $\mathbf{K}^2$) is $j(j+1)\hbar^2$, then the eigenvalues of I_3 and K_3 are of the form $m_1\hbar$ and $m_2\hbar$, respectively, with

$$m_1, m_2 = -j, -j+1, \ldots, j.$$

Hence, the degeneracy of the energy eigenvalue (12) is

$$(2j+1)(2j+1) = n^2.$$

Furthermore, m_1 and m_2 are both integers or half-integers according to whether j is an integer or half-integer, respectively; hence, the eigenvalues of L_3 and of A_3/p_0 will always be integral multiples of $\hbar$ [see Eqs. (9)].

The ladder operators

$$I_\pm \equiv I_1 \pm \mathrm{i}I_2, \qquad K_\pm \equiv K_1 \pm \mathrm{i}K_2, \tag{13}$$

act on each eigenspace of H. If $|j, m_1, m_2\rangle$ is a normalized common eigenket of $\mathbf{I}^2$, I_3, and K_3 with eigenvalues $j(j+1)\hbar^2$, $m_1\hbar$, and $m_2\hbar$, respectively, then its phase can be chosen in such a way that

$$I_\pm|j, m_1, m_2\rangle = \hbar \times \sqrt{j(j+1) - m_1(m_1 \pm 1)}\,|j, m_1 \pm 1, m_2\rangle, \tag{14}$$

$$K_\pm|j, m_1, m_2\rangle = \hbar \times \sqrt{j(j+1) - m_2(m_2 \pm 1)}\,|j, m_1, m_2 \pm 1\rangle. \tag{15}$$

In particular, the state $|j, j, j\rangle$ satisfies

$$I_+|j, j, j\rangle = 0, \qquad K_+|j, j, j\rangle = 0. \tag{16}$$

It should be remarked that all the foregoing relations do not involve any specific representation or the use of some coordinate system. As we shall show in the next section, the separable eigenfunctions of H in parabolic coordinates are also eigenfunctions of I_3 and K_3 (see also Refs. 3 and 5) and the ladder operators $I_\pm$, and $K_\pm$ take simple forms when expressed in parabolic coordinates. A similar result, in the case of the two-dimensional hydrogen atom, has been obtained in Ref. 6.

3. Separable solutions in parabolic coordinates

As pointed out in the Introduction, the Schrödinger equation for the hydrogen atom is separable in parabolic coordinates. In terms of the parabolic coordinates (ξ, η, φ), defined by

$$x = \sqrt{\xi\eta}\cos\varphi, \quad y = \sqrt{\xi\eta}\sin\varphi, \quad z = \frac{1}{2}(\xi - \eta), \tag{17}$$

the time-independent Schrödinger equation is given by [1,2]

$$\begin{aligned} &-\frac{\hbar^2}{2M}\left\{\frac{4}{\xi+\eta}\left[\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right) + \frac{\partial}{\partial\eta}\left(\eta\frac{\partial}{\partial\eta}\right)\right]\right. \\ &\left. + \frac{1}{\xi\eta}\frac{\partial^2}{\partial\varphi^2}\right\}\psi - \frac{2e^2}{\xi+\eta}\psi = E\psi. \end{aligned} \tag{18}$$

Looking for a separable solution $\psi = F(\xi)G(\eta)\mathrm{e}^{im\varphi}$, where m is an integer, one finds that F and G must obey the equations

$$\begin{aligned} &4\frac{\mathrm{d}}{\mathrm{d}\xi}\left(\xi\frac{\mathrm{d}F}{\mathrm{d}\xi}\right) + \left(\frac{2ME\xi}{\hbar^2} + \frac{2Me^2}{\hbar^2} - \frac{m^2}{\xi}\right)F = \lambda F, \\ &4\frac{\mathrm{d}}{\mathrm{d}\eta}\left(\eta\frac{\mathrm{d}G}{\mathrm{d}\eta}\right) + \left(\frac{2ME\eta}{\hbar^2} + \frac{2Me^2}{\hbar^2} - \frac{m^2}{\eta}\right)G = -\lambda G, \end{aligned} \tag{19}$$

where λ is another separation constant.

