Quantum mechanical treatment of the H atom:

Model:

Electron moving around positively charged nucleus in a Coulombic field from the nucleus. Potential energy term $V(r)$ arises from this Coulombic field.

The centrifugal potential due to angular motion of the electron also contributes to the potential energy term. Both terms are spherically symmetric.

Quantum mechanical treatment of H & H - like atoms

Coulombic P.E.

Quantum Mechanics predicts a stable system as opposed to the classical mechanical prediction of the demise of the atom.

Because $r = \sqrt{x^2 + y^2 + z^2}$ Separation of variables is not possible.

Strategic: changing the coordinate system – to polar coordinates.

Cartesian volume element $d\tau = dx \, dy \, dz$

Polar coordinate volume element $d\tau = r^2 \sin \theta \, d\theta \, d\phi \, dr$
Hamiltonian in Polar Coordinates (spherical symmetry):

H atom Hamiltonian

$$\begin{align*}
\frac{1}{2R^2} \left[ \frac{1}{2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{1}{2} \frac{\partial^2}{\partial \theta^2} \left( \sin^2 \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{2} \frac{\partial^2}{\partial \phi^2} \right] \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)
\end{align*}$$

Rigid rotor Hamiltonian (note)

$$-\frac{\hbar^2}{2mr^2} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right] \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

Substituting for $\psi(r, \theta, \phi)$; $\psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)$

And using the rigid rotor Hamiltonian,

Time-independent Schrödinger Equation for H atom:

$$\begin{align*}
\frac{\hbar^2}{2m_r^2} \frac{d^2}{dr^2} R(r) + \frac{1}{2m_r^2} R(r) \frac{d^2}{d\theta^2} \Theta(\theta) \Phi(\phi) - \Theta(\theta) \Phi(\phi) \left[ \frac{e^2}{4\pi\epsilon_0 r^2} \right] R(r) &= E R(r) \Theta(\theta) \Phi(\phi)
\end{align*}$$

Defining $R(r) \Theta(\theta) \Phi(\phi) = R \Theta \Phi$

Note this form of the SE for H:
Recall that for rigid rotor \((r \text{ constant and } I = \mu r^2)\):

\[
\hat{H}_\text{total} Y^m_l(\theta, \phi) = \frac{\hbar^2}{2I} l(l + 1) Y^m_l(\theta, \phi).
\]

\[E_n = \frac{l^2}{2I} \Rightarrow \hat{H} = \frac{l^2}{2I}\]

For an electron in an atom where \(r\) is a variable substituting for \(I = m_e r^2\) in the following term of SE;

\[
\frac{l^2}{2I} Y^m_l(\theta, \phi) = \frac{\hbar^2}{2I} l(l + 1) Y^m_l(\theta, \phi)
\]

Using the result in the SE:

\[
-\frac{\hbar^2}{2m_e r^2} \Theta \Phi \frac{d}{dr} \left[ r^2 \frac{dR(r)}{dr} \right] + \frac{1}{2m_e} \frac{\hbar^2}{r^2} \Theta \Phi - \Theta \Phi \left[ \frac{e^2}{4\pi \varepsilon_0 r} \right] R = ER\Theta\Phi
\]

\[
-\frac{\hbar^2}{2m_e r^2} \Theta \Phi \frac{d}{dr} \left[ r^2 \frac{dR(r)}{dr} \right] + \frac{\hbar^2}{2m_e} \frac{l(l+1)}{r^2} \Theta \Phi - \Theta \Phi \left[ \frac{e^2}{4\pi \varepsilon_0 r} \right] R = ER\Theta\Phi
\]

Differential equation in \(R(r)\) result in;

\[
\frac{\hbar^2}{2m_e r^2} \frac{d}{dr} \left[ r^2 \frac{dR(r)}{dr} \right] + \left[ \frac{\hbar^2}{2m_e r^2} \frac{1}{r^2} - \frac{e^2}{4\pi \varepsilon_0 r} \right] R(r) = ER(r)
\]

Solution of the above DE to find the radial part, \(R\), of the eigen functions and their eigen values.

Quantum numbers \(n\) and \(E_n\).

