The Laplace-Runge-Lenz Vector, the Accidental Degeneracy of the Hydrogen Atom, and Hidden Symmetry

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Our ultimate goal in these notes is to understand the eigenvalues of the non-relativistic Hamiltonian of the hydrogen atom and the degeneracy of each energy level. Our approach is primarily two-fold. First we will give an accounting of Pauli's derivation of the hydrogen spectrum [Pa26]. This method involves the famous Laplace-Runge-Lenz vector, and so before delving into the quantum mechanical problem, we first review the use of this vector in the Newtonian two-body problem. After developing the algebraic approach of Pauli, we will see that there should be an additional symmetry which would account for the higher-than-expected degeneracy of each energy subspace. We then show how an appropriate transformation can elucidate this hidden symmetry. For this, we take the approach detailed in the paper of Bander and Itzykson [Ba66].

I) The Newtonian Two-Body Problem

The classical Hamiltonian for two particles interacting via an inverse-square force law is

$$H(p_1, p_2, q_1, q_2) = \frac{|p_1|^2}{2m_1} + \frac{|p_2|^2}{2m_2} + \frac{\alpha}{|q_1 - q_2|}$$

where p_i, q_i, and m_i are the momentum, position, and mass of the ith particle. The constant α depends on the exact type of interaction ($\alpha < 0$ would be an attractive interaction). The first reduction we do is to separate off the center-of-mass motion via the canonical transformation

$$Q_{cm} = \frac{m_1 q_1 + m_2 q_2}{m_1 + m_2} \qquad q = q_1 - q_2$$
$$P_{cm} = p_1 + p_2 \qquad p = \frac{m_2 p_1 - m_1 p_2}{m_1 + m_2}$$

which transforms our original Hamiltonian into

$$H(P_{cm}, p, Q_{cm}, q) = \frac{|P_{cm}|^2}{2m} + \frac{|p|^2}{2\mu} + \frac{\alpha}{|q|}$$

where $m = m_1 + m_2$ and $\mu = \frac{m_1 m_2}{m_1 + m_2}$ (known as the reduced mass).

The conspicuous absence of Q_{cm} in the Hamiltonian shows that the total momentum P_{cm} is conserved! Hence, we can perform a boost into the coordinate system where $Q_{cm} = 0$ and $P_{cm} = 0$. In this frame, our Hamiltonian becomes

$$H_r(p, q) = \frac{|p|^2}{2\mu} + \frac{\alpha}{|q|}$$

which is known as the *reduced Hamiltonian* for the relative coordinates of the two-body problem.

Theorem. *The following quantities are constant along trajectories determined by H_r:*

1) $H_r(p, q) = \frac{|p|^2}{2\mu} + \frac{\alpha}{|q|}$

2) $L(p, q) = q \times p$

3) $M(p, q) = p \times L(p, q) + \mu\alpha \frac{q}{|q|}$

Proof:
1) is a direct consequence of the canonical equations of motion:

$$\begin{aligned} \dot{q}(t) &= (\nabla_p H_r)\,(p(t), q(t)) \\ &= \frac{1}{\mu} p(t) \\ \dot{p}(t) &= (-\nabla_q H_r)\,(p(t), q(t)) \\ &= \frac{\alpha}{|q(t)|^3}\, q(t) \end{aligned}$$

Explicitly,

$$\begin{aligned} \frac{d}{dt} H_r(p(t), q(t)) &= (\nabla_p H_r)\,(p(t), q(t)) \cdot \dot{p}(t) \\ &\quad + (\nabla_q H_r)\,(p(t), q(t)) \cdot \dot{q}(t) \\ &= (\nabla_p H_r)\,(p(t), q(t)) \cdot (-\nabla_q H_r)\,(p(t), q(t)) \\ &\quad + (\nabla_q H_r)\,(p(t), q(t)) \cdot (\nabla_p H_r)\,(p(t), q(t)) \\ &= 0 \end{aligned}$$

For 2), $\dot{L}(p(t), q(t)) = \dot{q}(t) \times p(t) + q(t) \times \dot{p}(t)$. Since $\dot{q}(t)$ is parallel to $p(t)$ and $\dot{p}(t)$ is parallel to $q(t)$, the result follows.

