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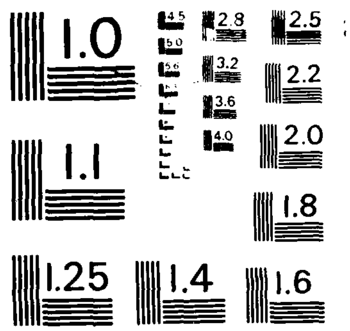

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A Taylor Series in Symmetry-adaptable Functions

by

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We present a Taylor series in spherical polar coordinates for a general class of functions of the form $Y_{\lambda\mu}(\hat{r})f_{\lambda}(r)$ which separate into purely angular and purely radial parts. The series depends upon the spherical harmonic functions, and, therefore, is symmetry adaptable. The general expression for the series is developed and some specific examples are considered. In particular, we note that the Taylor series coincides with the Laplace expansion for the

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A Taylor Series in Symmetry-adaptable Functions

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Abstract

We present a Taylor series in spherical polar coordinates for a general class of functions of the form $Y_{\lambda\mu}(\hat{r})f_{\lambda}(r)$ which separate into purely angular and purely radial parts. The series depends upon the spherical harmonic functions, and, therefore, is symmetry-adaptable. The general expression for the series is developed and some specific examples are considered. In particular, we note that the Taylor series coincides with the Laplace expansion for the Coulomb potential. We then display the particular series for the exponential, e^{-ar}, and the inverse power law, r^{-q}.

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Introduction

It is often the case in examining systems of interacting atoms and molecules that one wishes to isolate a single coordinate with its associated canonically conjugate momentum, or equivalently, a single element of symmetry in the system. We show here that for an arbitrary, well-behaved potential energy function, a Taylor series can be constructed which takes direct advantage of the available symmetry. In this sense, the Taylor series exploits the use of symmetry in the same sense as is the case with the more familiar Laplace expansion of the Coulomb interaction.

A few years ago, Briels[1] demonstrated the advantages of the use of symmetry-adapted functions in the general consideration of intermolecular interactions which arise in and are of importance to statistical mechanics. Our interest also focuses on the expansion of intermolecular and interatomic interactions. However, we have found it to be useful to consider expansions in the form of the Taylor series in terms of functions which can also be adapted to symmetry. With reference to vibrational quantum mechanics and chemical rate processes in particular, the Taylor series proves to be easier to handle.

In the next section, we outline the general methods which are required for the development of the Taylor series in symmetry-adaptable functions. Following that outline, we present the expansions for two potential energy functions: the exponential, e^{-ar}, and the general inverse power r^{-q}. A test of the method is reported in a subsequent paper; the assay involves the inversion spectrum of ammonia.[2]

The Taylor Series for an Expansion About One Center

We develop the Taylor series for functions which are separable into purely

radial and purely angular parts, *viz.*,

$$G(\underset{\sim}{r}) = Y_{\lambda\mu}(\hat{r})F_{\lambda}(r) \qquad (1)$$

for which $Y_{\lambda\mu}(\hat{r})$ is the spherical harmonic function (the unit vector in the r-space is $\hat{r}$). Still more general functions can be expressed as superpositions of such functions.

The function $G(\underset{\sim}{r})$ at the displaced point $\underset{\sim}{r}+\underset{\sim}{R}$ is given by the vectorial Taylor series[3]

$$G(\underset{\sim}{r}+\underset{\sim}{R}) = \sum_{n=0}^{\infty} \frac{1}{n!}(\underset{\sim}{r}\cdot\underset{\sim}{\nabla})^n G(\underset{\sim}{R}). \qquad (2)$$

The Fourier transform of $G(\underset{\sim}{r})$ is $g(\underset{\sim}{k})$:

$$g(\underset{\sim}{k}) = Y_{\lambda\mu}(\hat{k})f_{\lambda}(k) \qquad (3)$$

with

$$f_{\lambda}(k) = 4\pi i^{\lambda}\int_0^{\infty} dr\, r^2 F_{\lambda}(r) j_{\lambda}(kr). \qquad (4)$$

The function $j_n(x)$ is the spherical Bessel function of the first kind.[4]

An individual term in the Taylor series can be written as

$$\frac{1}{n!}(\underset{\sim}{r}\cdot\underset{\sim}{\nabla})^n G(\underset{\sim}{R}) = \frac{(-ir)^n}{(2\pi)^3 n!}\int d^3k\, k^n f_{\lambda}(k)(\hat{r}\cdot\hat{k})^n \exp(-i\underset{\sim}{k}\cdot\underset{\sim}{R}) \qquad (5)$$

where $\hat{r}$ and $\hat{k}$ are unit vectors. The following relationship is easily derived:

$$(\underset{\sim}{r}\cdot\underset{\sim}{k})^n = 4\pi\sum_{\ell,m}(2\ell+1)^{-1}A_{n\ell}Y^{*}_{\ell m}(\hat{k})Y_{\ell m}(\hat{r}) \qquad (6)$$

with[6]

$$A_{n\ell} = 0 \qquad \text{for } \ell > n \text{ and } n - \ell \text{ odd}$$

$$= \frac{(2\ell+1)n!(n-\ell+1)!!}{(n-\ell+1)!(n+\ell+1)!!} \qquad \text{for } \ell \le n \text{ and } n - \ell \text{ even.} \tag{7}$$

