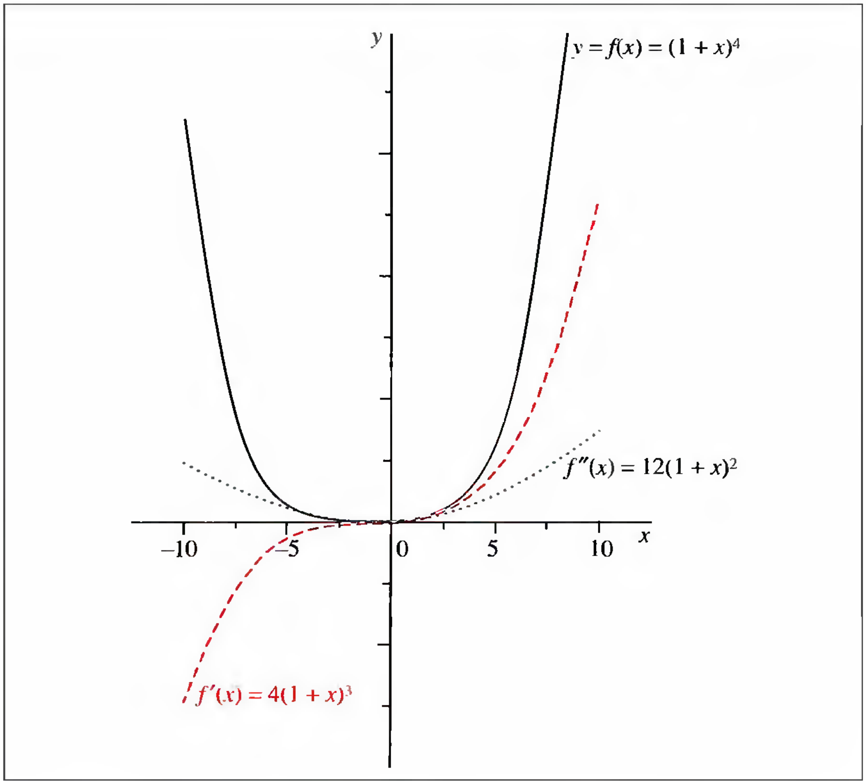

Figure 4.4 Plots of the function $f(x)=(1+x)^4$ and its first two derivatives

positive. The fact that the value of $f'(x)=4(1+x)^3$ is zero at $x=-1$ indicates that the slope of the function is zero at this point. Such a point is identified as a **stationary point**, which, in this case, corresponds to a minimum (as we can see from the plot). We shall see later in Section 4.4 how to prove whether a stationary point is a maximum or minimum (or point of inflection) without needing to plot the function. Similarly, the form of the second derivative, $f''(x)=12(1+x)^2$, gives us the slope, or rate of change, of the first derivative and by extension the slope of the slope of the original function $f(x)$. The form of the second derivative provides us with the means to characterize the nature of any stationary points in the original function, while that of the first derivative tells us if and where the stationary points exist (see Section 4.4).

Problem 4.8

Find the second and third derivatives of (a) $y=1/x$ and (b) $y=N\sin ax$ (N, a are constants).

4.3.1 Operators Revisited: an Introduction to the Eigenvalue Problem

In Section 4.2.2 we defined the act of differentiation as an operation in which the operator $\hat{D} = \mathrm{d}/\mathrm{d}x$ acts on some function $f(x)$. Similarly, we can express the act of differentiating twice in terms of the operator $\hat{D}^2 = \mathrm{d}^2/\mathrm{d}x^2$.

Worked Problem 4.4

Q For the function $f(x) = \cos kx$, find $\hat{A}(f(x))$, where $\hat{A} = \mathrm{d}^2/\mathrm{d}x^2$.

A For $f(x) = \cos kx$, $\mathrm{d}/\mathrm{d}x(f(x)) = -k \sin kx$ and $\mathrm{d}^2/\mathrm{d}x^2(f(x)) = -k^2 \cos kx$ and so $\hat{A} \cos kx = -k^2 \cos kx$.

The Eigenvalue Problem

A problem common to many areas in physical chemistry is the following: given an operator, $\hat{A}$, find a function $\phi(x)$, and a constant a, such that $\hat{A}$ acting on $\phi(x)$ yields a constant multiplied by $\phi(x)$. In other words, the result of operating on the function $\phi(x)$ by $\hat{A}$ is simply to return $\phi(x)$, multiplied by a constant factor, a. This type of problem is known as an **eigenvalue problem**, and the key features may be described schematically as follows:

The key eigenvalue equation in chemistry is the Schrödinger equation, $\hat{H}\psi = E\psi$. The solution of this equation for a particular system (such as an electron bound by the field of a nucleus) yields so called wavefunctions, ψ, that completely describe the system of interest and from which any property of the system can be extracted.

