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Legendre Polynomials and Angular Momentum

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I. INTRODUCTION USING CARTESIAN COÖRDINATES AND GUESSWORK

There are so many different ways to introduce Legendre Polynomials that one searchs for a path into this subject most suitable for chemists.

Consider Laplace's Equation:

$$\nabla^2\chi = \frac{\partial^2\chi}{\partial x^2} + \frac{\partial^2\chi}{\partial y^2} + \frac{\partial^2\chi}{\partial z^2} = 0 \tag{1.1}$$

which is a partial differential equation for $\chi(x, y, z)$. For our purposes, the solutions can be obtained by guessing, starting with $\chi = 1$, and proceeding to $\chi = x$, $\chi = y$ and $\chi = z$. It takes only a little more imagination to obtain $\chi = xy$ and its associates $\chi = yz$ and $\chi = xz$. It takes just a little more imagination to guess $\chi = x^2 - y^2$, but once done, one immediately guesses its two companions $\chi = x^2 - z^2$ and $\chi = y^2 - z^2$.

Reviewing, there was one simple (order 0) solution, three not so simple, but not particularly difficult solutions (of order 1) and six slightly more complicated solutions of order 2. Note that the first third-order solution one might guess would be $\chi = xyz$!

If one looks at these solutions, knowing that they are quantum mechanically important, the 1, x, y, and z solutions, accompanied by the xy, xz, yz, and $x^2 - y^2$ solutions suggest something having to do with wave functions, where the first function (1) is associated in some way with s-orbitals, the next three (x, y, and z) are associated with p-orbitals, and the next (of order 2) are associated with d-orbitals. If all this is true, the perceptive student will wonder where is the d_{z^2} orbital, the fifth one, and how come there are six functions of order two listed, when, if memory serves correctly, there are 5 d-orbitals! Ah.

$$\left(y^2 - z^2\right) + \left(x^2 - z^2\right)$$

can be rewritten as

$$\left(y^2 - z^2\right) + \left(x^2 - z^2\right) + \left(z^2 - z^2\right)$$

which is

$$x^2 + y^2 + z^2 - 3z^2$$

or as

$$r^2 - 3z^2$$

which combines the last two (linearly dependent) solutions into one, the one of choice, which has been employed for more than 50 years as the d_{z^2} orbital.

II. CONVERTING TO SPHERICAL POLAR COÖRDINATES

In Spherical Polar Coördinates, these solutions become

$$\begin{aligned}
1 &\Leftrightarrow 1\\
x &\Leftrightarrow r\sin\theta\cos\varphi\\
y &\Leftrightarrow r\sin\theta\sin\varphi\\
z &\Leftrightarrow r\cos\theta\\
xy &\Leftrightarrow r\sin\theta\cos\varphi r\sin\theta\sin\varphi = r^2\sin^2\theta\cos\varphi\sin\varphi\\
xz &\Leftrightarrow r\sin\theta\cos\varphi r\cos\theta = r^2\sin\theta\cos\theta\cos\varphi\\
yz &\Leftrightarrow r\sin\theta\sin\varphi r\cos\theta = r^2\sin\theta\cos\theta\sin\varphi\\
x^2 - y^2 &\Leftrightarrow r^2\sin^2\theta\cos^2\varphi - r^2\sin^2\theta\sin^2 = r^2\left(\sin^2\theta\left[\cos^2\varphi - \sin^2\varphi\right]\right)\\
r^2 - 3z^2 &\Leftrightarrow r^2 - 3r^2\cos^2\theta = r^2\left(1 - 3\cos^2\theta\right)\\
&\vdots
\end{aligned} \tag{2.1}$$

Now, Laplace's equation in spherical polar coördinates is

$$\nabla^2\chi = \frac{1}{r^2}\frac{\partial r^2\frac{\partial\chi}{\partial r}}{\partial r} + \frac{1}{r^2\sin^2\theta}\left[\sin\theta\frac{\partial\sin\theta\frac{\partial\chi}{\partial\theta}}{\partial\theta} + \frac{\partial^2\chi}{\partial\varphi^2}\right] = 0 \tag{2.2}$$

Next, we notice that our earlier solutions were all of the form

$$\chi = r^\ell\mathcal{Y}_{\ell,m_\ell}(r,\theta,\varphi) \tag{2.3}$$

where ℓ specifies the order, 0, 1, 2, etc., and the function of angles is dependent on this order, and on another quantum number as yet unspecified. Memory suggests that this last quantum number, m_ℓ is the famous substate quantum number in elementary atomic structure discussions.