For 3), note that

$$\begin{aligned}
\frac{d}{dt}(p(t) \times L(p(t), q(t))) &= \dot{p}(t) \times L(p(t), q(t)) \\
&= \frac{\alpha}{|q(t)|^3}\, q(t) \times (q(t) \times p(t)) \\
&= \frac{\alpha}{|q(t)|^3} \left[q(t)(q(t) \cdot p(t)) - p(t)|q(t)|^2 \right] \\
&= \frac{\alpha}{|q(t)|^3} \left[q(t)(q(t) \cdot \mu\dot{q}(t)) - \mu\dot{q}(t)|q(t)|^2 \right] \\
&= -\frac{\mu\alpha}{|q(t)|}\, \dot{q}(t) + \frac{\mu\alpha}{|q(t)|^3}(q(t) \cdot \dot{q}(t))q(t) \\
&= -\frac{d}{dt}\left(\frac{\mu\alpha}{|q(t)|}\ \ q(t) \right) \quad \square
\end{aligned}$$

The vector $M(p, q)$ is known as the Laplace-Runge-Lenz vector. Note that we have found 7 functions of phase space which are constant along each trajectory! Since our phase space is 6 dimensional, the quantities above cannot be totally independent.

Lemma. *The following relations hold amongst H_r, L and M:*

i) $L(p, q) \cdot M(p, q) = 0$

ii) $|M(p, q)|^2 = 2\mu H_r(p, q)|L(p, q)|^2 + \mu^2\alpha^2$

Proof:
i) is clear from the definition of $M(p, q)$.
ii) is verified directly:

$$M(p, q) \cdot M(p, q) = |p \times L(p, q)|^2 + 2\mu\alpha \frac{q}{|q|} \cdot (p \times L(p, q)) + \mu^2\alpha^2$$

The first term is just $|p|^2|L(p, q)|^2$ since these two vectors are perpendicular. For the second term, note that since the scalar triple product is cyclic in its arguments, we have

$$\begin{aligned}
q \cdot (p \times L(p, q)) &= L(p, q) \cdot (q \times p) \\
&= L(p, q) \cdot L(p, q) \\
&= |L(p, q)|^2
\end{aligned}$$

Putting all this into the expression for $|M(p,q)|^2$ and collecting the terms with $|L(p,q)|^2$ proves the relation. $\square$

Note that the remaining constants of motion are algebraically independent and, hence, the dynamical system is completely integrable.

We now show that the motion is along conic sections and provide a geometric interpretation for the L-R-L vector. For brevity, we use the following notation:

$$E = H_r(p(0), q(0))$$
$$L_0 = L(p(0), q(0))$$
$$M_0 = M(p(0), q(0)).$$

We assume that the angular momentum is non-zero (as then the motion is along a ray emanating from the origin; evidently, the motion may then encounter a singularity in finite time). By an appropriate choice of coordinates, we can take the angular momentum to lie on the positive z-axis. This restricts the plane of motion $q \cdot L_0 = 0$ to the xy-plane. Since M_0 must be in this plane and its length is given as above, the only thing undetermined about the L-R-L vector is its direction in the plane. Again by suitable choice of coordinates, we can take M_0 to be along the positive x-axis. Let $r(t)$ and $\theta(t)$ be the polar coordinates for $q(t)$ in the plane of motion. By the definition of the dot product, we have

$$q(t) \cdot M_0 = |M_0| r(t) \cos\theta(t).$$

On the other hand, we can calculate this dot product directly:

$$\begin{aligned} q(t) \cdot M_0 &= q(t) \cdot (p(t) \times L_0) + \mu\alpha |q(t)| \\ &= |L_0|^2 + \mu\alpha r(t). \end{aligned}$$

Solving for $r(t)$ gives

$$r(t) = \frac{|L_0|^2}{|M_0| \cos\theta(t) - \mu\alpha}$$

which is the polar form of a conic section! We also note the following consequences of our derivation:

- The motion is along a hyperbola whenever $E > 0$ (since $|M_0| > \mu\alpha$).
- The motion is along a parabola whenever $E = 0$ (which can only happen when $\alpha < 0$).

- The motion is along an ellipse whenever $E < 0$ (which can also only happen when $\alpha < 0$).
- The Laplace-Runge-Lenz vector points in the direction of the orbit's closest approach to the origin (e.g. the perihelion in planetary motion).
- The length of the Laplace-Runge-Lenz vector is the eccentricity of the orbit.

II) Pauli's Computation of the Hydrogen Spectrum

We first give a brief outline of the "quantization" procedure that Pauli had at his disposal thanks to Heisenberg's Matrix Mechanics. After showing that this is equivalent to Schrödinger's Wave Mechanics, we then outline the derivation of the Hydrogen spectrum purely through algebraic manipulations with operators.

