Workshop: Series expansion—A Swiss army knife for calculations and analysis

Quantum aspects of physical chemistry

http://quantum.bu.edu/courses/PLTL/4/4.pdf
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In this workshop we will explore series expansions and how they are helpful in analyzing quantum mechanical expressions and carrying out calculations with them. This workshop is based in part on McQuarrie and Simon, *Physical Chemistry* (University Science Books, 1997), MathChapter I. My hope is that once you have digested this workshop, you will have some confidence that you can actually *use* series expansions to do certain kinds of calculations and analyses much more easily.

■ Series expansions

The Taylor series

$$f(x) = f(x_0) + (x - x_0)\left(\frac{d f}{d x}\right)_{x_0} + \frac{(x - x_0)^2}{2!}\left(\frac{d^2 f}{d x^2}\right)_{x_0} + \frac{(x - x_0)^3}{3!}\left(\frac{d^3 f}{d x^3}\right)_{x_0} + \ldots$$

is a way of expressing the value of a function, $f(x)$, in terms of its values and derivatives at a single point, x_0. Notice that successive terms are proportional to successively higher powers of the separation $x - x_0$. This means that the closer x is to x_0, the fewer terms we need to include in the Taylor series, since successive terms more rapidly become negligible.

> 1. In textbooks, series are often represented as $f(x) = \sum_{i=0}^{\infty} g_i(x)$. Write the Taylor series in this form.

> 2. The Maclaurin series is a special case of the Taylor series for $x_0 = 0$. Write the down the general expression for the Maclaurin series.

■ Logarithmic functions

> 3. Use the Maclaurin series to find an expression for $\ln(1 + x)$ near $x = 0$. Include three non-vanishing terms in your series. Indicate the neglected terms by the notation $O(x^n)$, where the value of n is the power of x in the first non-zero neglected term.

> 4. Make a table of values of $\ln(1 + x)$ and of your three-term approximation to it for $-0.5 \leq x \leq 0.5$.

5. Make a sketch of the two functions for $-0.5 \leq x \leq 0.5$ and account for any differences.

■ Trigonometric functions

6. Use the Maclaurin series to find an expression for $\sin(x)$ near $x = 0$. Include two non-vanishing terms in your series. Indicate the neglected terms by the notation $O(x^n)$, where the value of n is the power of x in the first non-zero neglected term.

7. Make a table of values of $\sin(x)$ and of your two-term approximation to it for $0 \leq x \leq \pi$ radian.

8. Make a sketch of the two functions for $0 \leq x \leq \pi$ and account for any differences.

9. Use the Maclaurin series to find an expression for $\cos(x)$ near $x = 0$. Include two non-vanishing terms in your series. Indicate the neglected terms by the notation $O(x^n)$, where the value of n is the power of x in the first non-zero neglected term.

10. Make a table of values of $\cos(x)$ and of your two-term approximation to it for $0 \leq x \leq \pi$ radian.

11. Make a sketch of the two functions for $0 \leq x \leq \pi$ and account for any differences.

12. Account for any differences in accuracy of the two-expansions to $\sin(x)$ and $\cos(x)$ over the range $0 \leq x \leq \pi$.

■ Exponential functions

13. Use the Maclaurin series to find an expression for e^x near $x = 0$. Include four non-vanishing terms in your series. Indicate the neglected terms by the notation $O(x^n)$, where the value of n is the power of x in the first non-zero neglected term.

14. Make a table of values of e^x and of your four-term approximation to it for $0 \leq x \leq 2$.

15. Make a sketch of the two functions for $0 \leq x \leq 2$.and account for any differences.

16. Use the Maclaurin series to find an expression for $e^{i x}$ near $x = 0$. Include four non-vanishing terms in your series. Indicate the neglected terms by the notation $O(x^n)$, where the value of n is the power of x in the first non-zero neglected term.

17. The Euler relation is

$$e^{i x} = \cos(x) + i \sin(x).$$

Use your expansions for $\cos(x)$ and $\sin(x)$ to see whether or not this relation holds for small x. Account for any discrepancy.