Eigenvalues of SE are;

\[
E_n = \frac{-m_e e^4}{8\varepsilon_0^2 \hbar^2 n^2}, \text{ for } n = 1, 2, 3, 4,
\]

\[
E_n = \frac{2.179 \times 10^{-33} \text{ J}}{n^2} = -13.60 \text{ eV}
\]

Bohr radius: \(a_n = \frac{\varepsilon_0 \hbar^2}{m_e e^2}\)

\(R(r)\) solutions results in the radial part of the wave functions and the spherical harmonics results give the angular part of the wave function. The respective quantum numbers are \(n\) (principal), \(l\) (azimuthal) and \(m_l\) (magnetic) such that;

\[
\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)
\]

\[
\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)
\]
More accurately;

\[ E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2}. \]

Rydberg constant \( \frac{m_e e^4}{8\epsilon_0^2 h^2 c^2} \).

Isotope peaks in atomic spectra predictable.

Radial functions \( R_{nl} \sim \) product of an exponential function, power of \( r \) and a polynomial of \( (r/a_0) \) of order \( (n-\ell-1) \).

General form of Radial functions:

\[ R_{nl} = \text{constant} \times \text{polynomial} \left( \frac{r}{a_0} \right)^{n-\ell-1} \]

Hydrogen wave functions (orbitals) are a product of the radial and angular functions (spherical harmonics).

Real functions for \( m_l = 0 \) and complex functions if otherwise.

Normalized functions are shown.

Degeneracy (H atom and H like species only) = \( n^2 \)

Solution of the \( R \) Equation

<table>
<thead>
<tr>
<th>Quantum number</th>
<th>( n )</th>
<th>( \ell )</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>( R_{00} = \frac{Z}{a_0} )</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>( R_{01} = \frac{1}{2\sqrt{2}} )</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>( R_{11} = \frac{1}{2\sqrt{2}} )</td>
</tr>
</tbody>
</table>

Solution of the \( \Phi \) Equation

<table>
<thead>
<tr>
<th>Value of ( m_l )</th>
<th>Solution in Complex form</th>
<th>Real Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \Phi_0 = \frac{1}{\sqrt{2}} )</td>
<td>( \Phi_0 = \frac{1}{\sqrt{2}} )</td>
</tr>
<tr>
<td>1</td>
<td>( \Phi_1 = \frac{1}{\sqrt{2}} e^{i\theta} )</td>
<td>( \Phi_2 = \frac{1}{\sqrt{2}} (\Phi_0 + \Phi_1) = \frac{\cos \theta}{\sqrt{2}} + \frac{i \sin \theta}{\sqrt{2}} )</td>
</tr>
<tr>
<td>-1</td>
<td>( \Phi_{-1} = \frac{1}{\sqrt{2}} e^{-i\theta} )</td>
<td>( \Phi_{-2} = \frac{1}{\sqrt{2}} (\Phi_0 - \Phi_1) = \frac{\cos \theta}{\sqrt{2}} - \frac{i \sin \theta}{\sqrt{2}} )</td>
</tr>
</tbody>
</table>
Visualization of complex functions not possible \( m \neq 0 \).

Therefore linear combinations wave functions can be constructed to obtain equivalent orbitals; from the available 'complete set' of wave functions.

\[
\psi_{nlmn} = \text{combinations of } \psi_{nlm}, \psi_{nl-m} \text{ for } m \neq 0.
\]

e.g. two 2p orbitals

\[
\begin{align*}
\psi_{2p_x} &= \psi_{2,0,1} + \psi_{2,0,-1} \\
\psi_{2p_y} &= \psi_{2,0,1} - \psi_{2,0,-1} \\
\psi_{2p_z} &= \psi_{2,1,m} + \psi_{2,1,-m} \\
\psi_{2p_m} &= \psi_{2,1,m} - \psi_{2,1,-m}
\end{align*}
\]

At this point time independent SE provided us with eigen functions (orbitals) and eigen values (energies) for H atom that are independent of time.

All eigen values are negative, more stable than the reference energy (reference energy =0 at \( n = \infty \)).

\( n \geq 1 \) (positive and nonzero) and energy can never approach negative infinity; i.e. the electron will not fall into the nucleus!!

Visualization of orbitals

Orbitals described by \( \psi \)'s are not well defined shells, in keeping with the Heisenberg Principle.

They, \( \psi \)'s, are akin to probability functions.

Probability of finding an electron in a volume element \( d\tau \) is;

\[
\psi^* (r, \Theta, \Phi) \psi (r, \Theta, \Phi) d\tau
\]

Spherical nodal surfaces

#nodal surfaces (radial nodes) = \( n-l-l \);
not counting node at origin for \( l \neq 0 \).