In classical mechanics, physical properties of a system (such as the components of angular momentum) can be written as C^∞ functions of the basic phase space variables $(p_1, \ldots, p_N, q_1, \ldots, q_N)$ of the particles comprising the system. Let such a system property be given by the function

$$F(p_1, \ldots, p_N, q_1, \ldots, q_N)$$

where the system has Hamiltonian $H(p_1, \ldots, p_N, q_1, \ldots, q_N)$. We want to find a formula for the time derivative of this quantity along a trajectory of the system in phase space - $(p_1(t), \ldots, p_N(t), q_1(t), \ldots, q_N(t))$. Let

$$F(t) = F(p_1(t), \ldots, p_N(t), q_1(t), \ldots, q_N(t))$$

be the value of F at each point of the trajectory. Then by the chain rule, we have

$$\begin{aligned}
\dot{F}(t) &= \sum_{i=1}^{n} (\nabla_{p_i} F)(p_1(t), \ldots, p_N(t), q_1(t), \ldots, q_N(t)) \cdot \dot{p}(t) \\
&\quad + \sum_{i=1}^{n} (\nabla_{q_i} F)(p_1(t), \ldots, p_N(t), q_1(t), \ldots, q_N(t)) \cdot \dot{q}(t) \\
&= \sum_{i=1}^{n} (-\nabla_{p_i} F \cdot \nabla_{q_i} H)(p_1(t), \ldots, p_N(t), q_1(t), \ldots, q_N(t)) \\
&\quad + \sum_{i=1}^{n} (\nabla_{q_i} F \cdot \nabla_{p_i} H)(p_1(t), \ldots, p_N(t), q_1(t), \ldots, q_N(t))
\end{aligned}$$

$$= \sum_{i=1}^{n} (\nabla_{q_i} F \cdot \nabla_{p_i} H - \nabla_{p_i} F \cdot \nabla_{q_i} H)(p_1(t), \ldots, p_N(t), q_1(t), \ldots, q_N(t))$$

The final equality above leads to the definition of the *Poisson Bracket* of two C^∞ functions on phase space:

$$\{F, G\} \equiv \sum_{i=1}^{n} \nabla_{p_i} F \cdot \nabla_{q_i} G - \nabla_{q_i} F \cdot \nabla_{p_i} G.$$

Note the bracket of two C^∞ functions on phase space is another C^∞ function on phase space. Thus, we have that

$$\dot{F}(t) = \{H, F\}(t)$$

(where we again have used the short hand $\{H, F\}(t)$ to indicate that the actual trajectory $(p_1(t), \ldots, p_N(t), q_1(t), \ldots, q_N(t))$ is plugged into the function $\{H, F\}$). Note that the *fundamental brackets* are $\left\{p_i^m, q_j^n\right\} = \delta_{ij}\delta_{mn}$ where p_i^m is the m-th component of momentum for the i-th particle (and similar notation for q).

Heisenberg's Matrix Mechanics replaces these classical system properties (aka "observables") with infinite matrices (which we understand now as self-adjoint operators) acting on a fixed vector representing the quantum system, and replaces the Poisson Bracket above with $\frac{i}{\hbar}$ times the commutator of the matrices. The primary classical quantities q and p are now regarded as time-dependent matrices, and the fundamental brackets are translated into the *fundamental commutation relations*

$$[q_i, p_j] = i\hbar\delta_{ij}.$$

Other classical observables are converted into matrices appropriately (this can be delicate if the classical observable involves products of non-commuting variables; typically one uses the Weyl Rule, which means to symmetrize). The matrix corresponding to the observable F at time t would be given by the ODE

$$\dot{F}_t = \frac{i}{\hbar}[H, F_t].$$

Finally, the long-run average of many repetitions of an experiment designed to "measure the observable F at time t" would be $\langle F_t \rangle = (v, F_t v)$ where v is the fixed vector representing the system and the inner product is given in the usual way for vectors and matrices (i.e. $(v, F_t v) = v^T F_t v$).

