The Factorization Method and Its Applications in Quantum Chemistry

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Quantum chemistry today forms an integral part of all undergraduate curricula in chemistry. In order to acquire a workable knowledge of this subject which is essential in all fields related to molecular structure, spectra, and bonding, one should be fairly well acquainted with the techniques of solving certain second-order differential eigenvalue equations. The traditional method of solution by power series expansion involves complex mathematics to such an extent that an undergraduate student wishing to learn the technique, often starts developing a sort of fear complex toward quantum chemistry. This unhappy situation can be greatly averted by taking recourse to the factorization method which leads directly to the eigenvalues and a manufacturing process for the normalized eigenfunctions without tedious mathematical manipulations.

The factorization method was introduced by Schrodinger (*1*) about four decades ago. Since then his ideas have been generalized considerably in a number of sophisticated research papers (*2–5*). But curiously enough, this method as such has not yet been recognized as a textbook technique for the solution of quantum mechanical eigenvalue problems. An equivalent approach, called the ladder operator method, introduced by Dirac (*6*) has been followed in some quantum chemistry textbooks (*7, 8*) for the treatment of harmonic oscillator and angular momentum problems. But the great potential of the factorization method is not fully exposed by such treatments.

So far only two pedagogic articles, one by Salsburg (*9*) and the other by Peterson (*10*) have appeared on this subject. Salsburg, in his article, has shown how to factorize the radial equation of the hydrogen atom to obtain its eigenvalues and radial wavefunctions. Taking the same example, a comparison of this technique with the power series method has been carried out by Peterson. One very important aspect of the factorization method, namely, the simultaneous normalization of the eigenfunctions during their manufacturing process, has been overlooked in both the articles. Instead of demonstrating the usefulness of the factorization method to individual problems, it is more desirable to present its methodology to the reader, who himself can then explore its scope of application. The present article has been written with a view to meeting such an important pedagogic need.

Our treatment is based essentially on the works of Infeld (*2*), and Infeld and Hull (*5*). The theory of the factorization method is developed at first and then applied to solve some basic undergraduate problems.

Theory of the Factorization Method

To illustrate the basic idea of the factorization method, let us consider the following differential equation

$$\left(x^2 - \frac{d^2}{dx^2}\right) y = \lambda y \tag{1}$$

If we define a pair of operations, $R_\pm$, by

$$R_\pm = x \pm \frac{d}{dx}$$

then it is a simple matter to verify that eqn. (1) can be written in either of the following "factorized" forms

$$R_+R_-y = (\lambda + 1)y \tag{2}$$

$$R_-R_+y = (\lambda - 1)y \tag{3}$$

Thus if y be an eigenfunction of eqn. (1) with the eigenvalue λ, then it is also an eigenfunction of $R_\pm R_\mp$ with eigenvalues $(\lambda \pm 1)$. Left-multiplying eqn. (2) by R_- and (3) by R_+, we get

$$R_-R_+(R_-y) = (\lambda + 1)(R_-y) \tag{4}$$

$$R_+R_-(R_+y) = (\lambda - 1)(R_+y) \tag{5}$$

Now comparing eqn. (5) with eqn. (2), and eqn. (4) with eqn. (3), we see that $R_\pm y$ are also eigenfunctions of $R_\pm R_\mp$ with eigenvalues respectively decreased and increased by 2. Thus, we can write

$$R_+y_\lambda \sim y_{\lambda-2} \tag{6}$$

$$R_-y_\lambda \sim y_{\lambda+2} \tag{7}$$

where a suffix on y identifies the eigenfunction with respect to the eigenvalue. It is well-known that the operators R_+ and R_- are called a lowering and a raising operator, respectively. If we can find the minimum or the maximum value of λ corresponding to the bottom or the top of the eigenvalue ladder from some other consideration (this will be discussed fully later in this section), then we can write

$$R_+y_{\lambda\min} = 0 \tag{8}$$

or

$$R_-y_{\lambda\max} = 0 \tag{9}$$

These equations indicate that there is no solution with the eigenvalue $\lambda > \lambda_{max}$ and $\lambda < \lambda_{min}$. Once $y_{\lambda min}$ or $y_{\lambda max}$ is obtained by quadrature of the first-order differential eqn. (8) or (9), the rest can be found by the successive application of R_- or R_+.

The above discussion of the factorization method is of a very elementary nature. It does not lead us to the normalized eigenfunctions nor suggest any recipe for the determination of λ_{max} or λ_{min}. Moreover, a problem with degenerate eigenvalues cannot be represented by eqn. (1) which contains no parameter other than λ. To include all these aspects we now consider a general second order differential equation of the form

$$\frac{d^2y(\lambda,m)}{dx^2} + r(x,m)y(\lambda,m) + \lambda y(\lambda,m) = 0 \tag{10}$$

