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"HIDDEN" SYMMETRY OF HIGHLY EXCITED ATOMIC LEVELS

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A condition is derived, such that when it is satisfied the deviation of the potential V(r) at small distances from a pure Coulomb potential does not destroy the "hidden" symmetry of the spectrum of levels, as described by the group O(4).

THE spectrum of levels of the hydrogen atom possesses an "accidental" degeneracy with respect to the orbital angular momentum (in the nonrelativistic case, i.e., with neglect of the spin-orbit coupling). As was shown by Fock[1] and by Bargmann[2] (see also [3]) this degeneracy is explained by the existence of a group of higher (or "dynamical") symmetry, whose irreducible representations determine all of the quantum numbers, the spectrum of energy levels, and their degrees of degeneracy. For the discrete spectrum the group O(4)—the group of rotations of a four-dimensional sphere—is such a group. It has recently been shown[4] that the transition to the noncompact group O(3, 1) (the homogeneous Lorentz group) allows us to describe the symmetry of both the discrete and the continuous spectra of the hydrogen atom.

The exact symmetry of the group O(4) or O(3, 1) relates to the idealized case of a pure Coulomb field. Any deviation of V(r) from the Coulomb field destroys the higher symmetry (the energy of a level begins to depend on l). In the case of any atom (except the hydrogen atom) the potential V(r) surely differs from the pure Coulomb field for $r \lesssim r_0$ (r_0 is the radius of the atom), and therefore levels with small values of the principal quantum number n drop out of the scheme of the higher symmetry of O(4). For $n \gg 1$, however, the electron moves in a nearly Coulomb field and the question arises as to whether the symmetry of the group O(4) will not be applicable for the description of highly excited levels of any atom. We shall find a condition [see Eq. (10)] such that when it is satisfied the group O(4) still retains its meaning as a group of approximate dynamical symmetry of the levels with $n \gg 1$.

The motion of an electron in an arbitrary atom can be described with a selfconsistent potential V(r), which goes over into a Coulomb potential at large distances from the nucleus. We do not know the exact behavior of V(r) at small distances from the nucleus, and it varies from atom to atom. Therefore it is natural to solve the problem by the method of joining-on, which is well known from the theory of nuclear reactions (cf., e.g., [5]).

We introduce a distance r_0, which is of the order of magnitude of the radius of the atom, and assume that for $r > r_0$ the potential is a pure Coulomb potential:[1)]

$$V(r) = -\varkappa_c / r \quad \text{for} \quad r > r_0. \tag{1}$$

The behavior of V(r) for $r < r_0$ can be arbitrary. We are interested in studying only highly excited states ($n \gg 1$) whose wave functions are concentrated in the region $r \gg r_0$. Therefore we shall assume that $\kappa r_0 \ll 1$.

The solution outside the well which is regular at infinity is of the form (cf. [6])

$$R_{\varkappa l}(r) = e^{-\varkappa r}(2\varkappa r)^{\lambda-1} G(-\lambda + l + 1, -\lambda - l; -2\varkappa r), \tag{2}$$

$$G(\alpha, \beta; x) = 1 + \frac{\alpha\beta}{1!} x^{-1} + \frac{\alpha(\alpha+1)\beta(\beta+1)}{2!} x^{-2} + \ldots \tag{3}$$

Now $\lambda = \kappa_c/\kappa$ differs only slightly from an integer, $\lambda = n + \Delta n$, and

$$\Delta E = n^{-3} \Delta n \quad (n \gg 1). \tag{4}$$

We denote by h_l the logarithmic derivative of the internal solution at the edge of the well:

$$h_l = \frac{d \ln \chi_{nl}}{d \ln r}\bigg|_{r \to r_0 - 0}, \quad \chi_{nl}(r) = r R_{nl}(r) \tag{5}$$

[when $\kappa^2/2$ is much smaller than the average value of $|V(r)|$ in the internal region $r \leq r_0$ the quantity h_l is independent of κ]. With the condition $\kappa r \ll 1$ we get from (2)

[1)] The atomic system of units is used: $\hbar = m = e = 1$. In these units the energy of a level is $E_{nl} = -\kappa^2/2$.

$$\chi_{nl}(r) \approx A_{nl}(2\varkappa r)^{l+1}[1 - B_{nl}(2\varkappa r)^{-(2l+1)}], \quad (6)$$

$$A_{nl} = (-1)^{n-l-1}\frac{(n+l)!}{(2l+1)!},$$

$$B_{nl} = \frac{(2l+1)!(2l)!(n-l-1)!}{(n+l)!}\Delta n \quad (7)$$

In (6) it can already be assumed that $\kappa = \kappa_c/n$.