One of the advantages of Schrödinger's Wave Mechanics is that we replace this rather abstract notion of an ODE on operator space by a PDE for some L^2 function on $\mathbb{R}^{3N}$ (something far more tractable). That these two "pictures" of orthodox quantum theory are equivalent is easy to see from a formal standpoint. Let ψ_t be the wave function of a quantum system with Hamiltonian H. Formally we get that

$$\psi_t = e^{-\frac{i}{\hbar}tH}\psi_0.$$

If F is some fixed self-adjoint operator, then at time t

$$\begin{aligned}\langle F\rangle_t &= (\psi_t, F\psi_t)\\ &= (e^{-\frac{i}{\hbar}tH}\psi_0, Fe^{-\frac{i}{\hbar}tH}\psi_0)\\ &= (\psi_0, e^{\frac{i}{\hbar}tH}Fe^{-\frac{i}{\hbar}tH}\psi_0)\\ &= \langle F_t\rangle_0\end{aligned}$$

with

$$F_t = e^{\frac{i}{\hbar}tH}Fe^{-\frac{i}{\hbar}tH},$$

and by differentiating with respect to t we get

$$\begin{aligned}\dot{F}_t &= \frac{i}{\hbar}He^{\frac{i}{\hbar}tH}Fe^{-\frac{i}{\hbar}tH} - \frac{i}{\hbar}e^{\frac{i}{\hbar}tH}Fe^{-\frac{i}{\hbar}tH}H\\ &= \frac{i}{\hbar}[H, F_t]\end{aligned}$$

just as Heisenberg said! Incidentally, in Schrödinger's picture of Quantum Mechanics, p is replaced by the operator $-i\hbar\nabla$ while q becomes a multiplication operator. Hence, $[q_i, p_j] = i\hbar\delta_{ij}$ as required!

Of course, Pauli did not have Wave Mechanics at his disposal when he was working on the Hydrogen atom. So, the best one can do in that case is try to take advantage of algebraic properties of the operators coming from quantities that were useful in determining the motion of the classical two-body problem - namely, the Hamiltonian, orbital angular momentum, and the Laplace-Runge-Lenz vector [Pa26, pp. 397 and 402-403]!

The non-relativistic Hydrogen atom is modeled by the reduced Hamiltonian Operator:

$$H = \frac{|p|^2}{2\mu} - \frac{e^2}{|q|} = -\frac{\hbar^2}{2\mu}\Delta - \frac{e^2}{|q|}$$

where the reduced mass μ is as usual

$$\mu = \frac{m_e m_p}{m_e + m_p} \approx \frac{1836}{1837}\, m_e$$

and e is the charge of the proton (or the negative charge of the electron). We also introduce the Orbital Angular Momentum Operator:

$$L = q \times p = \frac{\hbar}{i} q \times \nabla$$

whose three components are well-defined self-adjoint operators. We also wish to make the L-R-L vector into an operator, but if we apply the usual procedure of replacing p by $-i\hbar\nabla$ we run into a slight difficulty - the operator obtained is not self-adjoint (due to non-commuting operators being multiplied together)! The standard trick to remedy such an issue is called symmetrization (i.e. the Weyl Rule). Using this, we introduce the Laplace-Runge-Lenz Operator:

$$M = \frac{1}{2}(p \times L - L \times p) + \mu\alpha \frac{q}{|q|}.$$

Our next step would be to calculate the various commutator relations among these quantities. These are long and tedious calculations involving the basic commutation relations and the fact that the commutator is a bi-derivation. To save space (and an extreme headache) we merely present the results:

$$\begin{aligned}
[H, L] &= 0 \\
[H, M] &= 0 \\
[L_i, L_j] &= i\hbar\, \epsilon_{ijk} L_k \\
[M_i, M_j] &= \frac{\hbar}{i} 2\mu\, \epsilon_{ijk} L_k H \\
[L_i, M_j] &= i\hbar \epsilon_{ijk} M_k
\end{aligned}$$

where ϵ_{ijk} is the Levi-Civita anti-symmetric tensor and the commutators involving vector operators are understood component-wise. In addition to these commutation relations, we also have the following relations among the operators (in complete analogy to the classical case):

a) $L \cdot M = M \cdot L = 0$

b) $M^2 - \mu^2 e^4 = 2\mu H(L^2 + \hbar^2)$

where the dot products are understood componentwise and

$$L^2 = L \cdot L = L_x^2 + L_y^2 + L_z^2$$

and similarly for M^2.