Eliminating E from Eqs. (19), one obtains

$$\begin{aligned} &\left\{\frac{4}{\xi+\eta}\left[\eta\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right) - \xi\frac{\partial}{\partial\eta}\left(\eta\frac{\partial}{\partial\eta}\right)\right]\right. \\ &\left. - \frac{\xi-\eta}{\xi\eta}\frac{\partial^2}{\partial\varphi^2} - \frac{2Me^2}{\hbar^2}\frac{\xi-\eta}{\xi+\eta}\right\}\psi = \lambda\psi \end{aligned} \tag{20}$$

and a straightforward computation shows that the operator appearing on the left-hand side of this last equation is $2A_3/\hbar^2$, which means that the separation constant λ is an eigenvalue of $2A_3/\hbar^2$ and that the separable solutions of the Schrödinger Eq. (18) in parabolic coordinates are simultaneous eigenfunctions of L_3 and A_3 (which do commute) or, equivalently, of I_3 and K_3 [see Eq. (9)].

From the definition of the Runge–Lenz vector (2), eliminating the terms proportional to e^2/r with the aid of the relation $\mathbf{p}^2/2M - e^2/r = -{p_0}^2/2M$, valid on each subspace $H = E$, one finds that the Cartesian components of the Runge–Lenz vector can be expressed in the form

$$A_i = \frac{1}{2}x_i(\mathbf{p}^2 - {p_0}^2) - (\mathbf{r}\cdot\mathbf{p})p_i + \mathrm{i}\hbar p_i. \tag{21}$$

Then, a straightforward but lengthy computation yields the following surprisingly simple expressions for the ladder operators $I_\pm$, $K_\pm$ [see Eqs. (9) and (13)]

$$\begin{aligned} I_+ &= \hbar\mathrm{e}^{\mathrm{i}\phi}\left(\sqrt{u}\frac{\partial}{\partial u} + \frac{\mathrm{i}}{2\sqrt{u}}\frac{\partial}{\partial\phi} + \frac{\sqrt{u}}{2}\right) \\ &\quad\times\left(\sqrt{v}\frac{\partial}{\partial v} + \frac{\mathrm{i}}{2\sqrt{v}}\frac{\partial}{\partial\phi} - \frac{\sqrt{v}}{2}\right), \\ I_- &= \hbar\mathrm{e}^{-\mathrm{i}\phi}\left(\sqrt{u}\frac{\partial}{\partial u} - \frac{\mathrm{i}}{2\sqrt{u}}\frac{\partial}{\partial\phi} - \frac{\sqrt{u}}{2}\right) \\ &\quad\times\left(\sqrt{v}\frac{\partial}{\partial v} - \frac{\mathrm{i}}{2\sqrt{v}}\frac{\partial}{\partial\phi} + \frac{\sqrt{v}}{2}\right), \\ K_+ &= -\hbar\mathrm{e}^{\mathrm{i}\phi}\left(\sqrt{u}\frac{\partial}{\partial u} + \frac{\mathrm{i}}{2\sqrt{u}}\frac{\partial}{\partial\phi} - \frac{\sqrt{u}}{2}\right) \\ &\quad\times\left(\sqrt{v}\frac{\partial}{\partial v} + \frac{\mathrm{i}}{2\sqrt{v}}\frac{\partial}{\partial\phi} + \frac{\sqrt{v}}{2}\right), \\ K_- &= -\hbar\mathrm{e}^{-\mathrm{i}\phi}\left(\sqrt{u}\frac{\partial}{\partial u} - \frac{\mathrm{i}}{2\sqrt{u}}\frac{\partial}{\partial\phi} + \frac{\sqrt{u}}{2}\right) \\ &\quad\times\left(\sqrt{v}\frac{\partial}{\partial v} - \frac{\mathrm{i}}{2\sqrt{v}}\frac{\partial}{\partial\phi} - \frac{\sqrt{v}}{2}\right), \end{aligned} \tag{22}$$

where we have made use of the dimensionless variables

$$u = \frac{p_0}{\hbar}\xi, \qquad v = \frac{p_0}{\hbar}\eta. \tag{23}$$

Note that, according to Eqs. (17), interchanging ξ with η (or, equivalently, interchanging u with v) amounts to a reflection on the xy-plane and, therefore, to interchanging $I_\pm$ with $-K_\pm$.

