Hydrogen

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Perhaps the most important applications of quantum mechanics is to the description of atoms, where quantum effects dominate the description. We now turn to the exact solution of the simplest problem in atomic physics – the study of the hydrogen atom.

1 The Hamiltonian

The Hamiltonian for hydrogen takes the form

$$\hat{H} = \frac{1}{2m}\hat{\mathbf{P}}^2 + V\left(\hat{\mathbf{X}}\right)$$

and satisfies the Schrödinger equation,

$$\hat{H}\left|\alpha, t\right\rangle = i\hbar\frac{\partial}{\partial t}\left|\alpha, t\right\rangle$$

where the potential is dependent only on $\hat{\mathbf{R}} = \sqrt{\hat{\mathbf{X}} \cdot \hat{\mathbf{X}}}$ and is given in a (spherical) coordinate basis by

$$\begin{aligned}\left\langle r, \theta, \varphi\right| V\left(\hat{\mathbf{X}}\right) &= \left\langle r, \theta, \varphi\right| V\left(\mathbf{x}\right) \\ &= \left\langle r, \theta, \varphi\right| \left(-\frac{e^2}{r}\right)\end{aligned}$$

Since the Hamiltonian is time-independent, we expect solutions of the form

$$\begin{aligned}\left|\alpha, t\right\rangle &= e^{-\frac{i}{\hbar}\hat{H}t}\left|\alpha\right\rangle \\ &= e^{-\frac{i}{\hbar}Et}\left|\alpha\right\rangle\end{aligned}$$

and making this substitution into the Schrödinger equation leads to the stationary state formulation,

$$\begin{aligned}\hat{H}\left|\alpha\right\rangle &= E\left|\alpha\right\rangle \\ \left[\frac{1}{2m}\hat{\mathbf{P}}^2 + V\left(\hat{\mathbf{X}}\right)\right]\left|\alpha\right\rangle &= E\left|\alpha\right\rangle\end{aligned}$$

2 Conservation of orbital angular momentum

We have studied the orbital angular momentum

$$\hat{\mathbf{L}} = \hat{\mathbf{X}} \times \hat{\mathbf{P}}$$

Exercise: Show that

$$\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{L}_k$$

so that the $\hat{L}_j$ form an irreducible representation of the rotation group. We know from our examination of angular momentum that

$$\begin{aligned}
\left[\hat{L}_i, \hat{\mathbf{P}}^2\right] &= \left[\hat{L}_i, \hat{P}_k\hat{P}_k\right] \\
&= \hat{P}_k\left[\hat{L}_i, \hat{P}_k\right] + \left[\hat{L}_i, \hat{P}_k\right]\hat{P}_k \\
&= \varepsilon_{ijm}\left(\hat{P}_k\left[\hat{X}_j\hat{P}_m, \hat{P}_k\right] + \left[\hat{X}_j\hat{P}_m, \hat{P}_k\right]\hat{P}_k\right) \\
&= \varepsilon_{ijm}\left(\hat{P}_k\hat{X}_j\left[\hat{P}_m, \hat{P}_k\right] + \hat{P}_k\left[\hat{X}_j, \hat{P}_k\right]\hat{P}_m + \hat{X}_j\left[\hat{P}_m, \hat{P}_k\right]\hat{P}_k + \left[\hat{X}_j, \hat{P}_k\right]\hat{P}_m\hat{P}_k\right) \\
&= \varepsilon_{ijm}\left(\hat{P}_k\left[\hat{X}_j, \hat{P}_k\right]\hat{P}_m + \left[\hat{X}_j, \hat{P}_k\right]\hat{P}_m\hat{P}_k\right) \\
&= \varepsilon_{ijm}\left(\hat{P}_k i\hbar\delta_{jk}\hat{P}_m + i\hbar\delta_{jk}\hat{P}_m\hat{P}_k\right) \\
&= \varepsilon_{ijm} i\hbar\left(\hat{P}_j\hat{P}_m + \hat{P}_m\hat{P}_j\right) \\
&= 0
\end{aligned}$$