■ Using series expansions to evaluate limits

Series expansions are helpful in determining the limit of a ratios when numerator and denominator both go to zero.

18.. Obtain an approximate expression for the ratio

$$\frac{\ln(1+x)-x}{x^2}$$

by doing a series expansion of the numerator and keeping the lowest two terms.

19. Obtain the limit

$$L = \lim_{x\to 0}\frac{\ln(1+x)-x}{x^2}$$

by evaluating your approximate expression for the ratio at $x = 0$.

■ Using series expansion to approximate integrals

The exact values of the integral

$$I = \int_0^a x^2\, e^{-x} \cos^2 x\, dx$$

for $a = 0.1$, 0.2 and 0.3 are

a	integral
0.1	0.000307
0.2	0.00224
0.3	0.00683

20. Obtain an approximate expression for the integrand, $x^2\, e^{-x} \cos^2 x$, by doing a series expansion of the integrand and keeping lowest two terms

21. Integrate your expansion from $x = 0$ to $x = a$.

22. Test your approximation to the integral by comparing its values for $a = 0.1$, 0.2 and 0.3 to the exact values given above.

■ Using series expansions to simplify expressions

One of the most powerful uses of series expansions is to simplify an expression by taking advantage of the constraints of the physical situation to which it applies. Here is an example.

To normalize unbound wave functions, special methods need to be used, since unbound wave functions extend to infinite distance (that's why we called them unbound). The problem is that the upper limit on the normalization integral extends to infinity, while the wave function oscillates about zero, and so it is not clear how to determine the numerical value of the integral.

23. In using the special methods (we'll discuss these elsewhere) to handle such integration, there arises the quantity $\sqrt{E} - \sqrt{E'}$, where E and E' are the kinetic energies of two different unbound wave functions. It turns out that only values of E' close to E need to be considered. Show that under these circumstances

$$\sqrt{E} - \sqrt{E'} \approx \frac{1}{2\sqrt{E}}(E - E').$$

Hint: Use the Taylor series to expand $\sqrt{E'}$ about the E.

I find that a good thing to keep in mind is that when I encounter an expression approximated in terms of another one, if the approximation is not obvious to me (as the one above is not obvious to me) then I see if there is a series expansion at work behind the scenes.

■ Using series expansions to evaluate electronic shielding

The periodicity in the properties of the elements reflects in part the different degree to which s electrons, p electrons, etc., penetrate into the region near the nucleus. Here are probability amplitudes, $P_{n\ell}(r)$, of the hydrogen 2s and 2p electron.

$$P_{2s}(r) = \frac{1}{2\sqrt{2}} e^{-r/2}(2 - r)\, r$$

$$P_{2p}(r) = \frac{1}{2\sqrt{6}} e^{-r/2}\, r^2$$

Here r is the distance of the electron from the nucleus, in units of the Bohr radius, $a_0 = 0.529$ Å. The fraction of the 2s and 2p electron within 0.1 a_0 of the nucleus is the value of the integrals

$$f_{2s}(0.1) = \int_0^{0.1} |P_{2s}(r)|^2\, dr$$

$$f_{2p}(0.1) = \int_0^{0.1} |P_{2p}(r)|^2\, dr$$

24. Use series expansions to show that an approximate expression for the integrand of the 2s integral is $(r^2/2) - r^3$.

25. Integrate your expansion from $r = 0$ to $r = 0.1$ to obtain an estimate of the fraction of the 2s electron within 0.1 a_0 of the nucleus. How does your result compare to the exact value, 0.00014?

26. Use series expansions to show that an approximate expression for the integrand of the 2p integral is $(r^4 - r^5)/24$.

27. Integrate your expansion from $r = 0$ to $r = 0.1$ to obtain an estimate of the fraction of the 2p electron within 0.1 a_0 of the nucleus. How does your result compare to the exact value, 7.7×10^{-8}?

28. Why do you suppose a larger fraction of the 2s electron is near the nucleus?