

## 39. The hydrogen atom, II

39.1. **Quantum numbers.** The number  $n$  in Theorem 38.2 is called the **principal quantum number**; it characterizes the energy of the state. The number  $\ell$  is called the **azimuthal quantum number**; it characterizes the eigenvalue of the spherical Laplacian  $\Delta_{\text{sph}}$ , which has the physical interpretation as (minus) the **orbital angular momentum operator**  $\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2$ . Note that the operators  $iL_x$ ,  $iL_y$  and  $iL_z$  are just the generators of the Lie algebra  $\text{Lie}(SO(3))$  acting on  $\mathbb{R}^3$ , i.e., we have

$$[L_x, L_y] = -iL_z, \quad [L_y, L_z] = -iL_x, \quad [L_z, L_x] = -iL_y.$$

Thus,  $\mathbf{L}^2$  is simply a Casimir of  $\text{Lie}(SO(3))$ . Namely, recall that the standard Casimir  $C$  acts on  $L_{2\ell}$  as  $\frac{2\ell(2\ell+2)}{4} = \ell(\ell+1)$ , so  $\mathbf{L}^2 = C$ .

Finally,  $m$  is called the **magnetic quantum number**, and it is the eigenvalue of  $L_z = -i\partial_\theta$  (in spherical coordinates).

**Corollary 39.1.** *The space  $W_n$  of states with principal quantum number  $n$  has dimension  $n^2$ .*

*Proof.* By Theorem 38.2, this dimension is  $\sum_{\ell=0}^{n-1} (2\ell+1) = n^2$ . □

In fact, this analysis applies not just to hydrogen but to other chemical elements whose nucleus has charge  $> 1$ , if we neglect interaction between electrons. Thus it can potentially be used to explain patterns of the periodic table.

39.2. **Coulomb waves.** We note, however, that  $\psi_{n\ell m}$  **do not** form a basis of  $L^2(\mathbb{R}^3)$ . Instead, they span (topologically) a proper closed subspace of  $L_0^2(\mathbb{R}^3)$  of  $L^2(\mathbb{R}^3)$  on which the operator  $H$  is bounded and negative definite. So if a smooth function  $\varphi$  on  $\mathbb{R}^3$  (say, with compact support away from the origin) satisfies  $(H\varphi, \varphi) \geq 0$  then  $\varphi \notin L_0^2(\mathbb{R}^3)$ . It is easy to construct such examples: let  $\varphi$  be a hat function and  $\varphi_s(\mathbf{r}) = \varphi(\mathbf{r} + s\mathbf{a})$ , where  $\mathbf{a}$  is any nonzero vector. We then have

$$(H\varphi_s, \varphi_s) = \frac{1}{2} \int_{\mathbb{R}^3} |\nabla\varphi(\mathbf{r})|^2 dV - \int_{\mathbb{R}^3} \frac{|\varphi(\mathbf{r})|^2}{|\mathbf{r} - s\mathbf{a}|} dV,$$

and we observe that the first term is positive and the second one goes to zero as  $s \rightarrow \infty$ , so for large  $s$  this expression is positive. This happens because besides bound states the hydrogen atom also has **continuous spectrum**  $[0, \infty)$  corresponding to free electrons which are not bound by the nucleus. This part of the spectrum can be computed similarly to the discrete (bound state) spectrum, except that the energy will take arbitrary **nonnegative** values. The corresponding wavefunctions are not normalizable (i.e., not in  $L^2$ ), and are given by similar formulas to

bound states but with imaginary  $n$ . Their continuous linear combinations satisfying appropriate boundary conditions are called **Coulomb waves**.