Exercise: Show that

$$\left[\hat{L}_i, \hat{\mathbf{X}}^2\right] = 0$$

The Hamiltonian is a function of $\hat{\mathbf{X}}^2$ and $\hat{\mathbf{P}}^2$,

$$\hat{H} = \frac{1}{2m}\hat{\mathbf{P}}^2 + V\left(\sqrt{\hat{\mathbf{X}}^2}\right)$$

so

$$\left[\hat{\mathbf{L}}, \hat{H}\right] = 0$$

and angular momentum is conserved. As a result, we may label states with eigenvalues (l, m) of $\hat{\mathbf{L}}^2$ and $\hat{L}_z$respectively, as well as energy. This makes it worthwhile expressing the Hamiltonian in terms of $\hat{\mathbf{L}}$.

From the definition of $\hat{\mathbf{L}}$, we see that

$$\begin{aligned}
\hat{\mathbf{L}}^2 &= \left(\hat{\mathbf{X}} \times \hat{\mathbf{P}}\right) \cdot \left(\hat{\mathbf{X}} \times \hat{\mathbf{P}}\right) \\
&= \left(\varepsilon_{ijk}\hat{X}_j\hat{P}_k\right)\left(\varepsilon_{ilm}\hat{X}_l\hat{P}_m\right) \\
&= \left(\delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl}\right)\hat{X}_j\hat{P}_k\hat{X}_l\hat{P}_m \\
&= \left(\delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl}\right)\hat{X}_j\left(\left[\hat{P}_k, \hat{X}_l\right] + \hat{X}_l\hat{P}_k\right)\hat{P}_m \\
&= -i\hbar\delta_{kl}\left(\delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl}\right)\hat{X}_j\hat{P}_m + \left(\delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl}\right)\hat{X}_j\hat{X}_l\hat{P}_k\hat{P}_m \\
&= -i\hbar\left(\hat{X}_j\hat{P}_j - 3\hat{X}_j\hat{P}_j\right) + \hat{X}_j\hat{X}_j\hat{P}_k\hat{P}_k - \hat{X}_j\hat{X}_k\hat{P}_k\hat{P}_j \\
&= \hat{\mathbf{X}}^2\hat{\mathbf{P}}^2 - \hat{X}_j\left(\hat{\mathbf{X}} \cdot \hat{\mathbf{P}}\right)\hat{P}_j + 2i\hbar\left(\hat{\mathbf{X}} \cdot \hat{\mathbf{P}}\right)
\end{aligned}$$

to arrive at

$$\hat{\mathbf{L}}^2 = \hat{\mathbf{X}}^2\hat{\mathbf{P}}^2 - \hat{X}_j\left(\hat{\mathbf{X}} \cdot \hat{\mathbf{P}}\right)\hat{P}_j + 2i\hbar\left(\hat{\mathbf{X}} \cdot \hat{\mathbf{P}}\right)$$

On any state where $\hat{\mathbf{X}}^2$ is nonvanishing, we may write

$$\hat{\mathbf{P}}^2 = \frac{1}{\hat{\mathbf{X}}^2}\hat{\mathbf{L}}^2 + \frac{1}{\hat{\mathbf{X}}^2}\hat{X}_j\left(\hat{\mathbf{X}} \cdot \hat{\mathbf{P}}\right)\hat{P}_j - \frac{2i\hbar}{\hat{\mathbf{X}}^2}\left(\hat{\mathbf{X}} \cdot \hat{\mathbf{P}}\right)$$

This may be used to replace $\hat{\mathbf{P}}^2$ in the Schrödinger equation.