With the use of eqn (6) together with the well-known Rayleigh expansion of $\exp(-i\underset{\sim}{k}\cdot\underset{\sim}{R})$, one finds

$$\frac{1}{n!}(\underset{\sim}{r}\cdot\nabla)^n G(\underset{\sim}{R}) = (4\pi)^{3/2}\frac{r^n}{n!}\sum_{L,M,\ell,m}(-i)^{L+n}A_{n\ell}Y_{LM}(\hat{R})Y_{\ell m}(\hat{r})$$

$$\times\left[\frac{2L+1}{(2\ell+1)(2\lambda+1)}\right]^{\frac{1}{2}}(L\ell 00|\lambda 0)(L\ell Mm|\lambda\mu)I_{nL}(R) \tag{8}$$

and $I_{nL}(R)$ is defined by

$$I_{nL}(R) = \frac{1}{(2\pi)^3}\int_0^\infty dk\; k^{n+2}f_\lambda(k)j_L(kR). \tag{9}$$

In eqn (8), $(L\ell Mm|\lambda\mu)$ is a Clebsch–Gordan coefficient.[5] The summation of terms of the form of eqn (8) yields the Taylor series, as indicated by eqn (2).

The Taylor series for a scalar function $G(r)$ has a simpler form. With the use of $\lambda=\mu=0$, and the addition theorem for the spherical harmonic functions, one finds

$$\sum_{n=0}^{\infty}\frac{1}{n!}(\underset{\sim}{r}\cdot\nabla)^n G(\underset{\sim}{R}) = (4\pi)^{\frac{1}{2}}\sum_{n=0}^{\infty}\frac{r^n}{n!}\sum_{\ell,m}(-i)^{n+\ell}A_{n\ell}P_\ell(\hat{r}\cdot\hat{R})I_{n\ell}(R) \tag{10}$$

where $P_\ell(x)$ is the Legendre polynomial of order ℓ and $\hat{r}\cdot\hat{R} = \cos\theta$ where θ is the angle between the vectors $\underset{\sim}{r}$ and $\underset{\sim}{R}$.

Taylor Series for Representative Potential Energy Functions

It is possible to derive several potential energy functions from one single form, the Yukawa, or Debye-Hückel, potential:

$$y(a,r) = \exp(-ar)/r. \tag{11}$$

The Coulomb electrostatic interaction follows as a limiting process:

$$1/r = \lim_{a\to 0} y(a,r). \tag{12}$$

The differentiation of $y(a,r)$ with respect to a yields the exponential:

$$e^{-ar} = -\frac{d}{da}y(a,r).$$

Finally, integration according to eqn (14) yields the inverse power law r^{-q}:

$$r^{-q} = \frac{1}{(q-2)!}\int_0^\infty da\; a^{q-2}y(a,r). \tag{14}$$

Each of these operations can be applied to the Taylor series for the Yukawa potential in order to derive the individual series.

The Taylor series for the Yukawa potential is

$$y(a,r+R) = a\sum_{n,\ell}\frac{(-ar)^n}{n!}A_{n\ell}P_\ell(\hat{r}\cdot\hat{R})k_\ell(aR) \tag{15}$$

where $k_n(x)$ is the modified spherical Bessel function of the third kind.[4]

The limit as a tends to zero yields the familiar Laplace expansion of the Coulomb potential; this is easily verified with the use of the limiting form of the Bessel function,[4]

$$\frac{(2n-1)!!}{x^{n+1}} \qquad \text{for} \quad x \ll 1,$$

for $k_n(x)$. The expansion for the exponential function is

$$\exp(-a(r+R)) = \sum_{n,\ell} \frac{(-ar)^n}{n!} A_{n\ell} P_\ell(\hat{r}\cdot\hat{R}) \left[aRk_{\ell-1}(aR) - (n-\ell)k_\ell(aR) \right]. \tag{16}$$

With the use of this form, one immediately can obtain an expansion for the Morse potential, for example:

$$M(r) = D \exp(a(r_0-r)) \left[\exp(a(r_0-r)) - 2 \right]. \tag{17}$$

Finally, with the use of[4]

$$k_\ell(x) = \frac{e^{-x}}{x} \sum_{s=0}^{\ell} \frac{(\ell-s)!}{(2s)!!(\ell-s)!} x^{-s} \tag{18}$$

in the integral (14), one finds[9]

$$\frac{1}{|\underset{\sim}{r}+\underset{\sim}{R}|^q} = \frac{1}{R^q} \sum_{n,\ell} A_{n\ell} P_\ell(\hat{r}\cdot\hat{R})(-r/R)^n \frac{(q+n-2+\ell)!!(q+n-2-\ell)!}{(q-2)!(q+n-2-\ell)!!} \tag{19}$$

The derivation of the Taylor series in symmetry-adaptable functions which we have sketched and the formulae which we have derived from the expansion apply to a great number of potential energy functions which are of interest in molecular physics. The utility of the expansion is demonstrated in several references, *cf.* refs. 2, 6-8

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