Quantum Mechanics

Problem Sheet 6

The Hydrogen Atom

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April 15, 2024

The Hydrogen Atom

6.1

The gross structure of the hydrogen atom is characterised by three quantum numbers: n, l, and m. The principal quantum number n determines the energy of the state, and the orbital angular momentum quantum number l determines the magnitude of the angular momentum. The spin quantum number m determines the projection of the angular momentum on the z-axis.

We require $n \in \mathbb{Z}^+$, $0 \leq l \leq n-1$, and $-l \leq m \leq l$. The energy of a state is given by:

$$E = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n^2} \equiv -\frac{E_R}{n^2} \tag{1}$$

where we define the Rydberg energy $E_R = m_e e^4/[2(4\pi\epsilon_0)^2\hbar^2] = 13.6\,\mathrm{eV}$.

For $n = 2$, i.e. the first excited state, there are two possible $l = 0, 1$ and three possible $m = 0, \pm 1$ so that the total degeneracy is $1 + 3 = 4$. For $n = 3$, there are three possible $l = 0, 1, 2$ and five possible $m = 0, \pm 1, \pm 2$ so that the total degeneracy is $1 + 3 + 5 = 9$. In general, for any n, the total degeneracy is n^2.

We write the ground state in position representation as:

$$\psi_{100} = R_{10}(r)Y_{00}(\theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0} \tag{2}$$

where $a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$ is the Bohr radius.

The reduced mass of the hydrogen atom is given by:

$$\mu = \frac{m_e m_p}{m_e + m_p} \approx m_e \tag{3}$$

For a hydrogen-like atom with Z protons, we replace m_e with $\mu = Zm_e m_p/(m_e + Zm_p)$. The energy levels are given by:

$$E_n = -\frac{E_R}{n^2}\frac{\mu Z^2}{m_e} \tag{4}$$

We also have the new Bohr radius:

$$a_Z = \frac{4\pi\epsilon_0\hbar^2}{\mu Z e^2} = \frac{m_e}{\mu Z}a_0 \approx \frac{a_0}{Z} \tag{5}$$

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6.2

We have the ground state wave function:

$$\psi_{100} = \frac{1}{\sqrt{\pi a_Z^3}} e^{-r/a_Z} \tag{6}$$

where $a_Z \approx a_0/Z$ is the Bohr radius for a hydrogen-like atom with Z protons.

(a) The average value of the radius is given by:

$$\begin{aligned}\langle r \rangle &= \iiint r |\psi_{100}|^2 r^2 \, \mathrm{d}r \mathrm{d}\theta \mathrm{d}\phi \\ &= \int_0^\infty 4\pi r^3 |\psi_{100}|^2 \, \mathrm{d}r \\ &= \frac{3}{2} a_Z\end{aligned} \tag{7}$$

(b) The probability amplitude has the form:

$$\frac{1}{\pi a_Z^3} e^{-2r/a_Z} \tag{8}$$

whose maximum is at $r = 0$ where the electron is most likely to be found.

We differentiate the following function:

$$|\psi|^2 \, r^2 \propto e^{-2r/a_Z} r^2 \tag{9}$$

and find the maximum at $r = a_Z$.

(c) The potential energy is given by the function:

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \tag{10}$$

Its expectation value is given by:

$$
\begin{aligned}
\langle V \rangle &= \iiint \psi^*_{100} V \psi_{100} r^2 \,\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi \\
&= \int_0^\infty 4\pi r^2 |\psi_{100}|^2 V \,\mathrm{d}r \\
&= -\frac{Ze^2}{4\pi\epsilon_0 a_Z}
\end{aligned} \tag{11}
$$

which agrees with Bohr's model of the hydrogen atom.

(d) The 'kinetic energy' is given the expectation of the operator:

$$
\hat{T} = -\frac{\hbar^2}{2m_e}\nabla^2 \tag{12}
$$

The expectation value is given by:

$$
\begin{aligned}
\left\langle \hat{T} \right\rangle &= \iiint \psi^*_{100} T \psi_{100} r^2 \,\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi \\
&= -2\pi \frac{\hbar^2}{m_e} \int_0^\infty \psi_{100} \frac{\mathrm{d}^2}{\mathrm{d}r^2} \left(r\psi_{100} \right) r \,\mathrm{d}r \\
&= \frac{\hbar^2}{2m_e a_Z^2} \\
&\approx Z^2 13.6\,\mathrm{eV}
\end{aligned} \tag{13}
$$

On the other hand, the combination given by Bohr model is:

$$
\frac{Ze^2}{8\pi\epsilon_0 a_Z} = Z^2 13.6\,\mathrm{eV} \tag{14}
$$

which numerically agrees with the expectation value of the kinetic energy, but the underlying physics is completely different.

