Hyperfocused Derivation of Hydrogen Energy Levels: From Scratch

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1 State Representation

1.1 The Hilbert Space

The defining postulate of quantum mechanics is that the state of a system is described with an element in a Hilbert space. Say the state of a system is a ket vector $|\alpha\rangle \in \mathcal{H}$. An observable property is represented by an operator $A : \mathcal{H} \to \mathcal{H}$. We presume the operator is normal, in which case it has a spectral decomposition

$$A = \int d\mu(\lambda)\lambda \, |\lambda\rangle \, \lambda.$$

A possible observed value is an eigenvalue λ of the operator, so all eigenvalues being real is equivalent to A being Hermitian, that is $A^\dagger = A$. When the system $|\alpha\rangle$ is observed with respect to the observable A, it randomly collapses to one of its eigenkets $|\lambda\rangle$ with probability $|\langle\lambda \,|\, \alpha\rangle|^2$. The total probability adding up to 1 can be stated as

$$1 = \int d\mu(\lambda) \, |\langle\lambda \,|\, \alpha\rangle|^2 = \langle\alpha| \left(\int d\mu(\lambda) \, |\lambda\rangle \, \langle\lambda| \right) |\alpha\rangle = \langle\alpha \,|\, \alpha\rangle \, .$$

This is succinctly referred to as $|\alpha\rangle$ being normalized.

1.2 Time Evolution

Suppose a system in state $|\alpha, t_0\rangle$ at time t_0 evolves to some other state $|\alpha, t_0; t\rangle$ at time t. We make four assumptions:

1. *Time evolution is linear:* $|\alpha, t_0; t\rangle = U(t_0, t) \, |\alpha, t_0\rangle$ for some linear operator $U(t_0, t) : \mathcal{H} \to \mathcal{H}$.
2. *Probability is conserved:* $\langle\alpha, t_0; t \,|\, \alpha, t_0; t\rangle = 1$. This is equivalent to $U^\dagger(t_0, t) = U^{-1}(t_0, t)$, which we call unitary.
3. *Time evolution composes:* $U(t_1, t_2)U(t_0, t_1) = U(t_0, t_2)$ for $t_0 < t_1 < t_2$.
4. *Time evolution is continuous:* $\lim_{t \to t_0^+} U(t_0, t) = 1$.

If we apply these to the infinitesimal evolution $U(t_0, t_0 + dt)$, we find that there is some Hermitian operator $H(t)$ such that

$$U(t_0, t_0 + dt) = 1 - \frac{iH(t_0)dt}{\hbar}.$$

This operator H is the generator of time evolution, which is also a description of the Hamiltonian/energy of a classical system. Therefore, we extend this terminology and say $H(t)$ is the operator corresponding to the Hamiltonian of the system.

1.3 3D Space

We want to describe the Hilbert space

$$\mathcal{H} = \text{span} \left\{ \, |\mathbb{r}'\rangle \;\middle|\; \mathbb{r}' \in \mathbb{R}^3 \, \right\}.$$

An element of this space would take the form

$$|\alpha\rangle = \int d^3x' \, |\mathbb{r}'\rangle \, \langle\mathbb{r}' \,|\, \alpha\rangle =: \int d^3x' \, |\mathbb{r}'\rangle \, \psi_\alpha \left(\mathbb{r}'\right)$$

where we have defined the wave function $\psi_\alpha(\mathbb{r}') := \langle \mathbb{r}' \,|\, \alpha \rangle$. This definition leads to the delta normalization:

$$\langle \mathbb{r}'' \,|\, \mathbb{r}' \rangle = \delta^3(\mathbb{r}'' - \mathbb{r}').$$