The idea now is to restrict our attention to a particular subspace corresponding to eigenfunctions of H with the same eigenvalue $E < 0$, i.e. we are looking for solutions to

$$H\psi = E\psi$$

for a fixed (negative) eigenvalue E. We now wish to determine the degeneracy of this subspace (that is, its dimension). Along the way, we also get out the admissible values of E! Since we have restricted our attention to this subspace, H merely acts by multiplication by E. With this in mind, we rescale the L-R-L operator by

$$\widetilde{M} = \sqrt{\frac{1}{-2\mu E}}\ M.$$

A simple check shows that all the commutators remain the same when we replace M by $\widetilde{M}$ except that

$$[\widetilde{M}_i, \widetilde{M}_j] = i\hbar\, \epsilon_{ijk} L_k.$$

Relation a) above still holds true since we have just rescaled M. Relation b) becomes

$$\widetilde{M}^2 + L^2 + \hbar^2 = \frac{-\mu e^4}{2E}.$$

We now define two new operators:

$$\begin{aligned} J_1 &= \frac{L + \widetilde{M}}{2} \\ J_2 &= \frac{L - \widetilde{M}}{2}. \end{aligned}$$

A simple calculation shows the following:

$$\begin{aligned} [J_1, J_2] &= 0 \\ [J_{1i}, J_{1j}] &= i\hbar\, \epsilon_{ijk} J_{1k} \\ [J_{2i}, J_{2j}] &= i\hbar\, \epsilon_{ijk} J_{2k} \end{aligned}$$

which shows that J_1 and J_2 are two commuting (generic) angular momenta on our subspace. As such, we can ask for simultaneous eigenfunction for the set of operators $\{J_1^2, J_2^2, J_{1z}, J_{2z}\}$ (see the notes on Angular Momenta in Quantum Mechanics for details). However, relation a) above shows that

$$\begin{aligned} J_1^2 &= \frac{1}{4}(L + \widetilde{M})^2 \\ &= \frac{1}{4}(L^2 + L \cdot \widetilde{M} + \widetilde{M} \cdot L + M^2) \\ &= \frac{1}{4}(L^2 + \widetilde{M}^2). \end{aligned}$$

A similar calculation shows that $J_1^2 = J_2^2 = \frac{1}{4}(L^2 + \widetilde{M}^2)$. Hence, the simultaneous eigenfunctions of $\{J_1^2 = J_2^2, J_{1z}, J_{2z}\}$ are characterized by three indices (or quantum numbers). We will label these functions by $|j, m_1, m_2\rangle$ where

$$\begin{aligned} J_1^2|j, m_1, m_2\rangle &= j(j+1)\hbar^2|j, m_1, m_2\rangle \\ J_2^2|j, m_1, m_2\rangle &= j(j+1)\hbar^2|j, m_1, m_2\rangle \\ J_{1z}|j, m_1, m_2\rangle &= m_1\hbar|j, m_1, m_2\rangle \\ J_{2z}|j, m_1, m_2\rangle &= m_2\hbar|j, m_1, m_2\rangle, \end{aligned}$$

$j \in \{0, \frac{1}{2}, 1, \frac{3}{2}, \ldots\}$, and for each j, both m_1 and m_2 can take on values in the set $\{-j, -j+1, \ldots, j-1, j\}$.

Note that our relation b) above now reads:

$$\begin{aligned} \frac{-\mu e^4}{2E} &= \widetilde{M}^2 + L^2 + \hbar^2 \\ &= 4J_1^2 + \hbar^2 \end{aligned}$$

and applying this to our eigenfunctions gives

$$\begin{aligned} \frac{-\mu e^4}{2E}|j, m_1, m_2\rangle &= (4J_1^2 + \hbar^2)|j, m_1, m_2\rangle \\ &= (4j(j+1) + 1)\hbar^2|j, m_1, m_2\rangle \\ &= (2j+1)^2\hbar^2|j, m_1, m_2\rangle \end{aligned}$$

and so we must have

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

or equivalently

$$E = \frac{-\mu e^4}{2\hbar^2}\frac{1}{(2j+1)^2}.$$

We define $n = 2j+1$ and from our results above $n \in \{0, 1, 2, \dots\}$. We now wish to use simultaneous eigenfunctions for the operators $\{L^2, L_z\}$ instead of the ones for $\{J_{1z}, J_{2z}\}$ (as the former operators are the ones traditionally used; also, these work with **any** spherical Schrödinger potential). Recall that the eigenvalue of J_1^2 is fixed for our subspace since it determines the energy! The only difficult part is recovering the possible values for ℓ (the quantum number for L^2) and m (the quantum number for L_z) given the values of m_1, m_2 and the fixed value j for our subspace. Since $L = J_1 + J_2$, the results on addition of angular momentum (see the notes) tells us that $\ell \in \{|j_1 - j_2|, |j_1 - j_2| + 1, \dots, j_1 + j_2 - 1, j_1 + j_2\}$, but $j_1 = j_2 = j$ and since $2j = n - 1$ we must have

