

Notes on the Factorization Method for Quantum Chemistry

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In a 1965 paper Salsburg³ demonstrated how to factorize the radial equation of the hydrogen atom to obtain the eigenvalues and eigenfunctions. He offered the procedures as pedagogically more appealing for introductory quantum courses than the polynomial method. The general treatment for the procedure as used by Salsburg can be found in a review article by Infeld and Hull.⁴ Following this example one of the writers, Peterson,⁵ compared the polynomial method with the factorization method for the radial equation of the hydrogen-like atom. It was a paper designed to stress the simplicity of the factorization technique. In a recent paper Das and Sannigrahi⁶ applied the factorization technique to the solution of the Schrodinger equation for the hydrogen atom, a linear harmonic oscillator, and the Morse oscillator. However, they presented the mathematics and techniques of the procedure in a manner that did not emphasize its simplicity and usefulness in teaching elementary quantum mechanics, although they pointed out the simultaneous normalization of the eigenfunctions during the generation process.

The factorization method can be applied to many of the partial differential equations that are used in quantum mechanics, and it does not involve the complex mathematics required by the traditional power series method, and it illustrates quantization more directly. However, the power series method has and continues to be the most used textbook approach for elementary quantum courses, especially quantum chemistry, although operator techniques are required for more advanced courses. The factorization method can serve as an excellent introduction to operator theory. It is also related to group theory.⁷ These are clear advantages of the factorization method over the power series method. A real pedagogical need is a presentation of the factorization procedure in such a manner that one explicitly demonstrates the simple algebraic techniques, without resorting to operator shorthand. Such a presentation does not undermine the simplicity of the procedure and hide it in obscure-appearing, raising and lowering operators, \hat{a}^+ and \hat{a} , before the student sees the need and utility for these operators. These notes were written in order to meet the above need.

We have chosen the harmonic oscillator for this demonstration since it has contributed so greatly to the understanding of the behavior of physical systems and it continues to be used for most demonstrations. Also, it is hoped that our paper will serve as a training paper for future students studying the factorization procedure.

Differential Notation and Commutation Relations

On solving the Schrodinger equation

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³ Salsburg, Z. W., *Amer. J. Phys.*, **33**, 36 (1965).

⁴ Infeld, L., and Hull, T. E., *Rev. Mod. Phys.*, **23** 21 (1965).

⁵ Peterson, C., *J. Chem. Educ.*, **52**, 92 (1975).

⁶ Das, R., and Sannigrahi, A. B., *J. Chem. Educ.*, **58**, 383 (1981).

⁷ The authors wish to thank their reviewer for pointing out the relation to group theory and the information source: B. G. Adams, J. Cizek, and J. Paldus, *Int. J. Quantum Chem.*, **21**, 153 (1982).

$$\hat{H}\Psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + \frac{1}{2} Kx^2 \Psi = E\Psi \quad (1)$$

by the factorization technique, it is convenient to introduce a change of variables for simplification as in the Sommerfeld polynomial method.⁵ We use the parameters:

$$\alpha = \frac{\omega m}{\hbar}$$

and

$$\beta = \frac{2mE}{\hbar^2}$$

where

$$\omega = \frac{K}{m}$$

the classical frequency of the harmonic oscillator, to obtain

$$\frac{\partial^2 \Psi}{\partial x^2} + (\beta - \alpha^2 x^2) \Psi = 0 \quad (2)$$

If we introduced $q = \sqrt{\alpha} x$ as the dimensionless position variable, we can proceed through the arithmetic as follows:

$$\begin{aligned} \frac{\partial \Psi}{\partial x} &= \frac{\partial \Psi}{\partial q} \cdot \frac{\partial q}{\partial x} = \sqrt{\alpha} \frac{\partial \Psi}{\partial q} \\ \frac{\partial^2 \Psi}{\partial x^2} &= \frac{\partial}{\partial q} \left(\frac{\partial \Psi}{\partial x} \right) \frac{\partial q}{\partial x} = \alpha \frac{\partial^2 \Psi}{\partial q^2} \end{aligned}$$