A translation by a vector $\mathbb{a}$ would be represented with an operator $\mathcal{T}(\mathbb{a})$ such that $\mathcal{T}(\mathbb{a})\,|\mathbb{r}'\rangle = |\mathbb{r}' + \mathbb{a}\rangle$. From $\mathcal{T}(\mathbb{a}) = \int d^3x' \,|\mathbb{r}' + \mathbb{a}\rangle\langle \mathbb{r}'|$, we can prove compositionality $\mathcal{T}(\mathbb{b})\mathcal{T}(\mathbb{a}) = \mathcal{T}(\mathbb{a}+\mathbb{b})$ and inversion $\mathcal{T}^\dagger(\mathbb{a}) = \mathcal{T}(-\mathbb{a}) = \mathcal{T}^{-1}(\mathbb{a})$. Assuming continuity, similar arguments as the time evolution operator allows us to write

$$\mathcal{T}(d\mathbb{r}') = 1 - \frac{i\mathbb{p}\cdot d\mathbb{r}'}{\hbar}$$

for some Hermitian operator $\mathbb{p}$. The two equations

$$\langle \mathbb{r}' \,|\, \mathcal{T}(d\mathbb{r}') \,|\, \alpha \rangle = \langle \mathbb{r}' - d\mathbb{r}' \,|\, \alpha \rangle = \langle \mathbb{r}' \,|\, \alpha \rangle - d\mathbb{r}' \cdot \nabla' \langle \mathbb{r}' \,|\, \alpha \rangle$$

and

$$\langle \mathbb{r}' \,|\, \mathcal{T}(d\mathbb{r}') \,|\, \alpha \rangle = \langle \mathbb{r}' \,|\, \alpha \rangle - \frac{i}{\hbar} d\mathbb{r}' \cdot \langle \mathbb{r}' \,|\, \mathbb{p} \,|\, \alpha \rangle$$

can be compared to find

$$\langle \mathbb{r}' \,|\, \mathbb{p} \,|\, \alpha \rangle = -i\hbar \nabla' \langle \mathbb{r}' \,|\, \alpha \rangle.$$

This representation allows for easy computation of the commutation relations:

$$[x_i, x_j] = [p_i, p_j] = 0, \quad [x_i, p_j] = i\hbar\delta_{ij}.$$

Here, we have defined the position operators

$$\mathbb{r} := \int d^3x' \mathbb{r}' \,|\mathbb{r}'\rangle\langle \mathbb{r}'|.$$

1.4 Rotation

For a 3D rotation $R \in SO(3)$, we expect there to be a corresponding rotation operator

$$\mathcal{D}(R)\,|\mathbb{r}'\rangle = |R\mathbb{r}'\rangle.$$

The rotation around a unit vector $\hat{\mathbb{n}}$ by an angle ϕ can be found as

$$R(\phi\hat{\mathbb{n}})\,\mathbb{r}' = \cos\phi\mathbb{r}' + (1-\cos\phi)(\mathbb{r}'\cdot\hat{\mathbb{n}})\,\hat{\mathbb{n}} + \sin\phi\hat{\mathbb{n}}\times\mathbb{r}',$$

which for small angles ϵ, becomes $R(\epsilon\hat{\mathbb{n}})\,\mathbb{r}' = \mathbb{r}' + \epsilon\hat{\mathbb{n}}\times\mathbb{r}'$. From this, we may write

$$\mathcal{D}(R(\epsilon\hat{\mathbb{n}}))\,|\mathbb{r}'\rangle = |\mathbb{r}' + \epsilon\hat{\mathbb{n}}\times\mathbb{r}'\rangle = \mathcal{T}(\epsilon\hat{\mathbb{n}}\times\mathbb{r}')\,|\mathbb{r}'\rangle = \left(1 - \frac{i\epsilon}{\hbar}\mathbb{p}\cdot(\hat{\mathbb{n}}\times\mathbb{r}')\right)|\mathbb{r}'\rangle.$$

Hence, defining the angular momentum operator $\mathbb{L} := \mathbb{r}\times\mathbb{p}$, we obtain $\mathcal{D}(R(\epsilon\hat{\mathbb{n}})) = 1 - \frac{i\mathbb{L}\cdot\epsilon\hat{\mathbb{n}}}{\hbar}$. The definition allows the following commutation relations:

$$[L_i, x_j] = \varepsilon_{ijk}x_k, \quad \left[L_i, r^2\right] = 0, \quad [L_i, p_j] = \varepsilon_{ijk}p_k, \quad \left[L_i, p^2\right] = 0, \quad [L_i, L_j] = \varepsilon_{ijk}L_k, \quad \left[L_i, \mathbb{L}^2\right] = 0.$$