$$\ell \in \{0, 1, \dots, n-1\}.$$

As usual, for each value of ℓ, m can take on any one of the $2\ell + 1$ values in

$$\{-\ell, -\ell + 1, \dots, \ell - 1, \ell\}.$$

So, we may label our eigenfunctions for the operators $\{H, L^2, L_z\}$ by $|n, \ell, m\rangle$ where

$$\begin{aligned} H|n,\ell,m\rangle &= \frac{-\mu e^4}{2\hbar^2}\frac{1}{n^2}|n,\ell,m\rangle \\ L^2|n,\ell,m\rangle &= \ell(\ell+1)\hbar^2|n,\ell,m\rangle \\ L_z|n,\ell,m\rangle &= m\hbar|n,\ell,m\rangle \end{aligned}$$

and each n, ℓ and m have the admissible ranges above. Hence the degeneracy of each energy subspace (the subspace corresponding to a specific choice of n) is given by

$$\sum_{\ell=0}^{n-1}(2\ell+1) = n^2.$$

As a final remark on this section, note that the entire argument hinges upon the (often tacit) assumption that the operators $\{H, L^2, L_z\}$ completely characterize the "state" of the electron in the hydrogen atom. This was certainly a reasonable assumption for Pauli, but of course we know better today! For instance, we know that electrons are spin $\frac{1}{2}$ particles. While the spin does not effect the energy (as long as no magnetic fields are present anyway), it does double the degeneracy of each energy subspace!

III) Fock's Transformation and the Hidden Symmetry of the Hydrogen Atom

From the outset, we could have easily predicted that the energy of a given eigenfunction should not depend on the eigenvalue of L_z. A cursory glance at the Hamiltonian shows that it is rotationally invariant - i.e. there is no preferred orientation in space (note that there IS a preferred origin)! However, there does not seem to be any obvious reason that the energy should be completely independent of the angular momentum. Lo and behold, our previous arguments show quite clearly that the energy eigenvalues only depend on n (with no dependence on ℓ). What accounts for this so-called *accidental degeneracy*?

Our calculations above used two distinct (though related) angular momentum operators to classify the eigenfunctions. Classically, we know that angular momentum conservation is associated to rotational invariance - i.e. invariance under the action of $SO(3)$. So, after much pondering, people hit upon the idea that we can project our problem from $\mathbb{R}^3$ onto some manifold where there is an obvious action of $SO(3) \times SO(3)$ (which can be thought of as a subgroup of $O(4)$ - the rotations and reflections in $\mathbb{R}^4$). This immediately suggests stereographic projection onto the unit sphere $\mathbb{S}^3$.

What is even more surprising is that this works much better in the "momentum representation" than the coordinate representation. Basically, this means that we take the Fourier Transform of our equation $H\psi = E\psi$. Instead of the standard transform used by mathematicians, we use the physicists' version:

$$\Phi(p) \;=\; \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int \psi(q) e^{-\frac{i}{\hbar} p\cdot q}\, d^3q.$$

Taking the indicated integrals on both sides and performing two integration-by-parts gives

$$\frac{p^2}{2\mu}\Phi(p) - \frac{e^2}{(2\pi\hbar)^{\frac{3}{2}}} \int \frac{\psi(q)}{|q|} e^{-\frac{i}{\hbar} p\cdot q}\, d^3q = E\Phi(p)$$

which upon simple rearrangement of terms gives

$$\left(p^2 - 2\mu E\right)\Phi(p) = \frac{2\mu e^2}{(2\pi\hbar)^{\frac{3}{2}}} \int \frac{\psi(q)}{|q|} e^{-\frac{i}{\hbar} p\cdot q}\, d^3q.$$

We can transform the integral on the right by using the following identity:

Proposition.

$$\frac{1}{|q|} = \frac{1}{2\pi^2} \int \frac{e^{-ir\cdot q}}{|r|^2}\, d^3r$$

Proof:

