Chapter 8: Spherical Coordinates

Triple Integrals

We've seen that *Mathematica* can compute integrals in Cartesian coordinates (x, y, z). However, atoms are better described using spherical coordinates (r, θ, ϕ). Here are some useful relationships:

$x = r \text{ Sin } \theta \text{ Cos } \phi$

$y = r \text{ Sin } \theta \text{ Sin } \phi$

$z = r \text{ Cos } \varphi$

$r^2 = x^2 + y^2 + z^2$

The volume of a 3D object can be thought of as: $V = \int\int\int f(x, y, z)\, dx\, dy\, dz$. Using the substitutions above: $V = \int\int\int f(r \text{ Sin } \theta \text{ Cos } \phi,\ r \text{ Sin } \theta \text{ Cos } \phi,\ r \text{ Cos } \theta)\, d\tau$ where $d\tau = r^2 \text{ Sin } \phi\, dr\, d\theta\, d\phi$. The limits of integration are generally:

$0 \le r \le \infty$, $0 \le \theta \le \pi$, $0 \le \phi \le 2\pi$.

From Physical Chemistry, 6th Edition by Peter Atkins:

Example 11.4

Normalize the wavefunction for the hydrogen atom over all space: $\psi = e^{\frac{-r}{ao}}$**, where ao is the bohr radius.**

Recall that a function is *normalized* if $\int\int\int A^2 \psi^2\, d\tau = 1$, where A is the normalization constant. In spherical coordinates, the integral becomes:

$\int\int\int A^2 r^2 \psi^2\, dr \text{ Sin } \theta\, d\theta\, d\phi$ with limits of $0 \le r \le \infty$, $0 \le \theta \le \pi$, $0 \le \phi \le 2\pi$.

For the special case of the H atom, $\psi = R(r)\, F(\theta)\, G(\phi)$, a product of functions of each variable. Then, the triple integral can be written as a product of three separate integrals:

$\int A^2 r^2 R(r)^2\, dr \int F(\theta)^2 \text{ Sin } \theta\, d\theta \int G(\phi)^2\, d\phi$

In this example, $\psi = \psi(r) = R(r)$ so $F(\theta) = 1$ and $G(\phi) = 1$.

Define the wavefunction ψ and set up the integrals one by one. Multiply the integrals together to get the answer.

```
psi = Exp[-r / ao];
integralr = Integrate[A^2 * r^2 * psi^2, {r, 0, Infinity}]
```

$A^2 \text{ If}\left[\text{Re}[ao] > 0, \frac{ao^3}{4}, \int_0^\infty e^{-\frac{2r}{ao}} r^2 \, dr\right]$

Mathematica sometimes will give a more complicated answer than what you're looking for. The output can be translated as:

$A^2 \left(\frac{ao^3}{4}\right)$ if ao > 0

$\int_0^\infty e^{-\frac{2r}{ao}} r^2 \, dr$ if ao < 0.

Define a new function using the answer above:

```
integralrNew = A^2 (ao^3 / 4)
```

$\frac{A^2 ao^3}{4}$

```
integralθ = Integrate[Sin[θ], {θ, 0, π}]
```

2

```
integralϕ = Integrate[1, {ϕ, 0, 2 * π}]
```

2π

```
ans = integralrNew * integralθ * integralϕ
```

$A^2 ao^3 \pi$

Solve for *A*:

```
Solve[ans == 1, A] // Flatten
```

$\left\{A \to -\frac{1}{ao^{3/2}\sqrt{\pi}}, A \to \frac{1}{ao^{3/2}\sqrt{\pi}}\right\}$

The normalization constant *A* can be chosen to be positive. Define *A* and print out the normalized wavefunction:

```
A = 1 / (ao^(3/2) Sqrt[π]);
Print["The normalized wavefunction is ψ =", A * psi]
```

The normalized wavefunction is $\psi = \frac{e^{-\frac{r}{ao}}}{ao^{3/2}\sqrt{\pi}}$

From Physical Chemistry, 6th Edition by Peter Atkins:

Problem 11.8
Normalize the wavefunction $\psi = x\, e^{-r/ao}$ to 1.:

Let x = r Sin θ Cos ϕ so ψ = r Sin θ Cos ϕ $e^{\frac{-r}{ao}}$. Then ψ(r) = r $e^{\frac{-r}{ao}}$, $\psi(\theta)$ = Sin θ, and $\psi(\phi)$ = Cos ϕ

```
Clear[A];
R = r * Exp[-r / ao];
integralr = Integrate[A^2 * r^2 * R^2, {r, 0, Infinity}]
```

$A^2 \text{ If}\left[\text{Re}[ao] > 0, \frac{3\, ao^5}{4}, \int_0^\infty e^{-\frac{2r}{ao}} r^4 \, dr\right]$

Define a new function for the output:

integralRNew = $A^2 * \left(\frac{3\, ao^5}{4}\right)$

$\frac{3 A^2 ao^5}{4}$

```
F = Sin[θ];
integralS = Integrate[Sin[θ] * F^2, {θ, 0, π}]
```

$\frac{4}{3}$

```
G = Cos[ϕ];
integralG = Integrate[G^2, {ϕ, 0, 2 * π}]
```

π

```
ans = integralRNew * integralS * integralG
```

$A^2\, ao^5\, \pi$

Solve for A:

```
Solve[ans == 1, A] // Flatten
```

$$\left\{A \to -\frac{1}{ao^{5/2}\sqrt{\pi}},\ A \to \frac{1}{ao^{5/2}\sqrt{\pi}}\right\}$$

The normalization constant *A* can be chosen to be positive. Define *A* and the normalized wavefunction ψ to print out the answer:

$$A = \frac{1}{ao^{5/2}\sqrt{\pi}};$$

```
psi = A * R * F * G;
Print["The normalized wavefunction is ψ =", psi]
```

The normalized wavefunction is $\psi = \frac{e^{-\frac{r}{ao}}\ r\ Cos[\phi]\ Sin[\Theta]}{ao^{5/2}\sqrt{\pi}}$

From Physical Chemistry, 6th Edition by Peter Atkins:

Problem 11.9
Normalize the following wavefunctions to 1:

a) $(2 - r / ao)\ e^{-r / 2ao}$

b) $r\ Sin\ \theta\ Cos\phi\ e^{-r / 2ao}$

From Physical Chemistry, 6th Edition by Peter Atkins:

Problem 11.16
Evaluate the expectation values of r and r2 for a hydrogen atom with wavefunctions:

a) $(2 - r / ao)\ e^{-r / 2ao}$

b) $r\ Sin\ \theta\ Cos\phi\ e^{-r / 2ao}$

Recall that the expectation of r is:
$\langle r \rangle = \int\int\int r\,\psi^2\, d\tau$ and for $\langle r^2 \rangle = \int\int\int r^2\,\psi^2\, d\tau$.

Use the normalized wavefunctions from Problem 11.9 to calculate the expectation values.

Answers: Problem 11.9

Part a:

$\psi = (2 - r / ao)\, e^{-r/2ao} = \psi(r) = R(r)$ so $F(\theta) = 1$ and $G(\phi) = 1$.

Define the wavefunction and integrate each integral separately:

```
Clear[A];
psi1 = (2 - (r / ao)) * Exp[-r / (2 * ao)];
integralr = Integrate[A^2 * r^2 * psi1^2, {r, 0, Infinity}]
```

$$A^2\,\mathrm{If}\left[\mathrm{Re}[ao] > 0,\ 8\,ao^3,\ \int_0^\infty e^{-\frac{r}{ao}}\, r^2 \left(2 - \frac{r}{ao}\right)^2 dr\right]$$

Define a new function using the answer above:

```
integralrNew = A^2 * 8 * ao^3
```

$8\,A^2\,ao^3$

```
integralθ = Integrate[Sin[θ], {θ, 0, π}]
```

2

```
integralϕ = Integrate[1, {ϕ, 0, 2 * π}]
```

$2\,\pi$

```
ans = integralrNew * integralθ * integralϕ
```

$32\,A^2\,ao^3\,\pi$

Solve for A:

```
Solve[ans == 1, A] // Flatten
```

$$\left\{A \to -\frac{1}{4\,ao^{3/2}\sqrt{2\,\pi}},\ A \to \frac{1}{4\,ao^{3/2}\sqrt{2\,\pi}}\right\}$$