Here (x,m) is a real function of x, and characterizes the given problem. We shall assume that m takes up different discrete values like m_0, $m_0 + 1$, $m_0 + 2$, . . . etc., where m_0 is zero or a constant. Thus (x,m) depends parametrically on m. By the notation $y(\lambda,m)$ we identify different solutions corresponding to the same λ but to different m's. The dependence of y on x has been suppressed here. In order to solve eqn. (10), we shall assume that it is possible to write it in *each* of the following factorized forms (cf. eqn. (2) and (3)):

$$D_+{}^{m+1}D_-{}^{m+1}y(\lambda,m) = [\lambda - L(m+1)]y(\lambda,m) \tag{11}$$

$$D_-{}^{m}D_+{}^{m}y(\lambda,m) = [\lambda - L(m)]y(\lambda,m) \tag{12}$$

where

$$D_\pm{}^{m} = k(x,m) \pm \frac{d}{dx} \tag{13}$$

and $L(m)$ is a function of m. In eqn. (13) $k(x,m)$ is a function

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of x depending parametrically on m. From a given expression of $r(x,m)$, $k(x,m)$ and $L(m)$ can be obtained as follows

Expanding eqn. (11), we get

$$[k^2(x,m+1) + k'(x,m+1) + L(m+1)]y(\lambda,m) = \frac{d^2y(\lambda,m)}{dx^2} + \lambda y(\lambda,m)$$

which on comparison with eqn. (10) yields

$$k^2(x,m+1) + k'(x,m+1) + L(m+1) = -r(x,m) \quad (14)$$

Replacing m by $m-1$, we obtain from eqn. (14)

$$k^2(x,m) + k'(x,m) + L(m) = -r(x,m-1) \quad (15)$$

Similarly from eqn. (12) we get

$$k^2(x,m) - k'(x,m) + L(m) = -r(x,m) \quad (16)$$

Adding eqns. (15) and (16), we obtain

$$k^2(x,m) + L(m) = -\frac{1}{2}[r(x,m) + r(x,m-1)] \quad (17)$$

which on differentiation with respect to x gives

$$2k(x,m)\,k'(x,m) = -\frac{1}{2}[r'(x,m) + r'(x,m-1)] \quad (18)$$

Again, subtracting eqn. (16) from (15), we get

$$k'(x,m) = \frac{1}{2}[r(x,m) - r(x,m-1)] \quad (19)$$

which on substitution into eqn. (18) gives

$$k(x,m) = \frac{1}{2}[r(x,m-1) - r(x,m)]^{-1}[r'(x,m) + r'(x,m-1)] \quad (20)$$

From a knowledge of $k(x,m)$ and using eqn. (17), we now obtain

$$L(m) = -\frac{1}{2}[r(x,m) + r(x,m-1)] - k^2(x,m) \quad (21)$$

Hence the criteria that the assumed factorization is possible are that $k(x,m)$ be given by eqn. (20) and $L(m)$ by eqn. (21). Of course, $L(m)$ determined in this way must be independent of x, as assumed earlier.

To proceed further we shall make use of the four theorems described in the following sections.

Theorem I

$D_{\pm}{}^m$ are mutually adjoint.

Proof: To prove this theorem we will have to show that

$$\langle D_-{}^m\phi_1|\phi_2\rangle = \langle\phi_1|D_+{}^m|\phi_2\rangle,$$

where ϕ_1 and ϕ_2 are well-behaved functions of x. Now,

$$\begin{aligned}\langle D_-{}^m\phi_1|\phi_2\rangle &= \int_a^b \left[k(x,m) - \frac{d}{dx}\right]{}^*\phi_1{}^*\phi_s\,dx \\ &= \int_a^b k(x,m)\phi_1{}^*\phi_2\,dx - \int_a^b \frac{d\phi_1{}^*}{dx}\phi_2\,dx \\ &= \int_a^b k(x,m)\phi_1{}^*\phi_2\,dx - [\phi_1{}^*\phi_2]_a^b + \int_a^b \frac{d\phi_s}{dx}\phi_1{}^*\,dx \\ &= \int_a^b k(x,m)\phi_1{}^*\phi_2\,dx + \int_a^b \frac{d\phi_2}{dx}\phi_1{}^*\,dx \\ &= \left\langle\phi_1\left|k(x,m) + \frac{d}{dx}\right|\phi_2\right\rangle \\ &= \langle\phi_1|D_+{}^m|\phi_2\rangle\end{aligned}$$

Theorem II

If $y(\lambda,m)$ be a solution of eqn. (10) then $D_-{}^{m+1}y(\lambda,m)$ and $D_+{}^m y(\lambda,m)$ are also its solutions.

Proof: Left-multiplying eqn. (11) by $D_-{}^{m+1}$ and (12) by $D_+{}^m$, we get

$$D_-{}^{m+1}D_+{}^{m+1}[D_-{}^{m+1}y(\lambda,m)] = [\lambda - L(m+1)][D_-{}^{m+1}y(\lambda,m)] \quad (22)$$

$$D_+{}^m D_-{}^m[D_+{}^m y(\lambda,m)] = [\lambda - L(m)][D_+{}^m y(\lambda,m)] \quad (23)$$

Comparison of eqns. (22) and (12), and of eqns. (23) and (11) reveals that $D_-{}^{m+1}y(\lambda,m)$ and $D_+{}^m y(\lambda,m)$ are solutions of eqn. (10) corresponding to the same λ, but m is now replaced by $m+1$ and $m-1$, respectively. Analogous to eqns. (6) and (7) we can now write

$$D_-{}^{m+1}y(\lambda,m) \sim y(\lambda,m+1) \quad (24)$$

$$D_+{}^m y(\lambda,m) \sim y(\lambda,m-1) \quad (25)$$

By these two transformations we can generate all the eigenfunctions corresponding to the same λ but to different m's.