#nodal surfaces (angular nodes) = \( l \)

Total # nodal surfaces = \( n-l \)
Radial Probability functions: $P(r)dr$

Probability per unit volume $= \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)$

Probability in volume $= \int \psi^*(r,\theta,\phi)\psi(r,\theta,\phi) d\tau$

Probability in nucleus $= \int \psi^*(r,\theta,\phi)\psi(r,\theta,\phi) d\tau$

$$= 9.0 \times 10^{-11}$$

See Example Problem 20.4

The electron distribution in general (for $l \neq 0$) is not spherically symmetric.

But radial part is always spherically symmetric.

To find the most probable position of finding electrons in an orbital would then be dictated by the radial function regardless of the spherical harmonics.

Probability of finding the electron in a spherical shell at radius $r$ of shell thickness $dr$ is defined as the Radial probability distribution function: $P(r)dr$.

$P(r)$ is a measure of the probability of electrons at a distance in a spherical shell of unit volume, $r$ distance away from the nucleus, for all angles $\theta$ and $\phi$.

$$P_{\psi}(r)dr = \int \frac{1}{2\pi a_0^2} \sigma d\phi \int \sin \theta d\theta \int_0^{2\pi} r^2 e^{-2r/a_0} dr$$

$$= 1$$

Radial Distribution Function

Example:

$$P_{\psi}(r)dr = \int \frac{1}{2\pi a_0^2} \sigma d\phi \int \sin \theta d\theta \int_0^{2\pi} r^2 e^{-2r/a_0} dr$$

$$= 1$$

$P(r)$ is the probability function of choice to determine the most likely radius to find the electron in an orbital.
2s is more dispersed than 1s.

Bohr Radius $= a_0$

$P(r)$ is the probability function of choice to determine the most likely radius to find the electron in an orbital.

Wave functions are a manifestation of the wave particle duality, so is the non-localization of orbitals.

Spherical harmonic wavefunctions and their shapes:

$l = 0$

$Y_0^0(\theta, \phi) = \frac{1}{(4\pi)^{1/2}}$

$l = 1$

$Y_1^0(\theta, \phi) = \frac{3}{4\pi} \cos \theta$

$Y_1^1(\theta, \phi) = \frac{3}{8\pi} \sin \theta e^{i\phi}$

$l = 2$

$Y_2^0(\theta, \phi) = \frac{5}{16\pi} \sin^2 \theta$

$Y_2^1(\theta, \phi) = \frac{11}{8\pi} \sin \theta \cos \theta e^{i\phi}$

$Y_2^2(\theta, \phi) = \frac{15}{32\pi} \sin^2 \theta e^{2i\phi}$

General form of Angular functions

$Y_l^m = \text{constant} (\sin \theta \text{ and } \cos \theta)^m e^{im\phi}$

$Y_1^0(\theta, \phi) = \left( \frac{3}{4\pi} \right)^{1/2} \cos \theta$
\[ y_1^0(\theta, \phi) = \left( \frac{3}{4\pi} \right)^{1/2} \cos \theta \]

Note the sign of the wavefunction!
Phase.

Under such situations alternate wave functions with same eigenvalues can be constructed from the 'complete set' of wave functions available, i.e. properly constructed linear combinations from the complete set of eigenfunctions.

\[
p_x = \frac{1}{\sqrt{2}} (Y_1^1 + Y_1^{-1}) = \frac{3}{\sqrt{4\pi}} \sin \theta \cos \phi
\]
\[
p_y = \frac{1}{\sqrt{2}i} (Y_1^1 - Y_1^{-1}) = \frac{3}{\sqrt{4\pi}} \sin \theta \sin \phi
\]
\[
p_z = Y_1^0 = \frac{3}{\sqrt{4\pi}} \cos \theta
\]

\[
d_{x^2} = Y_2^1 = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)
\]
\[
d_{xy} = \frac{1}{\sqrt{2}} (Y_2^1 + Y_2^{-1}) = \sqrt{\frac{15}{4\pi}} \sin \theta \cos \theta \cos \phi
\]
\[
d_{yz} = \frac{1}{\sqrt{2}i} (Y_2^1 - Y_2^{-1}) = \sqrt{\frac{15}{4\pi}} \sin \theta \cos \theta \sin \phi
\]
\[
d_{z^2} = Y_2^2 = \sqrt{\frac{15}{16\pi}} \sin^2 \theta \cos 2\phi
\]
\[
d_{xy} = \frac{1}{\sqrt{2}} (Y_2^2 + Y_2^{-2}) = \sqrt{\frac{15}{16\pi}} \sin^2 \theta \sin 2\phi
\]

Note the signs of the wavefunction!
all p

all d


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