The eigenfunction of the operator $\hat{A}$

$$\hat{A}\phi(x) = a\phi(x)$$

The eigenvalue of the operator $\hat{A}$

The solution to Worked Problem 4.4 is an example of an eigenvalue problem.

Worked Problem 4.4 *revisited*

For $f(x) = \cos kx$ and $\hat{A} = \mathrm{d}^2/\mathrm{d}x^2$:

$$\hat{A} \cos kx = -k^2 \cos kx$$

In this example, we see that by differentiating the function $f(x) = \cos kx$ twice, we regenerate our original function multiplied by a constant which, in this case, is $-k^2$. Hence, $\cos kx$ is an eigenfunction of $\hat{A}$, and its eigenvalue is $-k^2$.

Problem 4.9

Perform the following operations:

(a) For $f(x) = x^3$, find, $\hat{A}(f(x))$, where $\hat{A} = d^2/dx^2$.

(b) For $f(x) = \sin kx$, find $\hat{A}(f(x))$, where $\hat{A} = d^2/dx^2$.

(c) For $f(x) = \sin kx + \cos kx$, find $\hat{A}(f(x))$, where $\hat{A} = d^2/dx^2$.

(d) For $f(x) = e^{ax}$, find $\hat{A}(f(x))$, where $\hat{A} = d/dx$.

Which of (a)–(d) would be classified as eigenvalue problems? What is the eigenfunction and what is the eigenvalue in each case?

Problem 4.10

Show that $y = f(x) = e^{mx}$ is an eigenfunction of the operator $\hat{A} = \frac{d^2}{dx^2} - 2\frac{d}{dx} - 3$, and give its eigenvalue. For what values of m does $\hat{A}$ annihilate $f(x)$?

Annihilation of a function implies that the null function is produced after application of an operator.

Problem 4.11

The lowest energy solution of the **Schrödinger equation** for a particle (mass m) moving in a constant potential energy (V), and in a one-dimensional box of length L, takes the form:

$$\psi = \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}$$

If we take V as the zero of energy, then ψ satisfies the Schrödinger equation:

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} = E\psi$$

Find an expression for the total energy E in terms of L and the constants π, m and h. *Hint*: you may have noticed that the expression above is an example of an eigenvalue problem where the eigenfunction is $\psi = \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}$ and the eigenvalue is E. In this case, the total energy E is determined by operating on the function ψ using the operator $-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}$

In quantum mechanics, the operator $-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}$ is called the **Hamiltonian** and is given the symbol $\hat{H}$.

4.4 Maxima, Minima and Points of Inflection

We often encounter situations in the physical sciences where we need to establish at which value(s) of an independent variable a maximum or minimum value in the function occurs. For example:

- The probability of finding the electron in the ground state of the hydrogen atom between radii r and $r + \mathrm{d}r$ is given by $D(r)\mathrm{d}r$, where $D(r)$ is the radial probability density function shown in Figure 4.5. The most probable distance of the electron from the nucleus is found by locating the maximum in $D(r)$ (see Problem 4.12 below). It should come as no surprise to discover that this maximum occurs at the value $r = a_0$, the Bohr radius.

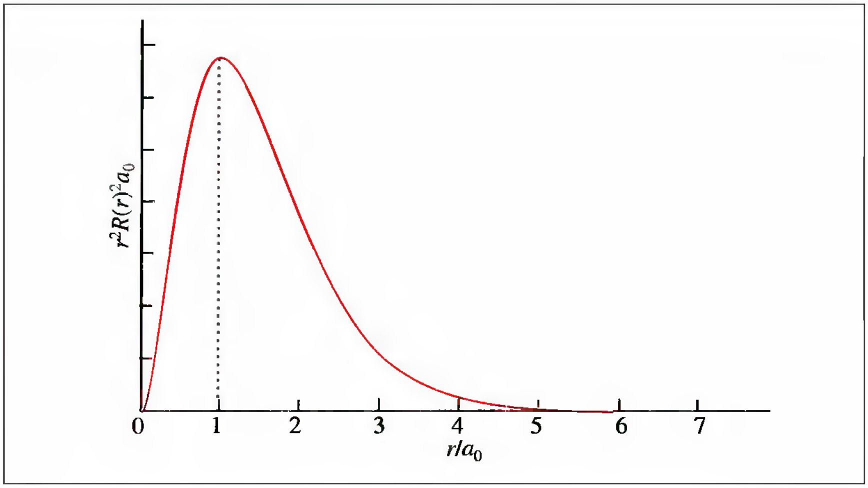

Figure 4.5 The radial probability density function for the 1s atomic orbital of the hydrogen atom