In quantum mechanics we are interested in obtaining eigenfunctions which are quadratically integrable. Otherwise, we cannot have the probabilistic interpretation of the wavefunction. The factorization method will, therefore, be of practical utility only when the functions generated by the application of $D_-{}^{m+1}$ or $D_+{}^m$ operators on a quadratically integrable function will be quadratically integrable as well. As we shall show below, this important requirement will restrict the value of m by the value of λ, and eventually leads to the eigenvalue λ. At this point we note that there may be two classes of problems, viz., class I and class II. In the former $L(m)$ is an increasing function of m, and in the latter it is a decreasing function. In order to establish the condition for quadratically integrability we prove below two other theorems.

Theorem IIIA

When $L(m)$ is an increasing function of m, then the necessary condition that $D_-{}^{m+1}$ will produce a quadratically integrable function from another such function is that

$$\lambda = \lambda_l = L(l+1)$$

where l is an integer and $m = 0, 1, 2, \ldots, l$.

Proof: Let $y(\lambda,m)$ be a quadratically integrable function, i.e. $\langle y(\lambda,m)|y(\lambda,m)\rangle \geq 0$. Then from eqns. (11) and (24), we get

$$\begin{aligned}\langle y(\lambda,m+1)|y(\lambda,m+1)\rangle &= \langle D_-{}^{m+1}y(\lambda,m)|D_-{}^{m+1}y(\lambda,m)\rangle \\ &= \langle y(\lambda,m)|D_+{}^{m+1}D_-{}^{m+1}|y(\lambda,m)\rangle \\ &= [\lambda - L(m+1)]\langle y(\lambda,m)|y(\lambda,m)\rangle \\ &\geq 0, \text{ if } \lambda \geq L(m+1)\end{aligned}$$

Similarly,

$$\begin{aligned}&\langle y(\lambda,m+2)|y(\lambda,m+2)\rangle \\ &\quad = [\lambda - L(m+2)][\lambda - L(m+1)]\langle y(\lambda,m)|y(\lambda,m)\rangle \\ &\quad \geq 0, \text{ if } \lambda \geq L(m+2).\end{aligned}$$

This process can be continued for $m+3$, $m+4$, and so on. But since $L(m)$ is an increasing function of m, the value of $\lambda - L(m)$ will gradually decrease (note that λ is fixed), and for some value of m, say $l+1$, we may have the contradiction

$$\langle y(\lambda,l+1)|y(\lambda,l+1)\rangle < 0$$

unless

$$y(\lambda,l+1) = 0$$

or

$$D_-{}^{l+1}y(\lambda,l) = 0 \quad (26)$$

Hence by virtue of eqn. (11), we have

$$\lambda_l + L(l+1)$$

where l is an integer, and $m = 0, 1, 2, \ldots . l$.

Theorem IIIB

When $L(m)$ is a decreasing function of m, the necessary condition that $D_+{}^m$ will produce a quadratically integrable function from another such function is that

$$\lambda_l = L(l)$$

where $m = l, l+1, l+2, \ldots\ldots$

Proof: Let $y(\lambda,m)$ be a quadratically integrable function. Then proceeding as for class I problems and making use of eqns. (12) and (25), we have

$$\langle y(\lambda,m-1)|y(\lambda,m-1)\rangle = [\lambda - \mathrm{L}(m)]\langle y(\lambda,m)|y(\lambda,m)\rangle \geq 0, \text{ if } \lambda \geq \mathrm{L}(m).$$

Continuing this process we shall reach a value of m, say l, for which $\lambda < \mathrm{L}(l)$, since $\mathrm{L}(m)$ is a decreasing function of m. This gives rise to the contradiction

$$\langle y(\lambda,l-1)|y(\lambda,l-1)\rangle < 0$$

unless

$$y(\lambda,l-1) = D_+{}^l y(\lambda,l) = 0 \tag{27}$$

Hence by virtue of eqn. (12), we have

$$\lambda_l = \mathrm{L}(l)$$

where

$$m = l, l+1, l+2, \ldots\ldots$$

If $m_0 \neq 0$, then theorems IIIA and IIIB warrant that $|l-m|$ rather than l be an integer. It can be seen also that for class I problems we have a finite number of solutions $y(\lambda,0), y(\lambda,1), \ldots. y(\lambda,l)$, but for class II problems we obtain an infinite number of solutions, $y(\lambda,l), y(\lambda,l+1), y(\lambda,l+2), \ldots.$