Substituting this form into the spherical polar form of Laplace's equation results in a new equation for the angular parts alone, which we know from our previous results. We substitute Equation 2.3 into Equation 2.2 to see what happens, obtaining

$$\nabla^2 r^\ell \mathcal{Y}_{\ell,m_\ell} = \frac{1}{r^2}\frac{\partial r^2 \frac{\partial r^\ell \mathcal{Y}_{\ell,m_\ell}}{\partial r}}{\partial r} + \frac{1}{r^2 \sin^2\theta}\left[\sin\theta \frac{\partial \sin\theta \frac{\partial r^\ell \mathcal{Y}_{\ell,m_\ell}}{\partial \theta}}{\partial \theta} + \frac{\partial^2 r^\ell \mathcal{Y}_{\ell,m_\ell}}{\partial \varphi^2}\right] = 0 \quad (2.4)$$

which, by the nature of partial differentiation, becomes

$$\nabla^2 r^\ell \mathcal{Y}_{\ell,m_\ell} = \mathcal{Y}_{\ell,m_\ell}\frac{1}{r^2}\frac{\partial r^2 \frac{\partial r^\ell}{\partial r}}{\partial r} + r^\ell \frac{1}{r^2 \sin^2\theta}\left[\sin\theta \frac{\partial \sin\theta \frac{\partial \mathcal{Y}_{\ell,m_\ell}}{\partial \theta}}{\partial \theta} + \frac{\partial^2 \mathcal{Y}_{\ell,m_\ell}}{\partial \varphi^2}\right] = 0 \quad (2.5)$$

and the first term in Equation 2.5 is

$$\frac{1}{r^2}\frac{\partial r^2 \frac{\partial r^\ell}{\partial r}}{\partial r} = \frac{1}{r^2}\ell(\ell+1)r^\ell \quad (2.6)$$

so, substituting into Equation 2.5 we obtain

$$\nabla^2 r^\ell \mathcal{Y}_{\ell,m_\ell} = \ell(\ell+1)r^{\ell-2}\mathcal{Y}_{\ell,m_\ell} + r^{\ell-2}\frac{1}{\sin^2\theta}\left[\sin\theta \frac{\partial \sin\theta \frac{\partial \mathcal{Y}_{\ell,m_\ell}}{\partial \theta}}{\partial \theta} + \frac{\partial^2 \mathcal{Y}_{\ell,m_\ell}}{\partial \varphi^2}\right] = 0 \quad (2.7)$$

which, of course, upon cancelling common terms, gives

$$\ell(\ell+1)\mathcal{Y}_{\ell,m_\ell} + \frac{1}{\sin^2\theta}\left[\sin\theta \frac{\partial \sin\theta \frac{\partial \mathcal{Y}_{\ell,m_\ell}}{\partial \theta}}{\partial \theta} + \frac{\partial^2 \mathcal{Y}_{\ell,m_\ell}}{\partial \varphi^2}\right] = 0 \quad (2.8)$$

Laplace's Equation in Spherical Polar Coördinates on the unit sphere, i.e. Legendre's Equation!

III. INTERPRETING ATOMIC ORBITAL DESIGNATORS

What then are these angular solutions we found?

$$\begin{aligned} \ell &= 0; 1 \\ \ell &= 1; \sin\theta\cos\varphi \\ \ell &= 1; \sin\theta\sin\varphi \\ \ell &= 1; \cos\theta \\ \ell &= 2; \sin^2\theta\cos\varphi\sin\varphi \\ \ell &= 2; \sin\theta\cos\theta\cos\varphi \\ \ell &= 2; \sin\theta\cos\theta\sin\varphi \\ \ell &= 2; \left(\sin^2\theta\left[\cos^2\varphi - \sin^2\varphi\right]\right) \\ \ell &= 2; \left(1 - 3\cos^2\theta\right) \\ &\vdots \end{aligned} \quad (3.1)$$

and if you check back concerning their origin, you will see where the Hydrogenic Orbitals naming pattern comes from for s, p and d orbitals.