Using (4), (5), and (7), we find from the condition of joining-on at the point $r = r_0$ the value of the level shift:2)

$$\Delta E_{nl} = \frac{1}{n^3}\left(1 - \frac{1^2}{n^2}\right)\left(1 - \frac{2^2}{n^2}\right)\ldots$$

$$\ldots\left(1 - \frac{l^2}{n^2}\right)\frac{(2\varkappa_c r_0)^{2l+1}}{(2l+1)!(2l)!}\,\frac{h_l - (l+1)}{h_l + l} \quad (8)$$

[for $l = 0$ Eq. (8) is the same as the formula derived by Zel'dovich[7]]. For arbitrary values of h_l except in a narrow region near $-l$ the quantity

$$|1 - (2l+1)/(h_l + l)|$$

is of the order of unity. The condition $h_l = -l$ corresponds to the appearance of a new bound state in the internal potential $(r \leq r_0)$.3) Excluding this possibility, we see that the level shift ΔE_{nl} falls off rapidly with increase of l, and the maximum value of ΔE_{nl} is at $l = l_0 \sim (\kappa_c r_0)^{1/2}$ (unlike the quantity κr_0, the quantity $\kappa_c r_0$ is of the order unity for the atom).

It can be seen from (8) that $|\Delta E_{nl}| \sim n^{-1}|E_{nl}|$, i.e., the level shift is small. This, however, is still insufficient for the preservation of the higher symmetry. It is necessary that the "shells" corresponding to different values of n not overlap with each other—that is, we must have the more severe condition

$$|\Delta E_{nl}| \ll (E_{n+1} - E_n) \quad \text{for all } l \ (0 \leqslant l \leqslant n-1). \quad (9)$$

By means of (8) we find that (9) is equivalent to the inequality

$$\varkappa_c r_0 \ll 1, \quad (10)$$

i.e., the radius r_0 of the region in which V(r) can differ from the pure Coulomb potential must be much smaller than the radius of the first Bohr orbit. This condition is well satisfied for the hydrogen atom (and also for the ions He^+, Li^{++}, and so on), for which r_0 is of the order of the size of the nucleus. For other atoms, including hydrogenlike atoms (with one valence electron), $\kappa_c r_0 \sim 1$. Therefore even for $n \gg 1$, with the electron moving far from the nucleus, in practically a Coulomb field, the levels E_{nl} do not group themselves according to the irreducible representations of the group O(4), and the higher symmetry of the group O(4) is destroyed.

In a medium with a large value of the dielectric constant ϵ (for example, in an impurity semiconductor, see [7]) the radius of the Bohr orbit is increased by a factor ϵ and the condition (10) may be satisfied, i.e., it may be possible to apply the approximate symmetry of the group O(4) for the classification of highly excited electronic levels.

In conclusion we make the following remark. It is usually stated that highly excited levels are described by the formula (cf., e.g., [6])

$$E_{nl} = -1/2(n + \Delta_l)^2, \quad (11)$$

where Δ_l is a constant not depending on the principal quantum number n (the so-called Rydberg correction). Comparing (11) with (8), we find the following expression for Δ_l:

$$\Delta_l = \left(1 - \frac{1^2}{n^2}\right)\ldots\left(1 - \frac{l^2}{n^2}\right)$$

$$\times\frac{(2\varkappa_c r_0)^{2l+1}}{(2l+1)!(2l)!}\,\frac{h_l - (l+1)}{h_l + l}, \quad (12)$$

i.e., Δ_l depends explicitly on n. The contradiction here is only apparent, since one usually considers the case $n \gg l$, for which the dependence on n in (12) can be neglected. On the other hand, from accurate experimental data one gets the empirical formula[8] $\Delta_l = \alpha + \beta/n^2 + \ldots$, which obviously agrees with (12). Reference is also sometimes made to the example of the potential

$$U(r) = -1/r + \alpha/2r^2, \quad (13)$$

for which the Schrödinger equation can be solved exactly and the energy levels are of the form

$$E_{nl} = -\frac{1}{2(n + \Delta_l)^2},$$

$$\Delta_l = \frac{\alpha}{(l + 1/2) + [(l + 1/2)^2 + \alpha]^{1/2}}. \quad (14)$$

In this case the formula (12) for Δ_l is incorrect, but this occurs because of the fact that the potential (13) has an inadmissible singularity $\sim r^{-2}$ at zero. The factor

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2) We note that apart from a numerical factor of order unity we can derive (8) by means of perturbation theory [see Appendix, Eq. (A.9)]. There is, however, no prior basis for applying perturbation theory, since the deviation of V(r) from the Coulomb potential for small r can be arbitrarily large.

3) Indeed, in the external region $r > r_0$, where the potential is zero, the wave function is of the form

$$\chi_l(r) = C(\varkappa r)^{1/2}K_{l+1/2}(\varkappa r)$$

($\kappa^2/2$ is the binding energy). For $\kappa \to 0$ we have $\chi_l(r) \approx (\kappa r)^{-l}$, and by (5) $h_l = -l$.

$$\left(1-\frac{1^2}{n^2}\right)\left(1-\frac{2^2}{n^2}\right)\dots\left(1-\frac{l^2}{n^2}\right)$$

in (8) and (12) arises because of $|\psi_{nlm}(0)|^2$, where ψ_{nlm} is the exact solution in the Coulomb field. This is particularly easily seen if we regard the deviation of U(r) from the Coulomb field as small (see Appendix).