Notice that $\mathcal{D}(R_2)\mathcal{D}(R_1) = \mathcal{D}(R_2R_1)$ and $\mathcal{D}^\dagger(R) = \mathcal{D}\left(R^{-1}\right) = \mathcal{D}^{-1}(R)$, implying $\mathbb{L}^\dagger = \mathbb{L}$. We can obtain the representation of $\mathbb{L}$ in spherical coordinates by comparing

$$\langle \mathbb{r}' \,|\, \mathcal{D}(\epsilon\hat{\mathbb{n}}) \,|\, \alpha \rangle = \langle \mathbb{r}' - \epsilon\hat{\mathbb{n}}\times\mathbb{r}' \,|\, \alpha \rangle = \langle \mathbb{r}' \,|\, \alpha \rangle - \epsilon(\hat{\mathbb{n}}\times\mathbb{r}')\cdot\nabla'\langle \mathbb{r}' \,|\, \alpha \rangle$$

and

$$\langle \mathbb{r}' \,|\, \mathcal{D}(\epsilon\hat{\mathbb{n}}) \,|\, \alpha \rangle = \langle \mathbb{r}' \,|\, \alpha \rangle - \frac{i\epsilon\hat{\mathbb{n}}}{\hbar}\cdot\langle \mathbb{r}' \,|\, \mathbb{L} \,|\, \alpha \rangle,$$

which then yields

$$\langle \mathbb{r}' \,|\, \mathbb{L} \,|\, \alpha \rangle = -i\hbar\mathbb{r}'\times\nabla'\langle \mathbb{r}' \,|\, \alpha \rangle = \left(-i\hbar\frac{\partial}{\partial\theta'}\hat{\phi}' + i\hbar\csc\theta'\frac{\partial}{\partial\phi'}\hat{\theta}'\right)\langle \mathbb{r}' \,|\, \alpha \rangle$$

or

$$\langle \mathbb{r}' \,|\, L_x \,|\, \alpha \rangle = \left(-i\hbar \sin\phi' \frac{\partial}{\partial \theta'} - i\hbar \cot\theta' \cos\phi' \frac{\partial}{\partial \phi'} \right) \langle \mathbb{r}' \,|\, \alpha \rangle$$

$$\langle \mathbb{r}' \,|\, L_y \,|\, \alpha \rangle = \left(i\hbar \cos\phi' \frac{\partial}{\partial \theta'} - i\hbar \cot\theta' \sin\phi' \frac{\partial}{\partial \phi'} \right) \langle \mathbb{r}' \,|\, \alpha \rangle$$

$$\langle \mathbb{r}' \,|\, L_z \,|\, \alpha \rangle = -i\hbar \frac{\partial}{\partial \phi'} \langle \mathbb{r}' \,|\, \alpha \rangle .$$

We could square these and add them up to find the representation of $\mathbb{L}^2$, but we can more easily get it by observing

$$\mathbb{L}^2 = \varepsilon_{ijk}\varepsilon_{lmk} x_i p_j x_l p_m = \cdots = r^2 p^2 - (\mathbb{r} \cdot \mathbb{p})^2 + i\hbar \mathbb{r} \cdot \mathbb{p},$$

which thus leads to

$$\langle \mathbb{r}' \,|\, \mathbb{L}^2 \,|\, \alpha \rangle = -\hbar^2 r'^2 \left(\nabla'^2 - \frac{\partial^2}{\partial r'^2} - \frac{2}{r'} \frac{\partial}{\partial r'} \right) \langle \mathbb{r}' \,|\, \alpha \rangle = -\hbar^2 \left(\frac{1}{\sin\theta'} \frac{\partial}{\partial \theta'} \left(\sin\theta' \frac{\partial}{\partial \theta'} \right) + \frac{1}{\sin^2\theta'} \frac{\partial^2}{\partial \phi'^2} \right) \langle \mathbb{r}' \,|\, \alpha \rangle .$$

2 Hydrogen Atom

2.1 Compatible Observables

Suppose two observables A and B commute, i.e., $[A, B] = 0$. We prove that the two have a common eigenbasis of $\mathcal{H}$. Let $|a, \lambda\rangle$ denote an eigenbasis of A with eigenvalue a. Notice that

$$A\,(B\,|a, \lambda\rangle) = BA\,|a, \lambda\rangle = a\,(B\,|a, \lambda\rangle),$$

so $B\,|a, \lambda\rangle$ is also an eigenket of A with eigenvalue a. This allows us to write

$$B\,|a, \lambda\rangle = \int d\mu(\lambda') K(\lambda', \lambda)\,|a, \lambda'\rangle$$

where the kernel K is defined to be

$$K(\lambda', \lambda) := \langle a, \lambda' \,|\, B \,|\, a, \lambda \rangle .$$