These functions have been written in "real" form, and they have "complex", (not complicated) forms which allow a different simplification:

$$\begin{aligned} 1s &\Leftrightarrow \ell = 0; 1 \\ 2p_x &\Leftrightarrow \ell = 1; \sin\theta\frac{e^{\imath\varphi} + e^{-\imath\varphi}}{2} \\ 2p_y &\Leftrightarrow \ell = 1; \sin\theta\left(\frac{e^{\imath\varphi} - e^{-\imath\varphi}}{2\imath}\right) \\ 2p_z &\Leftrightarrow \ell = 1; \cos\theta \\ 3d_{xy} &\Leftrightarrow \ell = 2; \sin^2\theta\left(\frac{e^{\imath\varphi} + e^{-\imath\varphi}}{2}\right)\left(\frac{e^{\imath\varphi} - e^{-\imath\varphi}}{2\imath}\right) \\ 3d_{xz} &\Leftrightarrow \ell = 2; \sin\theta\cos\theta\frac{e^{\imath\varphi} + e^{-\imath\varphi}}{2} \end{aligned}$$

$$
\begin{aligned}
3d_{yz} &\Leftrightarrow \ell = 2; \sin\theta\cos\theta\left(\frac{e^{\imath\varphi}-e^{-\imath\varphi}}{2\imath}\right)\\
3d_{x^2-y^2} &\Leftrightarrow \ell = 2; \left(\sin^2\theta\left[\left(\frac{e^{\imath\varphi}+e^{-\imath\varphi}}{2}\right)^2-\left(\frac{e^{\imath\varphi}-e^{-\imath\varphi}}{2\imath}\right)^2\right]\right)\\
3d_{z^2} &\Leftrightarrow \ell = 2; \left(1-3\cos^2\theta\right)\\
&\vdots
\end{aligned}
\tag{3.2}
$$

Once they have been written in imaginary form, we can create intelligent linear combinations of them which illuminate their underlying structure. Consider the linear combination of p_x and p_y, i.e., $2p_x + \imath 2p_y$ which becomes

$$\sin\theta e^{\imath\varphi}$$

aside from irrelevant constants. Next consider $2p_x - \imath 2p_y$ which becomes

$$\sin\theta e^{-\imath\varphi}$$

We have a trio of functions

$$
\begin{aligned}
2p_{m_\ell=-1} &= \sin\theta e^{-\imath\varphi}\\
2p_{m_\ell=0} &= \cos\theta \qquad (3.4)\\
2p_{m_\ell=+1} &= \sin\theta e^{+\imath\varphi} \qquad (3.3)
\end{aligned}
$$

which correspond to the m_ℓ values expected of p-orbitals.

You will see that the same "trick" can be applied to d_{xz} and d_{yz}.

Finally, the same trick, almost, can be applied to d_{xy} and $d_{x^2-y^2}$ with the $m_\ell = 0$ value reserved for d_{z^2}, all by itself.

IV. CONNECTION TO THE H-ATOM

Perhaps the next best place to introduce Spherical Harmonics and Legendre Polynomials is the Hydrogen Atom, since its eigenfunctions have angular components which are known to be Legendre Polynomials.

The Schrödinger Equation for the H-atom's electron is

$$-\frac{\hbar^2}{2m_e}\nabla^2|n,\ell,m_\ell> -\frac{Ze^2}{r}|n,\ell,m_\ell>= E_n|n,\ell,m_\ell> \tag{4.1}$$

We know that this equation is variable separable, in the sense that

$$|n,\ell,m_\ell>= R_{n,\ell}(r)\mathcal{Y}_{\ell,m_\ell}(\theta,\varphi)$$

Here, $R_{n,\ell}$ is the radial wave function, and $\mathcal{Y}_{\ell,m_\ell}$ is the angular wave function (a function of two variables), Since

$$\nabla^2 = \frac{1}{r^2}\frac{\partial r^2\frac{\partial}{\partial r}}{\partial r} + \frac{1}{r^2\sin^2\theta}\left[\sin\theta\frac{\partial\sin\theta\frac{\partial}{\partial\theta}}{\partial\theta} + \frac{\partial^2}{\partial\varphi^2}\right]$$