We shall now show how the eigenfunctions can be generated in their normalized form. It is obvious that once the starting or the key function is obtained by solving eqn. (26) or (27), then whole spectrum of eigenfunctions can be generated by making use of eqn. (25) or (24). The eigenfunctions thus generated are, however, not normalized. For example,

$$\langle y(\lambda,m+1)|y(\lambda,m+1)\rangle = [\lambda - \mathrm{L}(m+1)]\langle y(\lambda,m)|y(\lambda,m)\rangle$$

and

$$\langle y(\lambda,m-1)|y(\lambda,m-1)\rangle = [\lambda - \mathrm{L}(m)]\langle y(\lambda,m)|y(\lambda,m)\rangle$$

Thus even if $y(\lambda,m)$ is normalized to unity, $y(\lambda,m \pm 1)$ are not. The normalization constants for these functions are $[\lambda - \mathrm{L}(m+1)]^{-1/2}$ and $[\lambda - \mathrm{L}(m)]^{-1/2}$, respectively. If we, therefore, define two operators ${}_lD_\pm{}^m$ by

$${}_lD_\pm{}^m = \begin{cases} [\mathrm{L}(l+1) - \mathrm{L}(m)]^{-1/2} D_\pm{}^m & \text{for class I problems,} \\ [\mathrm{L}(l) - \mathrm{L}(m)]^{-1/2} D_\pm{}^m & \text{for class II problems,} \end{cases}$$

and modify eqns. (24) and (25), respectively as

$${}_lD_-{}^{m+1} y(l,m) = y(l,m+1) \tag{28}$$

$${}_lD_+{}^m y(l,m) = y(l,m-1) \tag{29}$$

then it is easy to verify that if $y(l,m)$ is a normalized function, so also are $y(l,m \pm 1)$. For class I problems, for instance,

$$\begin{aligned} &\langle y(l,m+1)|y(l,m+1)\rangle \\ &= \langle {}_lD_-{}^{m+1} y(l,m)|{}_lD_+{}^{m+1} y(l,m)\rangle \\ &= [\mathrm{L}(l+1) - \mathrm{L}(m+1)]^{-1}\langle y(l,m)|D_+{}^{m+1} D_-{}^{m+1}|y(l,m)\rangle \\ &= [\mathrm{L}(l+1) - \mathrm{L}(m+1)^{-1}[\mathrm{L}(l+1) - \mathrm{L}(m+1)]\langle y(l,m)|y(l,m)\rangle \\ &= 1 \end{aligned}$$

The case of class II problems can be proved similarly.

Having described the essential features of the factorization method, we now summarize its working steps.

1) Transform the equation at hand into the standard form (10) by a suitable substitution. All equations of the form

$$\frac{\mathrm{d}}{\mathrm{d}\varphi}\left(p\frac{\mathrm{d}P}{\mathrm{d}\varphi}\right) + \mathrm{q}P + \lambda\rho P = 0$$

where p and ρ are never negative, and ρ/p exists everywhere, can be transformed (11) into the standard form by the substitution

$$y = (p\rho)^{1/4} P$$

2) Evaluate $k(x,m)$ and $\mathrm{L}(m)$ using eqns. (20) and (21), respectively.

3) Identify the class of the problem and determine the eigenvalue.

4) Define ${}_lD_\pm{}^m$

5) Solve $D_-{}^{l+1} y(l,l) = 0$ for class I problems, and $D_+{}^l y(l,l) = 0$ for class II problems to obtain the starting function $y(l,l)$ in an unnormalized form.

6) Normalize $y(l,l)$ and obtain the eigenfunction spectrum by means of eqn. (28) or (29) depending on the class of the problem. More explicitly, the normalized eigenfunctions for class I and II problems are given respectively by

$$y(l,m-1) = {}_lD_+{}^m y(l,m) = [\mathrm{L}(l+1) - \mathrm{L}(m)]^{-1/2} D_+{}^m y(l,m) \tag{30}$$

$$y(l,m+1) = {}_lD_-{}^{m+1} y(l,m) = [\mathrm{L}(l) - \mathrm{L}(m+1)^{-1/2} D_-{}^{m+1} y(l,m) \tag{31}$$

Applications

In this section we have applied the factorization method to solve the Schrodinger equation for the hydrogen atom, a linear harmonic oscillator and the Morse oscillator.

The Hydrogen Atom

The Schrodinger equation for hydrogen-like one electron systems is given by

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{r}\right)\psi = 0 \tag{32}$$

To solve this equation we start by the usual technique of separation of variables. Letting

$$\psi = R(r)T(\theta)f(\phi) = RTf \tag{33}$$

and substituting eqn. (33) into eqn. (32), we obtain the following three equations for the three variables

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \left[\frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{r}\right) - \frac{\lambda^1}{r^2}\right]R = 0 \tag{34}$$

$$\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}T}{\mathrm{d}\theta}\right) - \frac{m^2 T}{\sin^2\theta} + \lambda^1 T = 0 \tag{35}$$

$$\frac{\mathrm{d}^2 f}{\mathrm{d}\phi^2} + m^2 f = 0 \tag{36}$$

where λ^1 and m^2 are constants of separation.