Since q is fixed in the integration and $r \cdot q = |r||q| \cos\phi$ where ϕ is the angle between q and r, we may take q to be on the positive z-axis (by an appropriate choice of coordinates). In such coordinates, the azimuthal angle ϕ is precisely the angle between q and r. Hence

$$\begin{aligned}
\int \frac{e^{-ir\cdot q}}{|r|^2}\, d^3r &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{e^{-i|q||r|\cos\phi}}{|r|^2} |r|^2 \sin\phi \; d\theta \; d\phi \; d|r| \\
&= 2\pi \int_0^\infty \int_0^\pi e^{-i|q||r|\cos\phi} \sin\phi \; d\phi \; d|r| \\
&= \frac{2\pi}{|q|} \int_0^\infty \frac{e^{-i|q||r|\cos\phi}}{i|r|} \Big|_0^\pi \; d|r| \\
&= \frac{4\pi}{|q|} \int_0^\infty \frac{\sin|r|}{|r|}\, d|r| \\
&= \frac{2\pi^2}{|q|} \qquad \square
\end{aligned}$$

As an interesting aside, the proposition above is true for any dimension! That is, if q is a vector in $\mathbb{R}^n$ and $\omega_n = \frac{2\pi^{\frac{n}{2}}}{\Gamma(\frac{n}{2})}$ is the area of the unit sphere $\mathbb{S}^{n-1}$ then

$$\frac{1}{|q|} = \frac{1}{\pi\omega_{n-1}} \int \frac{e^{-ir\cdot q}}{|r|^{n-1}}\, d^nr.$$

Returning to our problem, plugging in the formula from the proposition to our eigenvalue equation (and performing a few change of variables) gives

$$\left(p^2 - 2\mu E\right) \Phi(p) = \frac{2\mu e^2}{2\pi^2\hbar} \int \frac{\Phi(r)}{|r-p|^2}\, d^3r.$$

So far, this equation seems to only exhibit invariance under the action of $SO(3)$. We define $p_0 = \sqrt{-2\mu E}$ and stereographically project $\frac{p}{p_0}$ onto the unit sphere in $\mathbb{R}^4$ through the point $(0,0,0,1)$. Specifically, we make the transformation

$$\begin{aligned}
T\left(p_x, p_y, p_z\right) &= \frac{p_0}{p^2 + p_0^2} \left(2p_0p_x, 2p_0p_y, 2p_0p_z, p^2 - p_0^2\right) \\
T^{-1}\left(x, y, z, w\right) &= \frac{p_0}{1-w} \left(x, y, z\right)
\end{aligned}$$

where $p = (p_x, p_y, p_z)$ is an arbitrary vector in $\mathbb{R}^3$ and (x, y, z, w) is an arbitrary point of $\mathbb{S}^3 \setminus \{(0, 0, 0, 1)\}$. To keep things concise, we use the notation u_p to stand for $u = T(p)$ and $\widetilde{\Phi}(u_p) = \Phi(p)$. Some rather long and tedious calculations give the following facts:

$$\begin{aligned} |p - r|^2 &= \frac{(p^2 + p_0^2)(r^2 + p_0^2)}{(2p_0)^2} \ |u_p - v_r|^2 \\ d^3r &= \left(\frac{p^2 + p_0^2}{2p_0}\right)^3 \ d^4\Omega \end{aligned}$$

where the (non-standard) symbol $d^4\Omega$ stands for the surface measure on the unit sphere $\mathbb{S}^3$ in $\mathbb{R}^4$. Plugging these various results into our eigenvalue equation gives

$$(p^2 + p_0^2)\widetilde{\Phi}(u_p) = \frac{\mu e^2}{2\pi\hbar p_0} \frac{1}{p^2 + p_0^2} \int_{S^3} \frac{(r^2 + p_0^2)^2 \widetilde{\Phi}(v_r)}{|u_p - v_r|^2} \ d^4\Omega_{v_r}.$$

To ease the notation, we now drop the subscripts on the 4-vectors. Defining $\widehat{\Phi}(u) = \frac{1}{\sqrt{p_0}} \left(\frac{p^2+p_0^2}{2p_0}\right)^2 \widetilde{\Phi}(u)$ gives

$$\widehat{\Phi}(u) = \frac{\mu e^2}{2\pi^2\hbar p_0} \int_{S^3} \frac{\widehat{\Phi}(v)}{|u - v|^2} \ d^4\Omega_v.$$

This equation clearly shows invariance under the action of $O(4)$!