$$\nabla^2|n,\ell,m_\ell>= \nabla^2 R_{n,\ell}(r)\mathcal{Y}_{\ell,m_\ell}(\theta,\varphi) = \frac{\mathcal{Y}}{r^2}\frac{\partial r^2\frac{\partial R}{\partial r}}{\partial r} + \frac{R}{r^2\sin^2\theta}\left[\sin\theta\frac{\partial\sin\theta\frac{\partial\mathcal{Y}}{\partial\theta}}{\partial\theta} + \frac{\partial^2\mathcal{Y}}{\partial\varphi^2}\right]$$

which means that the Schrödinger Equation has the form

$$-\frac{\hbar^2}{2m_e}\left\{\frac{\mathcal{Y}}{r^2}\frac{\partial r^2\frac{\partial R}{\partial r}}{\partial r} + \frac{R}{r^2\sin^2\theta}\left[\sin\theta\frac{\partial\sin\theta\frac{\partial\mathcal{Y}}{\partial\theta}}{\partial\theta} + \frac{\partial^2\mathcal{Y}}{\partial\varphi^2}\right]\right\} - \frac{Ze^2}{r}R\mathcal{Y} = E_n R\mathcal{Y}$$

Dividing through by $R_{n,\ell}\mathcal{Y}_{\ell,m_\ell}$ (abreviated as $R\mathcal{Y}$) we have

$$-\frac{\hbar^2}{2m_e}\left\{\frac{1}{Rr^2}\frac{\partial r^2\frac{\partial R}{\partial r}}{\partial r} + \frac{1}{r^2\mathcal{Y}\sin^2\theta}\left[\sin\theta\frac{\partial\sin\theta\frac{\partial\mathcal{Y}}{\partial\theta}}{\partial\theta} + \frac{\partial^2\mathcal{Y}}{\partial\varphi^2}\right]\right\} - \frac{Ze^2}{r} = E_n$$

Multiplying through by r^2 shows that the expected variable separation has resulted in a proper segregation of the angles from the radius.

$$\frac{1}{R}\frac{\partial r^2\frac{\partial R}{\partial r}}{\partial r} + \underbrace{\frac{1}{\mathcal{Y}\sin^2\theta}\left[\sin\theta\frac{\partial\sin\theta\frac{\partial\mathcal{Y}}{\partial\theta}}{\partial\theta} + \frac{\partial^2\mathcal{Y}}{\partial\varphi^2}\right]} + \frac{2mZe^2r}{\hbar^2} = -\frac{2m}{\hbar^2}E_n r^2$$

We can see this by noting that the underbracketed part of this last equation is a pure function of angles, with no radius explicitly evident.

It is now standard to obtain (recover?) the equation (2.8)

$$\frac{1}{\mathcal{Y}\sin^2\theta}\left[\sin\theta\frac{\partial\sin\theta\frac{\partial\mathcal{Y}}{\partial\theta}}{\partial\theta}+\frac{\partial^2\mathcal{Y}}{\partial\varphi^2}\right]=-\ell(\ell+1) \tag{4.2}$$

where the minus sign (which is essentially arbitrary) is demanded by convention.

Cross multipilying by $\mathcal{Y}$, one has

$$\frac{1}{\sin^2\theta}\left[\sin\theta\frac{\partial\sin\theta\frac{\partial\mathcal{Y}}{\partial\theta}}{\partial\theta}+\frac{\partial^2\mathcal{Y}}{\partial\varphi^2}\right]=-\ell(\ell+1)\mathcal{Y} \tag{4.3}$$

which is written in traditional eigenfunction/eigenvalue form.