We shall solve these equations in the reverse order. The normalized solution of eqn. (36) is given by

$$f = \frac{1}{\sqrt{2\pi}}\exp(im\phi) \tag{37}$$

where the periodic boundary condition of f warrants that $m = 0, \pm1, \pm2, \ldots.$

We now turn our attention to eqn. (35). To bring it to the standard form we make the substitution

$$Y = \sqrt{\sin\theta}\, T \tag{38}$$

to obtain

$$\frac{\mathrm{d}^2 Y}{\mathrm{d}\theta^2} - \frac{\left(m^2 - \frac{1}{4}\right)}{\sin^2\theta}Y + \left(\lambda^1 + \frac{1}{4}\right)Y = 0 \tag{39}$$

Comparing eqns. (39) and (10), we find

$$r(\theta,m) = -\left(m^2 - \frac{1}{4}\right)\Big/\sin^2\theta$$

$$\lambda = \lambda^1 + \frac{1}{4}$$

Hence by virtue of relations (20) and (21)

$$k(\theta,m) = \left(m - \frac{1}{2}\right)\cot\theta$$

$$\mathrm{L}(m) = \left(m - \frac{1}{2}\right)^2$$

Since L(m) is an increasing function of m, it is a class I problem. The eigenvalues are given by

$$\lambda^1 + \frac{1}{4} = \mathrm{L}(l+1) = \left(l + \frac{1}{2}\right)^2$$

or

$$\lambda^1 = l(l+1) \tag{40}$$

where $l = 0, 1, 2, \ldots \geq m$.
The operators, ${}_lD_\pm{}^m$ are given by

$${}_lD_\pm{}^m = [\mathrm{L}(l+1) - \mathrm{L}(m)]^{-1/2} D_\pm{}^m$$

$$= [\mathrm{L}(l+1) - m(m-1)]^{-1/2} \left[\left(m - \frac{1}{2}\right)\cot\theta \pm \frac{\mathrm{d}}{\mathrm{d}\theta}\right]$$

The starting function $Y_{l,l}$ is obtained by solving

$$D_-{}^{l+1} Y_{l,l} = 0$$

or

$$\left[\left(l + \frac{1}{2}\right)\cot\theta - \frac{\mathrm{d}}{\mathrm{d}\theta}\right] Y_{l,l} = 0$$

Integration of this equation yields

$$Y_{l,l} = A \sin^{l+1/2}\theta$$

where A is the normalization constant and can be found by requiring

$$A^2 \int_0^\pi \sin^{2l+1}\theta \, \mathrm{d}\theta = 1 \tag{41}$$

Integrating eqn. (41) l times by parts, we get

$$A = \left(\frac{1.3.5 \ldots (2l+1)}{2.2.4.6 \ldots 2l}\right)^{1/2} = \left[\frac{(2l+1)!}{2}\right]^{1/2} \frac{1}{2^l l!}$$

Thus

$$Y_{l,l} = \left[\frac{(2l+1)!}{2}\right]^{1/2} \frac{1}{2^l l!} \sin^{l+1/2}\theta \tag{42}$$

and

$$Y_{l,m\mp1} = [\mathrm{L}(l+1) - m(m \mp 1)]^{-1/2} \times \left[\left(m \mp \frac{1}{2}\right)\cot\theta \pm \frac{\mathrm{d}}{\mathrm{d}\theta}\right] Y_{l,m} \tag{43}$$

Though in eqn. (37) m can be both positive and negative integers leading to different values of f, the Y function will be the same for the pair $\pm m$ because m appears as a squared term in eqn. (39).

Now we solve the radial equation, viz., eqn. (34). Substituting $\lambda^1 = l(l+1)$, and $g(r) = rR$ in this equation we obtain after a little rearrangement

$$\frac{\mathrm{d}^2 g}{\mathrm{d}r^2} + \left[\frac{8\pi^2\mu Z e^2}{h^2 r} - \frac{l(l+1)}{r^2}\right] g + \frac{8\pi^2\mu E}{h^2} g = 0$$

or

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \left[\frac{\vartheta}{r} - \frac{l(l+1)}{r^2}\right] g + \lambda g = 0 \tag{44}$$

where

$$\vartheta = \frac{8\pi^2\mu Z e^2}{h^2} \quad \text{and} \quad \lambda = \frac{8\pi^2\mu E}{h^2}$$

Comparing eqn. (44) with (10), we find that (m is now replaced by l, x by r, and r by p)

$$p(r,l) = \frac{\vartheta}{r} - \frac{l(l+1)}{r^2}$$

Therefore,

$$k(r,l) = \frac{l}{r} - \frac{\vartheta}{2l}$$

$$\mathrm{L}(l) = -\vartheta^2/4l^2$$

Thus L(l) is an increasing function of l, and consequently

$$\lambda = \mathrm{L}(l_{\max+1}) = \frac{-\vartheta^2}{4(l_{\max+1})^2}$$

where $l = 0, 1, 2, \ldots \leq l_{\max}$
Then from the relation

$$\lambda = 8\pi^2\mu E/h^2$$

we have

$$E = \frac{2\mu\pi^2 Z^2 e^4}{h^2 (l_{\max+1})^2} = -\frac{2\pi^2\mu Z^2 e^4}{n^2 h^2} \tag{45}$$

where $n = l_{\max+1}$.