3 Spin, orbital angular momentum, and degeneracy

The state $|\alpha\rangle$ describes the electron in a hyrogen atom. Since the electron has spin-$\frac{1}{2}$, part of its state will be described by $|j, m\rangle = \left|\frac{1}{2}, m\right\rangle$ where $m = \pm\frac{1}{2}$. Because the spin operators $\hat{\mathbf{S}}^2$ and $\hat{S}_z$ act only on the $|j, m\rangle$ states, while $\hat{\mathbf{X}}$ and $\hat{\mathbf{P}}$ act on phase space, these operators commute. The electron state will therefore be a direct product,

$$|\alpha\rangle = |\beta\rangle \otimes \left|\frac{1}{2}, m\right\rangle$$

Any presence of $\hat{\mathbf{S}}^2$ or $\hat{S}_z$ in the Hamiltonian will act on the spin ket, while $\hat{\mathbf{X}}$ and $\hat{\mathbf{P}}$ act only on the $|\beta\rangle$ part.

This will become relevant when we look at small corrections to the Hamiltonian, where we find coupling between orbital and spin angular momentum. It is also important if we place the atom in a magnetic field, since the magnetic moment depends on spin.

We now have found a maximal set of commuting operators,

$$\hat{H}, \hat{\mathbf{L}}^2, \hat{L}_z, \hat{\mathbf{S}}^2, \hat{S}_z$$

so we label our states with the corresponding eigenvalues. Separating orbital angular momentum kets in the same way as spin, we have

$$|\alpha\rangle = |E, l, m_l, m_s\rangle \otimes |l, m_l\rangle \otimes \left|\frac{1}{2}, m_s\right\rangle$$

where we retain the possibility that the energy eigenkets depend on the angular momentum eigenvalues.

Substituting for $\hat{\mathbf{P}}^2$, and writing the state in terms of the eigenvalues, the stationary state Schrödinger equation becomes

$$\left[\frac{1}{2m}\frac{1}{\hat{\mathbf{X}}^2}\hat{\mathbf{L}}^2 + \frac{1}{2m}\frac{1}{\hat{\mathbf{X}}^2}\hat{X}_j\left(\hat{\mathbf{X}}\cdot\hat{\mathbf{P}}\right)\hat{P}_j - \frac{i\hbar}{m}\frac{1}{\hat{\mathbf{X}}^2}\left(\hat{\mathbf{X}}\cdot\hat{\mathbf{P}}\right) + V\left(\hat{\mathbf{X}}\right)\right]|E, l, m_l\rangle \otimes \left|\frac{1}{2}, m_s\right\rangle = E\,|E, l, m\rangle \otimes \left|\frac{1}{2}, m_s\right\rangle$$

The first thing we notice is that the absence of any spin operators in the Hamiltonian means that there is no mixing of the $\left|\frac{1}{2}, \pm\frac{1}{2}\right\rangle$ states. This means that the final stationary state solutions will have the pure spin up or spin down form,

$$|E, l, m_l, m_s\rangle \otimes |l, m_l\rangle \otimes \left|\frac{1}{2}, m_s\right\rangle = |E, l, m_l\rangle \otimes |l, m_l\rangle \otimes \left|\frac{1}{2}, m_s\right\rangle$$

that is, the two energy eigenstates with $m_s = \pm\frac{1}{2}$ have the same energy.

The orbital angular momentum kets are eigenkets of $\hat{\mathbf{L}}^2$. Replacing this operator by its eigenvalue,

$$\left[\frac{\hbar^2}{2m}l\left(l+1\right)\frac{1}{\hat{\mathbf{X}}^2} + \frac{1}{2m}\frac{1}{\hat{\mathbf{X}}^2}\hat{X}_j\left(\hat{\mathbf{X}}\cdot\hat{\mathbf{P}}\right)\hat{P}_j - \frac{i\hbar}{m}\frac{1}{\hat{\mathbf{X}}^2}\left(\hat{\mathbf{X}}\cdot\hat{\mathbf{P}}\right) + V\left(\hat{\mathbf{X}}\right)\right]|E, l\rangle \otimes |l, m_l\rangle \otimes \left|\frac{1}{2}, m_s\right\rangle = E\,|E, l\rangle \otimes |l, m_l\rangle \otimes \left|\frac{1}{2}, m\right.$$

The Hamiltonian is independent of m_l, so we may drop this label from the energy eigenkets. This means that states of a given l, but different values of m_l will have the same energy. The total energy degeneracy is therefore

$$2 \times (2l + 1)$$

for states $|E, l\rangle$.