Assuming compactness of this kernel, therefore, we can find another basis $\{\, |a, \rho\rangle \,\}$ for this eigenspace, where

$$|a, \rho\rangle = \int d\mu(\lambda) L(\lambda, \rho)\,|a, \lambda\rangle$$

and

$$A\,|a, \rho\rangle = a\,|a, \rho\rangle, \quad B\,|a, \rho\rangle = b(\rho)\,|a, \rho\rangle .$$

Therefore, A and B are simultaneously diagonalizable.

2.2 Angular Momentum Basis

The Hamiltonian of a hydrogen atom is given by

$$H = \frac{p^2}{2\mu} - \frac{k}{r} \quad \left(k = \frac{e^2}{4\pi\epsilon_0} \right),$$

which incidentally commutes with $\mathbb{L}^2$ and L_z because the Coulomb potential shows spherical symmetry. This allows us to declare a simultaneous eigenbasis $\{\, |Eab\rangle \,\}$ with eigenvalues E, a, b for $H, \mathbb{L}^2, L_z$, respectively.

Let $L_\pm := L_x \pm i L_y$.

$$[L_z, L_\pm] = \pm\hbar L_\pm, \quad [L_+, L_-] = 2\hbar L_z, \quad L_+ L_- = L_x^2 + L_y^2 + \hbar L_z$$

$$\Rightarrow \mathbb{L}^2 = L_+ L_- + L_z^2 - \hbar L_z = L_- L_+ + L_z^2 + \hbar L_z$$

We now try to find what eigenvalues a, b are possible.

$$a = \langle Eab \,|\, \mathbb{L}^2 \,|\, Eab \rangle = \| L_-\,|Eab\rangle \|^2 + b^2 - \hbar b = \| L_+\,|Eab\rangle \|^2 + b^2 + \hbar b \Rightarrow a \geq b^2 + \hbar\,|b|$$

Hence, the range of b is bounded for a given a, say between b_{min} and b_{max}. But notice that $L_z\left(L_\pm\left|Eab\right\rangle\right) = (b \pm \hbar)\left(L_\pm\left|Eab\right\rangle\right)$. Thus, we must have $L_+\left|Eab_{max}\right\rangle = L_-\left|Eab_{min}\right\rangle = 0$, and also $b_{max} - b_{min} \in \hbar\mathbb{N}$. This also implies

$$a = b_{max}^2 - \hbar b_{max} = b_{min}^2 + \hbar b_{min}$$

$$\Rightarrow b_{max} = -b_{min} = \hbar j \ \left(j \in \frac{1}{2}\mathbb{N}\right), \quad a = j(j+1)\hbar^2, \quad b = -j, -j+1, \ldots, j-1, j.$$

Now, let us employ the position-basis representation of $\mathbb{L}$ to get further restrictions.

$$\left\langle \mathbb{r}' \,\middle|\, L_z \,\middle|\, Ejm \right\rangle = -i\hbar\frac{\partial}{\partial\phi'}\left\langle \mathbb{r}' \,\middle|\, Ejm \right\rangle = m\hbar\left\langle \mathbb{r}' \,\middle|\, Ejm \right\rangle \quad \Rightarrow \left\langle \mathbb{r}' \,\middle|\, Ejm \right\rangle \propto e^{im\phi'}$$

However, the wave function must be single-valued for ϕ' and $\phi' + 2\pi$; hence, m must be an integer and thus $j = l \in \mathbb{N}$.