**39.3. Spin.** Also, the answer  $n^2$  for the number of states in the  $n$ -th energy level does not quite agree with the periodic table, which suggests it should rather be  $2n^2$ : the numbers of electrons at each level are 2, 8, 18, 32.... This is because the Schrödinger model which we computed is not quite right, as it does not take into account an additional degree of freedom called **spin** (a sort of intrinsic angular momentum). Namely, it turns out that the space of states of an electron is not  $L^2(\mathbb{R}^3)$  but rather  $L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$ , with the same Hamiltonian as before but the Lie algebra  $\text{Lie}(SO(3))$  acting diagonally (where  $\mathbb{C}^2$  is the 2-dimensional irreducible representation of this Lie algebra). Thus the space of states of the  $n$ -th energy level taking spin into account is

$$V_n = (L_0 \oplus L_2 \oplus \dots \oplus L_{2n-2}) \otimes L_1 = 2L_1 \oplus 2L_3 \oplus \dots \oplus 2L_{2n-3} \oplus L_{2n-1}$$

and  $\dim V_n = 2n^2$ . In other words, we have the additional **spin operator**, which is just the operator

$$S = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$$

acting on the  $\mathbb{C}^2$  factor (in the standard basis  $\mathbf{e}_+, \mathbf{e}_-$ ). So the **total spin** (=angular momentum) of a state is  $m+s$ , where  $s$  is the eigenvalue of  $S$ , and we have the basic states  $\psi_{nlm+} = \psi_{nlm} \otimes \mathbf{e}_+$  and  $\psi_{nlm-} = \psi_{nlm} \otimes \mathbf{e}_-$  with spins  $m + \frac{1}{2}$  and  $m - \frac{1}{2}$  respectively.

Note also that  $V_n$  is **not** a representation of  $SO(3)$  but is only a representation of its double cover  $SU(2)$  where  $-\text{Id}$  acts by  $-1$ . However, this **anomaly** does not mean a violation of the  $SO(3)$  symmetry, since true quantum states are unit vectors in the Hilbert space **up to a phase factor**.

**39.4. The Pauli exclusion principle.** Suppose now that we have  $k$  electrons, each at the  $n$ -th energy level. If the electrons had been marked, the space of states for them would have been  $V_n^{\otimes k}$ . But in real life they are indistinguishable, so we need to mod out by permutations. So we might think the space of states is  $S^k V_n$ . However, as electrons are **fermions**, this answer turns out to be not correct: the correct answer is  $\wedge^k V_n$  rather than  $S^k V_n$ . In other words, when two identical electrons are switched, the corresponding vector changes sign. This is another example of a sign which does not violate symmetry since states are well defined only up to a phase factor.

In particular, this implies that if  $k > 2n^2$  then the space of states is zero, i.e., there cannot be more than  $2n^2$  electrons at the  $n$ -th energy level (the **Pauli exclusion principle**). This is exactly the kind of pattern we see in the periodic table.

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
Period 5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
Period 6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
Period 7	87 Fr	88 Ra	* 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			* 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

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Namely, the first energy level has two slots (the first row, or period, of the table), and the second one has 8 slots (the second period of the table). Further down interactions between electrons start to matter and the picture is modified (giving still 8 slots in the next period instead of 18), but we still see a similar pattern: 8 slots in the third period, 18 in periods 4,5, and 32 in periods 6,7. This arrangement is justified by the fact that the columns (groups) of elements, which have the same number of electrons at the last level, have similar chemical properties. For example, in the first column we have alkali metals (except hydrogen) and in the last one we have inert gases.

**Exercise 39.2.** Let  $\mathbf{r} = (x, y, z)$  and  $\mathbf{p} = (-i\partial_x, -i\partial_y, -i\partial_z)$  be the position and momentum operators in  $\mathbb{R}^3$ . Let  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$  be the angular momentum operator (these are actually vectors whose components are operators on functions in  $\mathbb{R}^3$ ). Let  $r = |\mathbf{r}| = \sqrt{x^2 + y^2 + z^2}$  (the operator of multiplication by this function) and  $H = \frac{1}{2}\mathbf{p}^2 + U(r) = -\frac{1}{2}\Delta + U(r)$  be a rotationally symmetric Schrödinger operator on  $\mathbb{R}^3$  with potential  $U(r)$  (smooth for  $r > 0$ ).