The definition of $\widehat{\Phi}(u)$ was chosen to make the following true:

Proposition. *If $\Phi(p)$ is normalized in $L_2(\mathbb{R}^3)$, then $\widehat{\Phi}(u)$ is normalized in $L_2(\mathbb{S}^3)$.*

Proof:

We need the Virial Theorem (see [Th02, p. 186]) from which we get

$$E = -\int \frac{p^2}{2\mu} |\Phi(p)|^2 \ d^3p$$

which gives

$$p_0^2 = \int p^2 |\Phi(p)|^2 \ d^3p.$$

By using the various facts and definitions, we have

$$\begin{aligned}\int_{S^3} |\widehat{\Phi}(u)|^2 \ d^4\Omega &= \int \frac{1}{p_0}\left(\frac{p^2+p_0^2}{2p_0}\right)^4 \left(\frac{2p_0}{p^2+p_0^2}\right)^3 |\Phi(p)|^2 \ d^3p \\ &= \frac{1}{2p_0^2}\int (p^2+p_0^2)|\Phi(p)|^2 \ d^3p \\ &= \frac{1}{2p_0^2}\left(\int p^2|\Phi(p)|^2 \ d^3p + p_0^2\right) \\ &= 1 \quad \square\end{aligned}$$

IV) Spherical Harmonics and the Hydrogen Atom

The familiar spherical harmonics in $\mathbb{R}^3$ can be generalized to similar functions in any dimension. We will be especially interested in the spherical harmonics $Y_\ell^m(u)$ defined on the unit sphere in $\mathbb{R}^4$. One way of characterizing these functions is by the following:

Define for any $x \in \mathbb{R}^n$

$$\mathscr{Y}_\ell^m(x) = |x|^\ell \, Y_\ell^m\left(\frac{x}{|x|}\right).$$

Then Y_ℓ^m is a spherical harmonic on the unit sphere in $\mathbb{R}^n$ if and only if both the following hold:

1) $\mathscr{Y}_\ell^m(x)$ is a homogeneous polynomial of degree ℓ in x.

2) $\Delta\mathscr{Y}_\ell^m(x) = 0$.

Note that ℓ can be any non-negative integer. The remaining index m indexes the independent functions satisfying the conditions above for the same ℓ. Using counting arguments, the two conditions above show that in $\mathbb{R}^4$ there are $(\ell+1)^2$ independent spherical harmonics for the same ℓ (which sounds slightly familiar).

Using Green's Formula and some standard estimates, we can show that the spherical harmonics on the unit sphere in $\mathbb{R}^3$ satisfy

$$Y_\ell^m(u) = \frac{\ell+1}{2\pi^2}\int_{S^3} \frac{Y_\ell^m(v)}{|v-u|^2} \ d^4\Omega_v$$

which is exactly the same form that we found for the functions $\widehat{\Phi}(u)$ above! Furthermore, recalling the definition of $p_0 = \sqrt{-2\mu E}$ and our results from section **II** where we found

$$E = \frac{-\mu e^4}{2\hbar^2}\frac{1}{n^2} \text{ where } n \in \{1, 2, \ldots\}$$

plugging this into the coefficient for our integral equation gives

$$\frac{\mu e^2}{2\pi^2 \hbar p_0} = \frac{n}{2\pi^2}$$

and so our integral equation becomes

$$\widehat{\Phi}(u) = \frac{n}{2\pi^2} \int_{S^3} \frac{\widehat{\Phi}(v)}{|u-v|^2} \ d^4\Omega_v.$$

Taking $\ell = n - 1$ in the spherical harmonic integral above gives us the exact form we found for $\widehat{\Phi}$. Since the Spherical Harmonics form a complete orthonormal basis on the unit sphere, we get that the eigenfunctions for the Hydrogen atom can be indexed by two parameters n and m where n is a positive integer and $m \in \{1, 2, \ldots, n^2\}$. Specifically, they are given by

$$\Phi_{n,m}(p) = \frac{4C_n^{\frac{5}{2}}}{(p^2 + C_n^2)^2} \ Y_{n-1}^m \circ T_n(p)$$

where T_n is the stereographic projection defined in the previous section (which depended on the energy!) and

$$C_n = \frac{\mu e^2}{n\hbar}.$$

Note that this form has the advantage of making the hidden $O(4)$ symmetry quite explicit. It of course has the disadvantage that the spherical harmonics in $\mathbb{R}^4$ are less familiar functions.

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