The normalization constant *A* can be chosen to be positive. Define *A* and print out the normalized wavefunction:

```
A = 1 / (4 ao^(3/2) Sqrt[2 π]);
Print["The normalized wavefunction is ψ =", A * psi1]
```

The normalized wavefunction is $\psi = \dfrac{e^{-\frac{r}{2\,ao}}\left(2 - \frac{r}{ao}\right)}{4\,ao^{3/2}\sqrt{2\,\pi}}$

Part b:
$\psi(r, \theta, \phi) = r \sin\theta \cos\phi\, e^{-r/2ao}$ so $R(r) = r\, e^{-r/2ao}$, $F(\theta) = \sin\theta$, and $G(\phi) = \cos\phi$.

```
Clear[A];
R = r * Exp[-r / (2 * ao)];
integralR = Integrate[A^2 * r^2 * R^2, {r, 0, Infinity}]
```

$A^2\ \mathrm{If}\left[\mathrm{Re}[ao] > 0,\ 24\, ao^5,\ \int_0^\infty e^{-\frac{r}{ao}} r^4\, dr\right]$

Define a new function for the output:

```
integralRNew = A^2 * 24 * ao^5
```

$24\, A^2\, ao^5$

```
F = Sin[θ];
integralF = Integrate[Sin[θ] * F^2, {θ, 0, π}]
```

$\frac{4}{3}$

```
G = Cos[ϕ];
integralG = Integrate[G^2, {ϕ, 0, 2 * π}]
```

π

```
ans = integralRNew * integralF * integralG
```

$32\, A^2\, ao^5\, \pi$

Solve for A:

```
Solve[ans == 1, A] // Flatten
```

$\left\{A \to -\frac{1}{4\, ao^{5/2} \sqrt{2\pi}},\ A \to \frac{1}{4\, ao^{5/2} \sqrt{2\pi}}\right\}$

The normalization constant *A* is positive. Define *A* and the normalized wavefunction ψ to print out the answer:

$A = \frac{1}{4\, ao^{5/2} \sqrt{2\pi}};$

```
psi = A * R * F * G;
Print["The normalized wavefunction is ψ =", psi]
```

The normalized wavefunction is $\psi = \frac{e^{-\frac{r}{2\,ao}}\, r\, \mathrm{Cos}[\phi]\, \mathrm{Sin}[\theta]}{4\, ao^{5/2} \sqrt{2\pi}}$

Answers: Problem 11.16

Part a:

From Problem 11.9, the normalized wavefunction is $\psi = \frac{e^{-\frac{r}{2\,ao}}\left(2-\frac{r}{ao}\right)}{4\,ao^{3/2}\sqrt{2\,\pi}}$.

Define this as a new function:

```
psi1 = E^(-r/(2 ao)) (2 - r/ao) / (4 ao^(3/2) Sqrt[2 π])
```

$$\frac{e^{-\frac{r}{2\,ao}}\left(2-\frac{r}{ao}\right)}{4\,ao^{3/2}\sqrt{2\,\pi}}$$

The normalized wavefunction contains only the variable *r* and is independent of *θ* and *ϕ*. This means that you can calculate the expectation of r as:

$\int\int\int r\,\psi^2\,d\tau = \int r^3\,\psi^2\,dr \int \mathrm{Sin}\,\theta\,d\theta \int d\phi$, with limits of

$0 \le r \le \infty$, $0 \le \theta \le \pi$, $0 \le \theta \le 2\pi$.

The expectation of r^2 is $\int\int\int r^2\,\psi^2\,d\tau = \int r^4\,\psi^2\,dr \int \mathrm{Sin}\,\theta\,d\theta \int d\phi$.