4 Stationary state Schrödinger equation in spherical coordinates

From here on, it becomes advantageous to choose a basis of spherical coordinates, $\langle r, \theta, \varphi|$. We also need basis kets for the intinsic spin. These may be chosen to be the $\hat{S}_z$ eigenkets, $\langle\pm|$ Bringing in the composit bra, $\langle r,\theta,\varphi| \otimes \langle \pm|$, from the left, the Hamiltonian ignores spin factor $\langle \pm|$, giving the wave function a factor of either $\alpha = \langle + \left| \frac{1}{2}, m_s \right\rangle$ or $\beta = \langle - \left| \frac{1}{2}, m_s \right\rangle$. We write a general linear combination of these as a complex 2-vector,

$$\chi = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

so the full state retains this factor in the form $\Psi = \psi(r,\theta\varphi)\,\chi(\alpha,\beta)$.

Returning to the coordinate part of the basis bra, we may immediately replace

$$\begin{aligned} \langle r,\theta,\varphi| \frac{1}{\hat{\mathbf{X}}^2} &= \langle r,\theta,\varphi| \frac{1}{r^2} \\ \langle r,\theta,\varphi| V\left(\hat{\mathbf{X}}\right) &= -\langle r,\theta,\varphi| \frac{e^2}{r} \end{aligned}$$

leaving only two terms to evaluate. We work through these in detail.

4.1 The first term, in detail

For the first,

$$\begin{aligned} \frac{1}{2m}\langle r,\theta,\varphi| \frac{1}{\hat{\mathbf{X}}^2}\hat{X}_j\left(\hat{\mathbf{X}}\cdot\hat{\mathbf{P}}\right)\hat{P}_j|E,l\rangle &= \frac{1}{2mr^2}\langle r,\theta,\varphi|\mathbf{x}_j\left(\mathbf{x}\cdot\hat{\mathbf{P}}\right)\hat{P}_j|E,l\rangle \\ &= \frac{1}{2mr^2}\langle r,\theta,\varphi|\mathbf{x}_j\left(\int d^3x'\,|\mathbf{x}'\rangle\langle\mathbf{x}'|\right)\left(\mathbf{x}\cdot\hat{\mathbf{P}}\right)\left(\int d^3x''\,|\mathbf{x}''\rangle\langle\mathbf{x}''|\right)\hat{P}_j\left(\int d^3x'''\,|\mathbf{x}'''\rangle\langle\mathbf{x} \end{aligned}$$

where we have inserted identities between operators. Now we may evaluate,

$$\begin{aligned} \langle\mathbf{x}'|\left(\mathbf{x}\cdot\hat{\mathbf{P}}\right)|\mathbf{x}''\rangle &= \mathbf{x}\cdot\langle\mathbf{x}'|\hat{\mathbf{P}}|\mathbf{x}''\rangle \\ &= i\hbar\mathbf{x}\cdot\boldsymbol{\nabla}_{x''}\delta^3\left(\mathbf{x}'-\mathbf{x}''\right) \\ \langle\mathbf{x}''|\hat{P}_j|\mathbf{x}'''\rangle &= i\hbar\nabla_{j,x'''}\delta^3\left(\mathbf{x}''-\mathbf{x}'''\right) \end{aligned}$$