- When we attempt to fit a theoretical curve to a set of experimental data points, we typically apply a least-squares fitting technique which seeks to minimize the deviation of the fit from the experimental data. In this case, differential calculus is used to find the minimum in the function that describes the deviation between fit and experiment.

4.4.1 Finding and Defining Stationary Points

Consider the function $y = f(x)$ in Figure 4.6. As we saw in our discussion of Worked Problem 4.3, values of x for which $f'(x) = 0$ are called stationary points. A stationary point may be:

- A maximum (point E, a turning point) or a minimum (point C, a turning point). The value of $\mathrm{d}y/\mathrm{d}x$ changes sign on passing through these points.
- A point of inflection: the tangent cuts the curve at this point (points A, B and D).

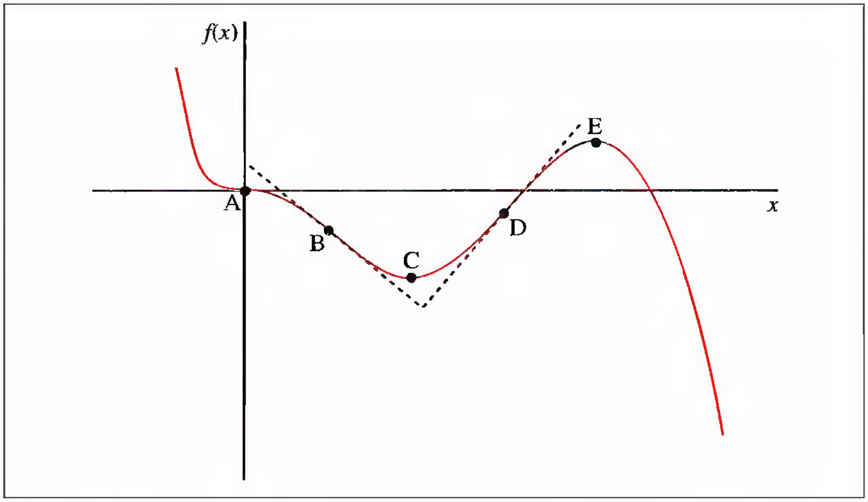

Figure 4.6 A plot of the function $y = f(x)$. Points A, C and E are all stationary points, for which $f'(x) = 0$. while points C and E are also turning points (minimum and maximum, respectively). Points A, B and D are all points of inflection, but B and D are neither stationary points nor turning points. Note that at the points of inflection, the tangents (*dashed lines*) cut the curve

Turning Points (Maxima and Minima)

Points E and C are called **turning points** because in passing through E and C the value of $\mathrm{d}y/\mathrm{d}x$ changes sign. The existence and nature of stationary points, which are also turning points, may be identified through the first and second derivatives of the function. If we consider point C, we see that as we pass through this point the gradient becomes less negative as we approach C, passes through zero at point C, and then becomes positive. Clearly the *rate of change* of the gradient is positive at point C (because the gradient changes from negative to positive), which suggests that the function has a minimum at this point:

A **minimum** exists if $f'(x) = 0$ and $f^{(2)}(x) > 0$.

Similarly, on passing through point E, the gradient becomes less positive, passes through zero at E and then becomes negative. In this case, the rate of change in the gradient is negative and we can identify point E as a maximum:

A **minimum** exists if $f'(x) = 0$ and $f^{(2)}(x) < 0$.

In general, $y = f(x)$ will display a number of turning points within the domain of the function.

Turning points corresponding to maxima and minima may be classified as either:

- A **global maximum** or minimum which has a value greater or smaller than all other points within the domain of the function.
- A **local maximum** or minimum which has a value greater or smaller than all neighbouring points.

Points of Inflection

At a **point of inflection** (A, B, D), which may or may not be a stationary point:

- The tangent cuts the curve.
- The slope of the tangent does not change sign.

Note that A is both a point of inflection and a stationary point, but while B and D are both points of inflection, they are not stationary points because $f'(x) \neq 0$.