Since $L_3 = I_3 + K_3$, the wave function, $\psi_{j,j,j}$, representing the state $|j, j, j\rangle$ must be of the form $F(u, v)\mathrm{e}^{\mathrm{i}2j\phi}$ and therefore, from Eqs. (16) and (22) we readily obtain

$$\psi_{j,j,j} = N\mathrm{e}^{-(u+v)/2}(uv)^j\mathrm{e}^{\mathrm{i}2j\phi}, \tag{24}$$

where N is a normalization constant. A simple computation, using the fact that the volume element is given by $(1/4)(\xi+\eta)\mathrm{d}\xi\mathrm{d}\eta\mathrm{d}\phi$, yields

$$|N| = \frac{(p_0/\hbar)^{3/2}}{(2j)!\sqrt{(2j+1)\pi}}.$$

Making use of Eqs. (14), (15), (22), and (24), one can obtain the explicit expression of all the *normalized* wave functions for the bound states of the hydrogen atom, separable in parabolic coordinates. Since these wave functions are given in terms of associated Laguerre polynomials (see Appendix), one is actually *deriving* the Rodrigues formula for these polynomials, as well as some recurrence relations. Note that, on a function ψ with a dependence on ϕ of the form $\mathrm{e}^{\mathrm{i}m\phi}$, we have the identity

$$\left(\sqrt{u}\frac{\partial}{\partial u} - \frac{\mathrm{i}}{2\sqrt{u}}\frac{\partial}{\partial \phi} - \frac{\sqrt{u}}{2}\right)\psi$$
$$= u^{(1-m)/2}\mathrm{e}^{u/2}\frac{\partial}{\partial u}\left(u^{m/2}\mathrm{e}^{-u/2}\psi\right),$$

with similar identities for the other operators appearing in Eqs. (22). Therefore, for $n \geqslant 0$ (on a function ψ with a dependence on ϕ of the form $\mathrm{e}^{\mathrm{i}m\phi}$),

$$(I_-)^n\,\psi = \hbar^n \mathrm{e}^{-\mathrm{i}n\phi}u^{(n-m)/2}\mathrm{e}^{u/2}$$
$$\times \frac{\partial^n}{\partial u^n}u^{m/2}\mathrm{e}^{-u/2}v^{(n-m)/2}\mathrm{e}^{-v/2}\frac{\partial^n}{\partial v^n}v^{m/2}\mathrm{e}^{v/2}\psi.$$

3.1. Interbasis expansions

The solution of the Schrödinger equation for the hydrogen atom is usually obtained making use of the spherical coordinates. The separable solutions in spherical coordinates, being proportional to the spherical harmonics, are eigenfunctions of $\mathbf{L}^2$ and L_3, and it must be possible to express the separable solutions in spherical coordinates (eigenfunctions of $\mathbf{L}^2$ and L_3) in terms of the separable solutions in parabolic coordinates (eigenfunctions of I_3 and K_3). Fortunately, according to Eqs. (9), $\mathbf{L}$ is the sum of two commuting angular momenta ($\mathbf{L}$=$\mathbf{I}$+$\mathbf{K}$) and, therefore, using the rules of addition of angular momenta, for a given value of E or, equivalently, of j, the possible values of the square of the angular momentum, $\mathbf{L}^2$, are $l(l+1)\hbar^2$, where [see Eq. (11)]