V. CHANGING THE ϑ VARIABLE

A change of variables can through this equation into a special form, which is sometimes illuminating. We write

$$\mu=\cos\theta$$

and

$$\frac{\partial\mu}{\partial\theta}=-\sin\theta=-\sqrt{1-\cos^2\theta}=-\sqrt{1-\mu^2}$$

so

$$\frac{\partial}{\partial\theta}=\left(\frac{\partial\mu}{\partial\theta}\right)\frac{\partial}{\partial\mu}$$

which is, substituting into Equation 4.3

$$\frac{\partial}{\partial\theta}=\left(-\sqrt{1-\mu^2}\right)\frac{\partial}{\partial\mu}$$

$$\frac{1}{(1-\mu^2)}\left[\sqrt{1-\mu^2}\sqrt{1-\mu^2}\frac{\partial\sqrt{1-\mu^2}\sqrt{1-\mu^2}\frac{\partial\mathcal{Y}}{\partial\mu}}{\partial\mu}+\frac{\partial^2\mathcal{Y}}{\partial\varphi^2}\right]=-\ell(\ell+1)\mathcal{Y} \tag{5.1}$$

where the $\ell(\ell+1)$ form is a different version of a constant, looking ahead to future results!

$$\left[\frac{\partial\left((1-\mu^2)\frac{\partial\mathcal{Y}}{\partial\mu}\right)}{\partial\mu}+\frac{\partial^2\mathcal{Y}}{\partial\varphi^2}\right]=-\ell(\ell+1)\mathcal{Y} \tag{5.2}$$

where

$$\mathcal{Y}_{\ell,m_\ell}(\theta,\varphi)=e^{\pm\imath m_\ell\varphi}S_{\ell,m_\ell}(\theta)$$

For $m_\ell=0$ we have

$$\left[\frac{\partial\left((1-\mu^2)\frac{\partial S_{\ell,0}}{\partial\mu}\right)}{\partial\mu}\right]=-\ell(\ell+1)S_{\ell,0} \tag{5.3}$$

which is Legendre's equation.

VI. SCHMIDT ORTHOGONALIZATION

We assume polynomials in μ^n and seek orthonormal combinations which can be generated starting with a constant (n=0) term. Then the normalization integral

$$<0|0>=\int_{+1}^{-1}\psi_0^2d\mu=1$$

[1] implies that

$$|0>=\sqrt{\frac{1}{2}}$$

We now seek a function $|1>$ orthogonal to $|0>$ which itself is normalizeable. We have

$$<1|0>=\int_{+1}^{-1}\psi_1\sqrt{\frac{1}{2}}d\mu=0$$

which has solution $\psi_1=N_1x$. Normalizing, we have

$$<1|1>=\int_{+1}^{-1}\psi_1^2d\mu=1=\int_{+1}^{-1}N_1^2\mu^2d\mu$$

which yields

$$1=N_1^2\frac{2}{3}$$

i.e.,

$$|1>=\sqrt{\frac{3}{2}}x$$

To proceed, we need to generate a function $|2>$ which is not only normalizeable but orthogonal to $|0>$ and $|1>$.

$$<2|0>=\int_{+1}^{-1}\psi_2\sqrt{\frac{1}{2}}d\mu=0$$

and

$$<2|1>=\int_{+1}^{-1}\psi_2\sqrt{\frac{2}{3}}\mu d\mu=0$$

where $|2>$ is a polynomial of order 2 in μ, i.e.,

$$\psi_2=|2>=a\mu^2+b$$

Substituting, we have

$$<2|0>=\int_{+1}^{-1}(a\mu^2+b)\sqrt{\frac{1}{2}}d\mu=0$$

and

$$<2|1>=\int_{+1}^{-1}(a\mu^2+b)\sqrt{\frac{3}{2}}\mu d\mu=0$$

We obtain two equations in two unknowns, a and b,

$$\sqrt{\frac{1}{2}}\left(\frac{2a}{3}+2b\right)=0$$

and the other integral vanishes automatically. i.e.,

$$\frac{a}{3}+b=0$$

i.e., $a=-3b$ so

$$|2>=-3b\mu^2+b=b(-3\mu^2+1)$$

in unnormalized form. Normalizing gives

$$<2|2>=\int_{+1}^{-1}(-3b\mu^2+b)^2d\mu=1$$

i.e.,

$$<2|2>=b^2\int_{+1}^{-1}(-3\mu^2+1)^2d\mu=1$$

which gives

$$b=\sqrt{\frac{1}{\int_{+1}^{-1}(-3\mu^2+1)^2d\mu}}$$

where, of course, we recognize the sign ambiguity in this result.

One can continue forever with this Schmidt Orthogonalization, but the idea is clear, and there are better ways, so why continue?

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[1] The limits correspond to $\theta=0$ to $\theta=\pi$