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APPENDIX

Let us find the level shift with perturbation theory, assuming that

$$U(r) = -1/r + \delta U(r).$$

The radial wave function in the Coulomb field is of the form

$$R_{nl}(r) = C_{nl}e^{-r/n}r^lF(-n+l+1,\ 2l+2;\ 2r/n),$$

$$C_{nl} = \frac{2^{l+1}}{(2l+1)!}\left[\frac{1}{n^3}\left(1-\frac{1^2}{n^2}\right)\dots\left(1-\frac{l^2}{n^2}\right)\right]^{1/2}. \quad \text{(A.1)}$$

From this we have

$$\Delta E_{nl} = C_{nl}^2\int\limits_0^\infty \delta U(r)\,e^{-2r/n}r^{2l+2}$$

$$\times F^2\left(-n+l+1, 2l+2; \frac{2r}{n}\right)dr. \quad \text{(A.2)}$$

Let us take δU(r) in the form

$$\delta U(r) = -\alpha e^{-2\mu r}/r \quad \text{(A.3)}$$

(a screened Coulomb potential). In this case the integral in (A.2) can be calculated exactly (see [6], page 696):

$$\Delta E_{nl} = -\frac{\alpha}{(2l+1)!\,\mu^{2l+2}}\left(\frac{n\mu}{1+n\mu}\right)^{2n}\frac{1}{n^3}\left(1-\frac{1^2}{n^2}\right)\dots$$

$$\dots\left(1-\frac{l^2}{n^2}\right)\cdot{}_2F_1(-n+l+1, -n+l+1;$$

$$2l+2;\ (n\mu)^{-2}). \quad \text{(A.4)}$$

For n ≫ 1, $\mu \sim 1$ the hypergeometric function has the asymptotic form

$${}_2F_1(-n+l+1,\ -n+l+1;\ 2l+2;$$

$$(n\mu)^{-2}) \sim (2l+1)!\,\mu^{2+1}I_{2l+1}(2/\mu)\cdot, \quad \text{(A.5)}$$

where $I_{2l+1}(z)$ is the Bessel function of imaginary argument. Substituting this in (A.4), we have

$$\Delta E_{nl}|_{n\mu\gg1} = -\frac{\alpha}{\mu n^3}\left(1-\frac{1^2}{n^2}\right)\cdots\left(1-\frac{l^2}{n^2}\right)e^{-2/\mu}I_{2l+1}\left(\frac{2}{\mu}\right) \quad \text{(A.6)}$$

i.e., the dependence on n is given by the same factor as in (8). On the other hand, for $\mu \to 0$ the first term in the polynomial

$${}_2F_1(-n+l+1,\ -n+l+1;\ 2l+2;\ (n\mu)^{-2})$$

is dominant, and (A.4) takes the form

$$\Delta E_{nl}|_{n\mu\ll1} = -\frac{\alpha}{n^2} = -\alpha\left\langle\frac{1}{r}\right\rangle_{nl}. \quad \text{(A.7)}$$

It can be seen from this that Eq. (8) does not give the level shift correctly if δU(r) has a slowly decreasing Coulomb "tail." This is in agreement with the derivation of (8) given in the main text.

It is not hard to extend the result we have obtained to any form of δU(r). To do so we note that for $n \to \infty$ and $r \lesssim n$ the wave function $R_{nl}(r)$ has the asymptotic form

$$R_{nl}(r) = \left[\frac{2}{n^3r}\left(1-\frac{1^2}{n^2}\right)\dots\left(1-\frac{l^2}{n^2}\right)\right]^{1/2}J_{2l+1}(\sqrt{8r}) \quad \text{(A.8)}$$

[here the numerical factor is chosen so that for $r \ll l$ this formula goes over into the exact formula (A.1)]. Therefore the shift of the level E_{nl} is given by

$$\Delta E_{nl}|_{n\gg1} = \frac{2}{n^3}\left(1-\frac{1^2}{n^2}\right)\dots\left(1-\frac{l^2}{n^2}\right)\int\limits_0^\infty \delta U(r)\,J_{2l+1}^2(\sqrt{8r})\,r\,dr \quad \text{(A.9)}$$

[for this formula to hold it is necessary that δU(r) fall off more rapidly than $r^{-3/2}$ for $r \to \infty$). The dependence of ΔE_{nl} on n again agrees with (8).

We note, finally, that the exact solution for the potential (13) is of the form

$$R_{\varkappa l}(r) = Ce^{-\varkappa r}r^{l'}F(l'+1-\varkappa^{-1},\ 2l'+2,\ 2\varkappa r), \quad \text{(A.10)}$$

where $l' = -1/2 + [(l+1/2)^2 + \alpha]^{1/2}$ [the energy level (14) is found from the condition $l' + 1 - \kappa^{-1} = -n + l + 1$]. For $r \to 0$ we have $R_{\kappa l}(r) \sim Cr^{l'}$, which does not agree with the usual behavior of the wave function. Therefore the potential (13) cannot be treated by perturbation theory.

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