Substituting and integrating by parts to free up the delta functions, we start from the right with

$$\begin{aligned} \int d^3x'''\,\langle\mathbf{x}''|\hat{P}_j|\mathbf{x}'''\rangle\langle\mathbf{x}'''|E,l\rangle &= i\hbar\int d^3x'''\nabla_{j,x'''}\delta^3\left(\mathbf{x}''-\mathbf{x}'''\right)\langle\mathbf{x}'''|E,l\rangle \\ &= -i\hbar\int d^3x'''\delta^3\left(\mathbf{x}''-\mathbf{x}'''\right)\nabla_{j,x'''}\langle\mathbf{x}'''|E,l\rangle \\ &= -i\hbar\nabla_{j,x''}\langle\mathbf{x}''|E,l\rangle \end{aligned}$$

Replacing this in the full expression,

$$\frac{1}{2m}\langle r,\theta,\varphi| \frac{1}{\hat{\mathbf{X}}^2}\hat{X}_j\left(\hat{\mathbf{X}}\cdot\hat{\mathbf{P}}\right)\hat{P}_j|E,l\rangle = -\frac{i\hbar}{2mr^2}\langle r,\theta,\varphi|\mathbf{x}_j\left(\int d^3x'\,|\mathbf{x}'\rangle\langle\mathbf{x}'|\right)\left(\mathbf{x}\cdot\hat{\mathbf{P}}\right)\left(\int d^3x''\,|\mathbf{x}''\rangle\langle\mathbf{x}''|\right)\nabla_{j,x''}\langle\mathbf{x}''|E,l\rangle$$

we next encounter

$$\begin{aligned} \int d^3x''\,\langle\mathbf{x}'|\left(\mathbf{x}\cdot\hat{\mathbf{P}}\right)|\mathbf{x}''\rangle\nabla_{j,x''}\langle\mathbf{x}''|E,l,m\rangle &= i\hbar\int d^3x''\mathbf{x}\cdot\boldsymbol{\nabla}_{x''}\delta^3\left(\mathbf{x}'-\mathbf{x}''\right)\nabla_{j,x''}\langle\mathbf{x}''|E,l\rangle \\ &= -i\hbar\int d^3x''\delta^3\left(\mathbf{x}'-\mathbf{x}''\right)\left(\mathbf{x}\cdot\boldsymbol{\nabla}_{x''}\right)\nabla_{j,x''}\langle\mathbf{x}''|E,l\rangle \\ &= -i\hbar\left(\mathbf{x}\cdot\boldsymbol{\nabla}_{x'}\right)\nabla_{j,x'}\langle\mathbf{x}'|E,l\rangle \end{aligned}$$

and then the final integral,

$$
\begin{aligned}
-\frac{\hbar^2}{2mr^2}\langle r,\theta,\varphi|\,\mathbf{x}_j\int d^3x'\,|\mathbf{x}'\rangle\left(\mathbf{x}\cdot\boldsymbol{\nabla}_{x'}\right)\nabla_{j,x'}\langle\mathbf{x}'\,|E,l\rangle &= -\frac{\hbar^2}{2mr^2}\int d^3x'\,\langle r,\theta,\varphi\,|\mathbf{x}'\rangle\,\mathbf{x}'_j\left(\mathbf{x}\cdot\boldsymbol{\nabla}_{x'}\right)\nabla_{j,x'}\langle\mathbf{x}'\,|E,l\rangle \\
&= -\frac{\hbar^2}{2mr^2}\int d^3x'\delta^3\left((r,\theta,\varphi)-\mathbf{x}'\right)\mathbf{x}'_j\left(\mathbf{x}\cdot\boldsymbol{\nabla}_{x'}\right)\nabla_{j,x'}\langle\mathbf{x}'\,|E,l\rangle \\
&= -\frac{\hbar^2}{2mr^2}\mathbf{x}_j\left(\mathbf{x}\cdot\boldsymbol{\nabla}\right)\nabla_j\langle r,\theta,\varphi\,|E,l\rangle
\end{aligned}
$$