$$\left\langle \mathbb{r}' \,\middle|\, \mathbb{L}^2 \,\middle|\, Elm \right\rangle = -\hbar^2\left(\frac{1}{\sin\theta'}\frac{\partial}{\partial\theta'}\left(\sin\theta'\frac{\partial}{\partial\theta'}\right) + \frac{1}{\sin^2\theta'}\frac{\partial^2}{\partial\phi'^2}\right)\left\langle \mathbb{r}' \,\middle|\, Elm \right\rangle = \hbar^2 l(l+1)\left\langle \mathbb{r}' \,\middle|\, Elm \right\rangle$$

$$\Rightarrow \left(\frac{1}{\sin\theta'}\frac{\partial}{\partial\theta'}\left(\sin\theta'\frac{\partial}{\partial\theta'}\right) - \frac{m^2}{\sin^2\theta'} - l(l+1)\right)\left\langle \mathbb{r}' \,\middle|\, Elm \right\rangle = 0$$

Thus, we may decompose the wavefunction into the radial part and the angular part:

$$\left\langle \mathbb{r}' \,\middle|\, Elm \right\rangle = R(r')\Theta_{lm}(\theta')e^{im\phi'}.$$

2.3 Energy Levels

We find the bound states of the hydrogen atom, i.e., $E < 0$.

$$\left\langle \mathbb{r}' \,\middle|\, H \,\middle|\, Elm \right\rangle = \left(-\frac{\hbar^2}{2\mu}\nabla'^2 - \frac{k}{r'}\right)\left\langle \mathbb{r}' \,\middle|\, Elm \right\rangle = \left(-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r'^2} + \frac{2}{r'}\frac{\partial}{\partial r'} - \frac{l(l+1)}{r'^2}\right) - \frac{k}{r'}\right)\left\langle \mathbb{r}' \,\middle|\, Elm \right\rangle$$

$$\Rightarrow \frac{d^2R}{dr'^2} + \frac{2}{r'}\frac{dR}{dr'} + \left(\frac{2\mu E}{\hbar^2} - \frac{l(l+1)}{r'^2} + \frac{2\mu k}{\hbar^2 r'}\right)R = 0$$

Let us define $\kappa := \frac{\sqrt{2\mu|E|}}{\hbar}$ and $\lambda := \frac{\mu k}{\hbar}$. For $r' \to \infty$, $\frac{d^2R}{dr'^2} \approx \kappa^2 R \Rightarrow R \sim e^{\pm\kappa r'}$. For $r' \to 0+$, similarly, we have

$$\frac{d^2R}{dr'^2} + \frac{2}{r'}\frac{dR}{dr'} - \frac{l(l+1)}{r'^2} \approx 0 \Rightarrow R \sim r'^l \text{ or } r'^{-l-1}.$$

For normalizability, hence, we require that $R(r') = f(r')r'^l e^{-\kappa r'}$ for some "well-behaved" function $f(r')$. Substitution yields the new differential equation

$$r'\frac{d^2f}{dr'^2} + 2(l+1-\kappa r')\frac{df}{dr'} + 2(\lambda - (l+1)\kappa)f = 0.$$

Suppose $f(r') = \sum_{k=0}^{\infty} c_k r'^k$ for unknown coefficients c_k. The differential equation then becomes

$$\sum_{k=0}^{\infty}\left((k+1)(k+2l+2)c_{k+1} - 2(\kappa(k+l+1) - \lambda)c_k\right)r'^k = 0$$

$$\Rightarrow c_{k+1} = \frac{2(\kappa(k+l+1) - \lambda)}{(k+1)(k+2l+2)}c_k.$$

Now, if every coefficient were nonzero, then for large k,

$$c_k \sim \frac{(2\kappa)^k}{k!} \Rightarrow f(r') \sim e^{2\kappa r'},$$

which would render $R(r')$ non-normalizable. Therefore, the sequence $\{ c_k \}$ must terminate, i.e., there must exist some $k_0 \in \mathbb{N}$ such that $\kappa(k_0 + l + 1) - \lambda = 0$. Relabelling as $n := k_0 + l + 1 \in \mathbb{Z}_>$ (rendering $l = 0, 1, \ldots, n-1$), we finally obtain

$$E_n = -\frac{\mu k^2}{2\hbar^2 n^2} = -\frac{Z^2 e^4 \mu}{32\pi^2 \epsilon_0^2 \hbar^2 n^2},$$

or using the fine-structure constant $\alpha := \frac{e^2}{4\pi\epsilon_0 \hbar c}$,

$$E_n = -\frac{\mu c^2 Z^2 \alpha^2}{2n^2} \approx -(13.6\mathtt{eV})\frac{Z^2}{n^2}$$

thus concluding the derivation. □