$$l = 2j, 2j-1, 2j-2, \ldots, 0,$$

which is the well-known result obtained by solving the Schrödinger equation in spherical coordinates (again, recall that $2j$+1 is the principal quantum number, n). Furthermore, if $|j,l,m\rangle$ is the (normalized) state with energy (12), that is an eigenket of $\mathbf{L}^2$ and L_3 with eigenvalues $l(l$+$1)\hbar^2$, and $m\hbar$, respectively, then, in terms of the common eigenkets of $\mathbf{I}^2$, I_3, and K_3, we have

$$|j,l,m\rangle$$
$$= \sum_{m_1,m_2=-j}^{j} \langle j,j,m_1,m_2|j,j,l,m\rangle\,|j,m_1,m_2\rangle, \qquad (25)$$

with m=m_1+m_2, where $\langle j_1,j_2,m_1,m_2|j_1,j_2,j,m\rangle$ denotes the Clebsch–Gordan coefficients (*cf*. Ref. 3). The analog of this result for the case of the two-dimensional hydrogen atom has been given, following other approaches, in Refs. 8 and 9.

Finally, it should be remarked that, as already pointed out at the Introduction, the SO(4) symmetry of the Schrödinger equation for the bound states of the hydrogen atom is more easily exhibited by considering its separable solutions in parabolic coordinates. In fact, owing to the homomorphism between SO(4) and $\mathrm{SU}(2)\times\mathrm{SU}(2)$, which comes from Eqs. (9) and (10), a given element of SO(4) corresponds to two SU(2) matrices (defined up to a common sign), whose action on the states $|j,m_1,m_2\rangle$ is given by the standard matrices (or Wigner D functions) $D^j_{mm'}$.

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Appendix

Following the standard procedure, making use of the dimensionless variables

$$u = \frac{p_0}{\hbar}\xi, \qquad v = \frac{p_0}{\hbar}\eta, \qquad k = \frac{\lambda\hbar}{2p_0} \qquad (A.1)$$

and writing

$$F = u^{|m|/2}\mathrm{e}^{-u/2}f(u), \qquad G = v^{|m|/2}\mathrm{e}^{-v/2}g(v),$$

from Eqs. (19) we find that f and g satisfy the associated Laguerre equations

$$u\frac{\mathrm{d}^2 f}{\mathrm{d}u^2} + (|m|+1-u)\frac{\mathrm{d}f}{\mathrm{d}u}$$
$$+ \frac{1}{2}\left(\frac{Me^2}{\hbar p_0} - |m| - 1 - k\right)f = 0 \qquad (A.2)$$

and

$$v\frac{\mathrm{d}^2 g}{\mathrm{d}v^2} + (|m|+1-v)\frac{\mathrm{d}g}{\mathrm{d}v}$$
$$+ \frac{1}{2}\left(\frac{Me^2}{\hbar p_0} - |m| - 1 + k\right)g = 0. \qquad (A.3)$$

These equations have acceptable solutions (which are associated Laguerre polynomials) only if

$$N_1 \equiv \frac{1}{2}\left(\frac{Me^2}{\hbar p_0} - |m| - 1 - k\right)$$

and

$$N_2 \equiv \frac{1}{2}\left(\frac{Me^2}{\hbar p_0} - |m| - 1 + k\right)$$

are non-negative integers (the degrees of these polynomials). Therefore,

$$\frac{Me^2}{\hbar p_0} = N_1 + N_2 + |m| + 1,$$

is an integer greater than or equal to 1. Letting

$$2j \equiv N_1 + N_2 + |m|, \qquad (A.4)$$

with $j = 0, 1/2, 1, 3/2, \ldots$, and recalling the definition of p_0, it follows that

$$E = -\frac{Me^4}{2\hbar^2(2j+1)^2},$$

which coincides with Eq. (12).

Following the conventions of Ref. 10, f and g are proportional to the associated Laguerre polynomials

$$L^{|m|}_{(2j-|m|-k)/2}(u)$$

and

$$L^{|m|}_{(2j-|m|+k)/2}(v),$$

respectively.

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