(e) Since both expectation values of the kinetic and potential energies both agree with Bohr's model, the total energy also agrees.

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6.3

In Bohr's model, the quantisation condition reads:

$$2\pi r = n\frac{h}{p} \tag{15}$$

so that the angular momentum is quantised as:

$$L = pr = n\hbar \tag{16}$$

where p and r also satisfy the relation:

$$\frac{p^2}{m_e r} = \frac{e^2}{4\pi\epsilon_0 r^2} \tag{17}$$

Putting $n = 1$ and solving for $v = p/m_e$, we find:

$$v = \frac{e^2}{4\pi\epsilon_0\hbar} = \alpha c \tag{18}$$

For a hydrogen-like ion with $Z = 26$, we replace e^2 with Ze^2 and find:

$$v = \frac{Ze^2}{4\pi\epsilon_0\hbar} = Z\alpha c \tag{19}$$

This means that the electron moves at a fraction $Z\alpha \approx Z/137$ of the speed of light. By ignoring relativistic effects, we must have incurred a fractional error at least of the order $\gamma - 1$, which is given by:

$$\gamma - 1 = \frac{1}{\sqrt{1-(Z\alpha)^2}} - 1 \approx \frac{1}{2}(Z\alpha)^2 \tag{20}$$

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6.4

The expected electric field experienced by an electron in the ground state is:

$$\begin{aligned} \langle E \rangle &= \frac{1}{4\pi\epsilon_0}\iiint \psi_{100}^*\frac{1}{r^2}\psi_{100}r^2\,\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi \\ &= \frac{1}{2\pi\epsilon_0 a_0^2} \end{aligned} \tag{21}$$

Treating an ideal laser as monochromatic plane wave, the intensity is given by:

$$I = \frac{1}{2}\epsilon_0 c E^2 \tag{22}$$

which gives the approximation:

$$E \approx \sqrt{2I\epsilon_0 c} \tag{23}$$

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6.5

We use the reduced mass:

$$\mu = \frac{m_e m_e}{m_e + m_e} = \frac{m_e}{2} \tag{24}$$

with $Z = 1$.

The energy levels are given by:

$$E_n = -\frac{E_R}{n^2}\frac{\mu Z^2}{m_e} = -\frac{E_R}{2n^2} \tag{25}$$

The characteristic length scale is given by:

$$a_Z = \frac{m_e}{\mu Z}a_0 = 2a_0 \tag{26}$$

which suggests that the size of the atom is twice that of the hydrogen atom.

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6.6

We have the reduced mass:

$$\mu = \frac{m_e m_\mu}{m_e + m_\mu} \approx 0.995 m_e \tag{27}$$

Following the same procedure, we have the energy levels:

$$E_n = -0.995\frac{E_R}{n^2} \tag{28}$$

and the characteristic length scale:

$$a_Z = 1.005a_0 \tag{29}$$

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6.7

The Pickering series is given by transitions to the $n = 4$ state in a Helium cation. The energy levels of this ion are given by:

$$E_n = -\frac{E_R}{n^2}\frac{\mu Z^2}{m_e} = -\frac{4E_R}{n^2} \tag{30}$$

Note that we can rewrite the energy levels as:

$$E_n = -\frac{E_R}{(n/2)^2} \tag{31}$$

which follows the same form as the hydrogen atom of energy levels $n/2$.

This suggests that the Pickering series characterised by $n = 4$ is equivalent to the Balmer series of the hydrogen atom characterised by $n = 2$. The small discrepancies are due to the approximation of the reduced mass. We should have used:

$$\begin{aligned} E_{n,He} &= -\frac{4E_R}{n^2}\frac{2m_p}{m_e + 2m_p} \approx -0.999728\frac{4E_R}{n^2} \\ E_{n,H} &= -\frac{E_R}{n^2}\frac{m_p}{m_e + m_p} \approx -0.999456\frac{E_R}{n^2} \end{aligned} \tag{32}$$

We can check the ratios:

$$\begin{aligned} \frac{0.999728}{0.999456} &\approx 1.00027 \\ \frac{0.456987}{0.456806} &\approx 1.00040 \\ \frac{0.616933}{0.616682} &\approx 1.00041 \end{aligned} \tag{33}$$

which suggests that the approximation used in reduced mass partially accounts for the discrepancy.

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