Finally, note that

$$
\begin{aligned}
\mathbf{x}_j\left(\mathbf{x}\cdot\boldsymbol{\nabla}\right)\nabla_j &= \mathbf{x}_j\left(r\frac{\partial}{\partial r}\right)\nabla_j \\
&= \left(r\frac{\partial}{\partial r}\right)\left(\mathbf{x}\cdot\boldsymbol{\nabla}\right)-\left(r\frac{\partial\mathbf{x}}{\partial r}\right)\cdot\boldsymbol{\nabla} \\
&= r\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)-\left(r\frac{\partial\mathbf{x}}{\partial r}\right)\cdot\boldsymbol{\nabla}
\end{aligned}
$$

In spherical coordinates,

$$
\frac{\partial\mathbf{x}}{\partial r}=\frac{\partial}{\partial r}\left(r\hat{\mathbf{r}}\right)=\left(\frac{\partial}{\partial r}r\right)\hat{\mathbf{r}}=\hat{\mathbf{r}}
$$

so that

$$
\begin{aligned}
\mathbf{x}_j\left(\mathbf{x}\cdot\boldsymbol{\nabla}\right)\nabla_j &= r\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)-r\hat{\mathbf{r}}\cdot\boldsymbol{\nabla} \\
&= r\frac{\partial}{\partial r}+r^2\frac{\partial^2}{\partial r^2}-r\frac{\partial}{\partial r} \\
&= r^2\frac{\partial^2}{\partial r^2}
\end{aligned}
$$

4.2 The third term

We are left with the evaluation of the third term

$$
\begin{aligned}
-\frac{i\hbar}{m}\langle r,\theta,\varphi|\,\frac{1}{\hat{\mathbf{X}}^2}\left(\hat{\mathbf{X}}\cdot\hat{\mathbf{P}}\right)|E,l\rangle &= -\frac{i\hbar}{mr^2}r\,\langle r,\theta,\varphi|\,\mathbf{x}\cdot\hat{\mathbf{P}}\,|E,l\rangle \\
&= -\frac{\hbar^2}{mr}\frac{\partial}{\partial r}\langle r,\theta,\varphi\,|E,l\rangle
\end{aligned}
$$

where we have used the same techniques as for the second term.

4.3 The final differential equation

Substituting these results into the full equation we have

$$
\left[\frac{l\left(l+1\right)\hbar^2}{2mr^2}-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}-\frac{\hbar^2}{mr}\frac{\partial}{\partial r}-\frac{e^2}{r}\right]\langle r,\theta,\varphi|\left(|E,l\rangle\otimes|l,m_l\rangle\right)\chi \quad = \quad E\,\langle r,\theta,\varphi|\left(|E,l\rangle\otimes|l,m_l\rangle\right)\chi
$$

Since the remaining operator depends only on r, the angular parts of the basis separate so that

$$
\begin{aligned}
\langle r,\theta,\varphi|\left(|E,l\rangle\otimes|l,m_l\rangle\right) &= \langle r\,|E,l\rangle\,\langle\theta,\varphi\,|l,m\rangle \\
&= \psi_{E,l}\left(r\right)Y_{lm}\left(\theta,\varphi\right)
\end{aligned}
$$

The functions $Y_{lm}(\theta, \varphi)$ are the spherical harmonics. They form a complete orthonormal set of functions on the 2-sphere. Writing the full wave function as

$$\Psi = \psi_{E,l}(r) \, Y_{lm}(\theta, \varphi) \, \chi(\alpha, \beta)$$

we have only the radial equation for $\psi_{E,l}(r)$ remaining

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}\psi_{E,l}(r) + \frac{2}{r}\frac{\partial}{\partial r}\psi_{E,l}(r)\right) + \left(\frac{l(l+1)\hbar^2}{2mr^2} - \frac{e^2}{r}\right)\psi_{E,l}(r) \quad = \quad E\psi_{E,l}(r)$$

The first terms combine to give the radial part of the Laplacian,

$$\frac{\partial^2}{\partial r^2}\psi_{E,l}(r) + \frac{2}{r}\frac{\partial}{\partial r}\psi_{E,l}(r) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi_{E,l}(r)\right)$$

Solutions for $\psi_{E,l}(r)$ may be expressed in terms of Laguerre polynomials.