Calculate each individual integral and multiply them together to get the answer:

```
integralr = Integrate[r^3 * psi1^2, {r, 0, Infinity}]
```

$$\frac{\mathrm{If}\left[\mathrm{Re}[ao] > 0,\ 48\,ao^4,\ \int_0^\infty e^{-\frac{r}{ao}}\,r^3\left(2-\frac{r}{ao}\right)^2 dr\right]}{32\,ao^3\,\pi}$$

```
integralrNew = 48 * ao^4 / (32 * ao^3 * π)
```

$$\frac{3\,ao}{2\,\pi}$$

```
integralθ = Integrate[Sin[θ], {θ, 0, π}]
```

2

```
integralϕ = Integrate[1, {ϕ, 0, 2 * π}]
```

$2\,\pi$

```
ans = integralrNew * integralθ * integralϕ;
Print["<r> = ", ans]
```

<r> = 6 ao

For <r^2>, the only integral that changes in value is the one involving the variable *r*. Define a new integral for *r* and multiply all the integrals together to get the answer.

```
integralr2 = Integrate[r^4 * psi1^2, {r, 0, Infinity}]
```

$$\frac{\text{If}\left[\text{Re}[\text{ao}] > 0,\ 336\ \text{ao}^5,\ \int_0^\infty e^{-\frac{r}{\text{ao}}}\, r^4 \left(2 - \frac{r}{\text{ao}}\right)^2 dr\right]}{32\ \text{ao}^3\ \pi}$$

$$\text{integralr2New} = \frac{336\ \text{ao}^5}{32\ \text{ao}^3\ \pi}$$

$$\frac{21\ \text{ao}^2}{2\ \pi}$$

```
ans = integralr2New * integralθ * integralϕ;
Print["<r^2> = ", ans]
```

<r^2> = 42 ao^2

Part b:

From Problem 11.9, the normalized wavefunction is

$$\psi = \frac{e^{-\frac{r}{2\,\text{ao}}}\ r\ \text{Cos}[\phi]\ \text{Sin}[\theta]}{4\ \text{ao}^{5/2}\sqrt{2\ \pi}}\ .$$

This function contains three variables (r, θ, ϕ), so <r> is:

$$\int r^3 R(r)^2\, dr \int \text{Sin}\,\theta\, F(\theta)^2\, d\theta \int G(\phi)^2\, d\phi$$

Define each part of the wavefunction separately and multiply the individual integrals together to get the answer.

$$\text{R} = \frac{e^{-\frac{r}{2\,\text{ao}}}\ r}{4\ \text{ao}^{5/2}\sqrt{2\ \pi}}$$

$$\frac{e^{-\frac{r}{2\,\text{ao}}}\ r}{4\ \text{ao}^{5/2}\sqrt{2\ \pi}}$$

```
integralR = Integrate[r^3 * R^2, {r, 0, Infinity}]
```

$$\frac{\text{If}\left[\text{Re}[\text{ao}] > 0,\ 120\ \text{ao}^6,\ \int_0^\infty e^{-\frac{r}{\text{ao}}}\, r^5\, dr\right]}{32\ \text{ao}^5\ \pi}$$

```
integralRNew = 120 ao^6 / (32 ao^5 π)
```

$$\frac{15\,ao}{4\,\pi}$$

```
F = Sin[θ];
integralθ = Integrate[Sin[θ] * F^2, {θ, 0, π}]
```

$$\frac{4}{3}$$

```
G = Cos[ϕ];
integralϕ = Integrate[G^2, {ϕ, 0, 2 * π}]
```

π

```
ans = integralRNew * integralF * integralG;
Print["<r> = ", ans]
```

```
<r> = 5 ao
```

For <r^2>, the only integral that changes in value is the one involving the variable *r*. Define a new integral for *r* and multiply all the integrals together to get the answer.

```
integralr2 = Integrate[r^4 * R^2, {r, 0, Infinity}]
```

$$\frac{\text{If}\left[\text{Re}[ao] > 0,\ 720\,ao^7,\ \int_0^\infty e^{-\frac{r}{ao}}\,r^6\,dr\right]}{32\,ao^5\,\pi}$$

```
integralr2New = 720 ao^7 / (32 ao^5 π)
```

$$\frac{45\,ao^2}{2\,\pi}$$

```
ans = integralr2New * integralF * integralG;
Print["<r^2> = ", ans]
```

```
<r^2> = 30 ao^2
```