In this case, the operators ${}_nD_\pm{}^l$ are given by

$${}_nD_\pm{}^l = [\mathrm{L}(n) - \mathrm{L}(l)]^{-1/2} \left[\frac{l}{r} - \frac{\vartheta}{2l} \pm \frac{\mathrm{d}}{\mathrm{d}r}\right]$$

$$= \frac{2nl}{\vartheta} [(n+l)(n-l)]^{-1/2} \left[\frac{l}{r} - \frac{\vartheta}{2l} \pm \frac{\mathrm{d}}{\mathrm{d}r}\right] \tag{46}$$

The solution corresponding to $l = l_{\max} = n - 1$ is obtained from the relation

$$D_-{}^n g_{n,n-1} = 0$$

or

$$\left[\frac{n}{r} - \frac{\vartheta}{2n} - \frac{\mathrm{d}}{\mathrm{d}r}\right] g_{n,n-1} = 0$$

which on integration gives

$$g_{n,n-1} = A r^n \exp(-\vartheta r/2n)$$

The constant A is determined from the normalization condition

$$A^2 \int_0^\infty r^{2n} \exp(-\vartheta r/n) \mathrm{d}r = 1$$

Making use of the standard integral

$$\int_0^\infty r^n \exp(-ar) \mathrm{d}r = \frac{n!}{a^{n+1}}$$

we obtain

$$g_{n,n-1} = \left(\frac{\vartheta}{n}\right)^{n+1/2} [(2n)!]^{-1/2} r^n \exp\left(-\frac{\vartheta r}{2n}\right) \tag{47}$$

The other solutions are obtained using the relations

$$g_{n,l} = {}_nD_-{}^l g_{n,l-1} \tag{48}$$

$$g_{n,l-1} = {}_nD_-{}^l g_{n,l} \tag{49}$$

In order to convince ourselves that the above procedure does generate the familiar hydrogenic orbitals we now find the explicit solution for $n = 3$.

Using eqn. (47) we get

$$g_{3,2} = \left(\frac{\vartheta}{3}\right)^{7/2} (6!)^{-1/2} r^3 \exp(-\vartheta r/6)$$

Recalling that

$$\vartheta = \frac{g\pi^2\mu Z e^2}{h^2} = \frac{2Z}{a_0}$$

where a_0 is the first Bohr radius, we have

$$g_{3,2} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{4}{81\sqrt{30}} \left(\frac{Zr}{a_0}\right)^2 r \exp\left(-\frac{Zr}{3a_0}\right)$$

Then

$$g_{3,1} = {}_3D_+{}^2 g_{3,2}$$

$$= \frac{2.3.2}{\vartheta} (5)^{-1/2} \left[\frac{2}{r} - \frac{\vartheta}{4} + \frac{\mathrm{d}}{\mathrm{d}r}\right] g_{3,2}$$

$$= \left(\frac{Z}{a_0}\right)^{3/2} \frac{4}{81\sqrt{6}} \left(6 - \frac{Zr}{a_0}\right) \left(\frac{Zr^2}{a_0}\right) \exp\left(-\frac{Zr}{3a_0}\right)$$

and

$$g_{3,0} = {}_3D_+{}^1 g_{3,1}$$

$$= \frac{2.3.1}{\theta} (8)^{-1/2} \left[\frac{1}{r} - \frac{\theta}{2} + \frac{\mathrm{d}}{\mathrm{d}r}\right] g_{3,1}$$

$$= \left(\frac{Z}{a_0}\right)^{3/2} \frac{2}{81\sqrt{3}} \left[27 - 18\left(\frac{Zr}{a_0}\right) + 2\left(\frac{Zr}{a_0}\right)^2\right] r \exp\left(-\frac{Zr}{3a_0}\right)$$

Since $g = rR$, the radial solutions corresponding to the $3d$, $3p$, and $3s$ hydrogen orbitals are given respectively by

$$R_{3,2} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{4}{81\sqrt{30}} \sigma^2 \exp(-\sigma/3)$$

$$R_{3,1} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{4}{81\sqrt{6}} (6 - \sigma)\sigma \exp(-\sigma/3)$$

$$R_{3,0} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{2}{81\sqrt{3}} (27 - 18\sigma + 2\sigma^2) \exp\left(-\frac{\sigma}{3}\right)$$

where

$$\sigma = \frac{zr}{a_0}$$

We now direct out attention to the $T(\theta)$ part of the solution. From eqns. (42) and (43), we have

$$Y_{2,2} = \frac{\sqrt{15}}{4} \sin^{5/2}\theta$$

$$Y_{2,1} = {}_2D_+{}^2Y_{2,2} = (4)^{-1/2}\left[\frac{3}{2}\cot\theta + \frac{\mathrm{d}}{\mathrm{d}\theta}\right] Y_{2,2}$$

$$= \frac{\sqrt{15}}{2} \sin^{3/2}\theta \cos\theta$$

$$Y_{2,0} = {}_2D_+{}^1Y_{2,1} = (6)^{-1/2}\left[\frac{1}{2}\cot\theta + \frac{\mathrm{d}}{\mathrm{d}\theta}\right] Y_{2,1}$$

$$= \frac{\sqrt{10}}{4} (3\cos^2\theta - 1) \sin^{1/2}\theta$$

Thus,

$$T_{2,\pm2} = \frac{\sqrt{15}}{4} \sin^2\theta$$

$$T_{2,\pm1} = \frac{\sqrt{15}}{2} \sin\theta\cos\theta$$

$$T_{2,0} = \frac{\sqrt{10}}{4} (3\cos^2\theta - 1)$$

The $f(\phi)$ part of the solution is as given by eqn. (37) where $m = 0, \pm1, \pm2$.