Points of inflection occur when the gradient is a maximum or minimum. This requires that $f^{(2)}(x) = 0$, but this in itself is not sufficient to characterize a point of inflection. We achieve this through the first non-zero higher derivative.

If $f'(x) = 0$, $f^{(2)}(x) = 0$ but $f^{(3)}(x) \neq 0$, then we have a point of inflection which is also a stationary point (such as point A). However, if $f'(x) \neq 0$, $f^{(2)}(x) = 0$ and $f^{(3)}(x) \neq 0$, then we have a point of inflection which is *not* a stationary point (B, D). The rules for identifying the location and nature of stationary points, turning points and points of inflection are summarized in Table 4.2.

Table 4.2 The location and nature of turning points, stationary points and points of inflection are given by the first, second and, where appropriate, third and fourth derivatives

	$f'(x)$	$f^{(2)}(x)$	$f^{(3)}(x)$	$f^{(4)}(x)$
Minimum	0	>0	–	–
Maximum	0	<0	–	–
Inflection point (stationary)	0	0	$\neq 0$	–
Inflection point (not stationary)	$\neq 0$	0	$\neq 0$	–
Turning points where $f^{(2)}(x) = 0$	0	0	0	$\neq 0$

Interestingly, in the last row of Table 4.2 we see that a turning point may exist for which $f^{(2)}(x) = 0$. In such cases, $f^{(3)}(x) = 0$, and the nature of the turning point is determined by the sign of the fourth derivative. An example of a function for which this latter condition applies is $y = f(x) = (x - 1)^4$. If there is any doubt over the nature of a stationary point, especially if the second derivative vanishes, it is always helpful to sketch the function!

Worked Problem 4.5

Q Consider the function $y = f(x)$, where $f(x) = x^2 - x^3/9$.

(a) Plot the function for selected values of x in the interval $-3.5 \le x \le 10$.

(b) Identify possible values of x corresponding to turning points and points of inflection.

(c) Derive expressions for the first and second derivatives of the function.

(d) Identify the nature of the turning points (*e.g.* maximum, minimum, global, local).

(e) Verify that there is a point of inflection where $f'(x) \neq 0$, $f^{(2)}(x) = 0$ and $f^{(3)}(x) \neq 0$.

A (a) See Figure 4.7.

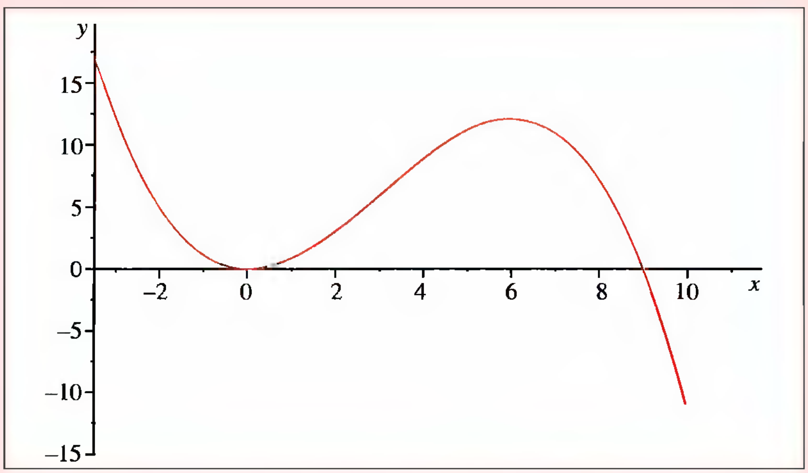

Figure 4.7 A plot of the function $y = f(x) = x^2 - x^3/9$ for $-3.5 \le x \le 10$

(b) By inspection, we can identify turning points at $x = 0$ and in the vicinity of $x = 6$; there is no turning point corresponding to a point of inflection.

(c) $f'(x) = 2x - x^2/3$; $f^{(2)}(x) = 2 - 2x/3$.

(d) $f'(x) = x(2 - \frac{x}{3}) = 0$ at $x = 0$ (local minimum; $f^{(2)}(x) > 0$) and $x = 6$ (local maximum; $f^{(2)}(x) < 0$).

(e) $f'(x) = 2x - x^2/3 \neq 0$ when $x = 3$; $f^{(2)}(x) = 2 - 2x/3 = 0$ when $x = 3$; $f^{(3)}(x) = -2/3 \neq 0$ when $x = 3$, corresponding to a point of inflection.