(i) Show that the components of  $i\mathbf{L}$  are vector fields that define the action of the Lie algebra  $\text{Lie}(SO(3))$  on functions on  $\mathbb{R}^3$  induced by rotations. Deduce that  $[\mathbf{L}, \mathbf{p}^2] = 0$  (componentwise).

(ii) Let  $\mathbf{A}_0 = \frac{1}{2}(\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p})$ . Show that  $[\mathbf{A}_0, \mathbf{p}^2] = 0$  (again componentwise).

(iii) Let  $\mathbf{A} := \mathbf{A}_0 + \phi(r)\mathbf{r}$ . Show that there exists a function  $\phi$  such that  $[\mathbf{A}, H] = 0$  if and only if  $U$  is the Coulomb potential  $\frac{C}{r} + D$ , and

then  $\phi$  is uniquely determined, and compute  $\phi$ . The corresponding operator  $\mathbf{A}$  is called the **quantum Laplace-Runge-Lenz vector**.<sup>20</sup>

(iv) (Hidden symmetry of the hydrogen atom). By virtue of (iii), the components of  $\mathbf{A}$  act (by second order differential operators) on functions on  $\mathbb{R}^3$  commuting with  $H$ . In particular, they act on each  $W_n$  (note that in this problem we ignore spin). Use these components to define an action of  $\mathfrak{so}_4 = \mathfrak{so}_3 \oplus \mathfrak{so}_3 = \mathfrak{sl}_2 \oplus \mathfrak{sl}_2$  on  $W_n$  so that the geometric one (generated by the components of  $\mathbf{L}$ ) is the diagonal copy.

(v) Show that  $W_n = L_{n-1} \boxtimes L_{n-1}$  as a representation of  $\mathfrak{sl}_2 \oplus \mathfrak{sl}_2$ .

(vi) Now include spin by tensoring with the representation  $\mathbb{C}^2$  of  $SU(2)$  and show that  $V_n = L_{n-1} \boxtimes L_{n-1} \boxtimes L_1$  as a representation of  $\mathfrak{so}_4 \oplus \mathfrak{su}_2 = \mathfrak{sl}_2 \oplus \mathfrak{sl}_2 \oplus \mathfrak{sl}_2$ . This representation is irreducible, which explains why the  $n$ -th energy level of  $H$  is degenerate, with multiplicity (i.e., dimension)  $2n^2$ .

**Exercise 39.3.** Let  $H = -\frac{1}{2}\Delta + \frac{1}{2}r^2$  be the Hamiltonian of the quantum harmonic oscillator in  $\mathbb{R}^n$ , where  $r = \sqrt{x_1^2 + \dots + x_n^2}$ . Compute the eigenspaces of  $H$  in  $L^2(\mathbb{R}^n)$  as representations of  $SO(n)$  and find the eigenvalues of  $H$  with multiplicities and an orthogonal eigenbasis.

**Hint.** Show that the operator  $e^{r^2/2} \circ H \circ e^{-r^2/2}$  preserves the space of polynomials  $\mathbb{C}[x_1, \dots, x_n]$ , and find an eigenbasis  $P_{i_1 i_2 \dots i_n}$  for this operator in this space (these should express via Hermite polynomials; use that  $H = H_1 + \dots + H_n$  is the sum of operators  $H_i$  depending only on  $x_i$ ). This will give orthogonal eigenfunctions

$$\psi_{i_1 \dots i_n}(\mathbf{r}) = P_{i_1 \dots i_n}(\mathbf{r})e^{-r^2/2}$$

in  $L^2(\mathbb{R}^n)$ . Using properties of Hermite polynomials, conclude that these are complete. Then use Exercise 31.11.

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<sup>20</sup>In the classical mechanics setting, the existence of this conservation law is the reason why orbits for Coulomb potential are periodic (Kepler's law), while this is not so for other rotationally invariant potentials, except harmonic oscillator. It was discovered many times over the last 300 years. This is one of the most basic examples of "hidden symmetry".

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