It is interesting to note that once the quantum number m is introduced in the problem, the other quantum numbers appear in a quite natural manner via the quadratically integrability condition of the problem.

A Linear Harmonic Oscillator

The Schrodinger equation for a linear harmonic oscillator is given by

$$-\frac{h^2}{8\pi^2\mu}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{k}{2}x^2\psi - E\psi = 0 \tag{50}$$

where μ is the reduced mass, and k is the force constant of the oscillator. Substituting $k = 4\pi^2\mu\nu^2$, where ν is the frequency of oscillation, in eqn. (50) we get

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - \alpha^2x^2\psi + \lambda\psi = 0 \tag{51}$$

where

$$\alpha = \frac{4\pi^2\mu\nu}{h}$$

and

$$\lambda = \frac{8\pi^2\mu E}{h^2}$$

Letting $X = \sqrt{\alpha}\,x$ and $\lambda' = \lambda/\alpha$, eqn. (51) can be reduced to the following dimensionless form

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}X^2} - X^2\psi + \lambda'\psi = 0 \tag{52}$$

which is identical to eqn. (1). It may be noted that m does not appear in eqn. (52). The factorization method, as has been developed in the last section, cannot therefore be applied as such. Infeld (2) has solved this equation by introducing m artificially and then following the general approach. In contrast to the H-atom problem where m appears automatically as a logical consequence of the solution, one has to assume here that m can take up only positive discrete values. In order to avoid this forced assumption, we shall solve this equation in a slightly different manner.

Since eqn. (52) is identical with eqn. (1), we can write

$$R_+R_-\psi_{\lambda'} = (\lambda' + 1)\psi_{\lambda'} \tag{53}$$

$$R_-R_+\psi_{\lambda'} = (\lambda' - 1)\psi_{\lambda'} \tag{54}$$

and analogous to eqns. (6) and (7)

$$R_+\psi_{\lambda'} \approx \psi_{\lambda'-2} \tag{55}$$

$$R_-\psi_{\lambda'} \approx \psi_{\lambda'+2} \tag{56}$$

To obtain the eigenvalues we investigate the conditions for quadratically integrability of $\psi_{\lambda'}$. Supposing $\langle\psi_{\lambda'}|\psi_{\lambda'}\rangle \geq 0$, we have from eqns. (54) and (55)

$$\langle\psi_{\lambda'-2}|\psi_{\lambda'-2}\rangle = (\lambda' - 1)\langle\psi_{\lambda'}|\psi_{\lambda'}\rangle$$

Similarly,

$$\langle\psi_{\lambda'-4}|\psi_{\lambda'-4}\rangle = (\lambda' - 3)(\lambda' - 1)\langle\psi_{\lambda'}|\psi_{\lambda'}\rangle$$

and so on.

Thus in this lowering process, the condition for quadratically integrability of $\psi_{\lambda'-(2N+2)}$ is

$$\{\lambda' - (2N + 1)\} \geq 0 \tag{57}$$

where $N = 0, 1, 2$, etc. Similarly for the raising process, the condition for quadratically integrability of $\psi_{\lambda'+(2N+1)}$ is

$$\{\lambda' + (2N + 1)\} \geq 0 \tag{58}$$

The minimum value of λ' which satisfies both the conditions is 1. Since λ''s are changing by 2, we have

$$\lambda' = 2N + 1 \tag{59}$$

Now, since $\lambda = \lambda'\alpha = 8\pi^2\mu E/h^2$ we have

$$E = \left(N + \frac{1}{2}\right) h\nu$$

Since there is no state below ψ_1, we can write

$$R_+\psi_1 = \left(X + \frac{\mathrm{d}}{\mathrm{d}X}\right)\psi_1 = 0$$

or

$$\psi_1 = A \exp(-X^2/2)$$

where the normalization constant A is found from the condition

$$\int_{-\infty}^{+\infty} \psi_1{}^2\mathrm{d}X = A^2 \int_{-\infty}^{\infty} \exp(-X^2)\mathrm{d}X = 1$$

or

$$A = \left(\frac{1}{\pi}\right)^{1/4}$$

If we assume that $\langle\psi_{\lambda'}|\psi_{\lambda'}\rangle = 1$, then from eqn. (53) we find

$$\langle\psi_{\lambda'+2}|\psi_{\lambda'+2}\rangle = \lambda' + 1$$

Thus $(\lambda' + 1)^{-1/2}\psi_{\lambda'+2}$ is normalized to unity. The normalized eigenfunctions are, therefore, related as

$$\psi_{\lambda'+2} = (\lambda' + 1)^{-1/2} R_-\psi_{\lambda'}$$

$$\psi_{\lambda'-2} = (\lambda' - 1)^{-1/2} R_+\psi_{\lambda'}$$

If we replace λ' by N, the natural quantum number for a linear harmonic oscillator, then we can write

$$\psi_0 = \left(\frac{1}{\pi}\right)^{1/4} \exp(-X^2/2) \tag{60}$$

$$\psi_{N+1} = (2N + 2)^{-1/2} R_-\psi_N \tag{61}$$

$$\psi_{N-1} = (2N)^{-1/2} R_+\psi_N \tag{62}$$

The Morse Oscillator

The Schrodinger equation for the pure vibrational motion of a diatomic molecule is given by (*12*)

$$\frac{d^2\psi}{dr^2} + \left[\frac{8\pi^2\mu}{h^2}\{E - U(r)\}\right]\psi = 0 \qquad (63)$$

where μ is the reduced mass, E is the total energy, and $U(r)$ is the potential energy of the system. In the preceding example we have solved eqn. (63) for a simple harmonic potential. Although a good many features of the vibrational spectroscopy can be understood from this model problem, there remains also a lot of problems like the dissociative behavior of a diatomic molecule, location of overtone bands etc., which cannot be accounted for. A more realistic potential function is needed for this purpose. The Morse potential is one such potential which is widely used. This potential has the following analytical form

$$U(r) = D[1 - \exp\{-a(r - r_e)\}]^2 \qquad (64)$$

where D is the depth of the potential function, a is an empirical parameter. Defining $q = r - r_e$, where r_e is the equilibrium internuclear separation, and substituting eqn. (64) into (63) we get

$$\frac{d^2\psi}{dq^2} + \frac{8\pi^2\mu}{h^2}[E - D - D\exp(-2aq) + 2D\exp(-aq)\psi = 0 \qquad (65)$$

If we put

$$x = -aq + \log\frac{(8\mu D)^{1/2}}{a\hbar}$$

$$S + \frac{1}{2} = (2\mu D)^{1/2}/a\hbar$$

$$m^2 = -2\mu(E - D)/a^2\hbar^2$$

eqn. (65) can be reduced to the standard form (m is now replaced by S, and λ by $-m^2$)

$$\frac{d^2\psi}{dx^2} + \left[-\frac{1}{4}\exp(2x) + \left(S + \frac{1}{2}\right)\exp(x)\right]\psi - m^2\psi = 0 \qquad (66)$$

Comparing eqn. (66) with (10) and making use of eqns. (20) and (21) we find that

$$k(x,S) = \frac{\exp(x)}{S^2\,2} - S$$

$$L(S) = -S^2\,2$$

Since $L(S)$ is a decreasing function of S, we have

$$\lambda = L(S_{min}) = -m^2$$

where $S = m, m + 1, m + 2, \ldots$.
But S as defined above is a constant. Therefore, we have only one energy level for each S. Since the minimum value of S is

$$\frac{(2\mu D)^{1/2}}{a\hbar} - \frac{1}{2}$$

the lowest possible energy of the Morse oscillator is given by

$$E_m = D + \frac{a^2\hbar^2}{2}L(S_{min})$$

$$= D - \frac{a^2\hbar^2}{2\mu}\left[\frac{\sqrt{2\mu D}}{a\hbar} - \frac{1}{2}\right]^2$$

Similarly,

$$E_{m+1} = D - \frac{a^2\hbar^2}{2\mu}\left[\frac{\sqrt{2\mu D}}{a\hbar} - \frac{3}{2}\right]^2$$

since, now

$$(S + 1) + \frac{1}{2} = \frac{\sqrt{2\mu d}}{a\hbar}$$

Defining $S - m = N$, we can write in general

$$E_N = D - \frac{a^2\hbar^2}{2\mu}\left[\frac{\sqrt{2\mu D}}{a\hbar} - \left(N + \frac{1}{2}\right)\right]^2$$

$$= \frac{ha}{2\pi}\left(N + \frac{1}{2}\right)\left(\frac{2D}{\mu}\right)^{1/2} - \frac{h^2a^2}{8\pi^2\mu}\left(N + \frac{1}{2}\right)^2 \qquad (67)$$

where $N = 0, 1, 2, \ldots$. Recalling that $\nu = (1/2\pi)(\sqrt{(12/\mu)}$, where

$$k = \left(\frac{\partial^2 U}{\partial q^2}\right)_{q=0} = 2a^2D$$

we can write the vibrational energy of the Morse oscillator as

$$E_N = \left(N + \frac{1}{2}\right)h\nu - \left(N + \frac{1}{2}\right)^2 h\nu\omega \qquad (68)$$

where ω is the anharmonicity constant of the potential function, and is given by

$$\omega = \frac{ha}{4\pi}\sqrt{\frac{1}{2D\mu}}$$

The vibrational wavefunctions of the Morse oscillator are quite complicated. We have, therefore, preferred not to include their determinations in this article which is meant for undergraduate students.

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