Now we introduce a dimensionless energy

$$\epsilon = \frac{\beta}{\alpha} = \frac{2E}{\omega \hbar}$$

and obtain

$$\alpha \frac{\partial^2 \Psi}{\partial q^2} + \left(\alpha \epsilon - \alpha^2 \cdot \frac{q^2}{\alpha} \right) \Psi = 0$$

which leads to

$$\frac{\partial^2 \Psi}{\partial q^2} + (\epsilon - q^2) \Psi = 0 \quad (3)$$

for the Schrödinger equation. If we define

$$\begin{aligned} \hat{p} &= \frac{1}{\hbar \sqrt{\alpha}} p_x = -\frac{i}{\sqrt{\alpha}} \frac{\partial}{\partial x} \\ &= -\frac{i}{\sqrt{\alpha}} \frac{\partial}{\partial q} \frac{\partial q}{\partial x} = -i \frac{\partial}{\partial q} = \frac{1}{i} \frac{\partial}{\partial q} \end{aligned}$$

then

$$\hat{p}^2 = -\frac{\partial^2}{\partial q^2}$$

From eqn. (3), one obtains

$$-\hat{p}^2 \Psi + \epsilon \Psi - \hat{q}^2 \Psi = 0$$

which yields on rearrangement

$$(\hat{p}^2 + \hat{q}^2) \Psi = \epsilon \Psi \quad (4)$$

We note that

$$i\hat{p}\hat{q}\Psi = \frac{\partial}{\partial q} (q)\Psi = q \frac{\partial \Psi}{\partial q} + \Psi$$

which implies that

$$i\hat{p}\hat{q}\Psi = i\hat{q}\hat{p}\Psi + \Psi$$

This gives

$$(\hat{p}\hat{q} - \hat{q}\hat{p})\Psi = -i\Psi$$

which leads to

$$[\hat{p}, \hat{q}]\Psi = -i\Psi$$

or the value for the commutativity of \hat{p} and \hat{q} .

Now

$$\begin{aligned} (\hat{q} + i\hat{p})(\hat{q} - i\hat{p})\Psi &= (\hat{q}^2 - i\hat{q}\hat{p} + i\hat{p}\hat{q} + \hat{p}^2)\Psi \\ &= [\hat{q}^2 + \hat{p}^2 + i(\hat{p}\hat{q} - \hat{q}\hat{p})]\Psi \\ &= (\hat{q}^2 + \hat{p}^2)\Psi + \Psi \end{aligned} \quad (5)$$

In a similar manner

$$(\hat{q} - i\hat{p})(\hat{q} + i\hat{p})\Psi = (\hat{q}^2 + \hat{p}^2)\Psi - \Psi \quad (6)$$

The use of eqns. (4), (5), and (6) then gives

$$(\hat{q} + i\hat{p})(\hat{q} - i\hat{p})\Psi = \epsilon\Psi + \Psi \quad (7)$$

and

$$(\hat{q} - i\hat{p})(\hat{q} + i\hat{p})\Psi = \epsilon\Psi - \Psi \quad (8)$$

If eqn. (8) is multiplied on the left by $q + ip$ one obtains

$$(q + ip)(\hat{q} - i\hat{p})(\hat{q} + i\hat{p})\Psi = (\epsilon - 1)(q + ip)\Psi$$

If one renames $(q + ip)\Psi = \varphi$, then one obtains

$$(q + ip)(\hat{q} - i\hat{p})\varphi = (\epsilon - 1)\varphi, \quad (9)$$

which gives

$$(\hat{q}^2 + \hat{p}^2)\varphi + \varphi = (\epsilon - 1)\varphi$$

or

$$(\hat{q}^2 + \hat{p}^2)\varphi = (\epsilon - 2)\varphi \quad (10)$$

That is, if Ψ is an eigenfunction of the operator $[(\hat{q} + i\hat{p})(\hat{q} - i\hat{p}) - 1]$ corresponding to energy level ϵ , then $(\hat{q} + i\hat{p})\Psi = \varphi$ is an eigenfunction corresponding to the new eigenvalue $\epsilon - 2$. There is a lowest energy ϵ_0 since the energy states of the harmonic oscillator must always correspond to positive energies. This is a well-known result in classical mechanics and can be accepted in quantum mechanics by the correspondence principle. However, it can be proved formally by setting up the equation for the expectation value of the energy. Therefore from eqn. (4)

$$\langle \epsilon \rangle = \int_{-\infty}^{\infty} \Psi^*(p^2 + q^2)\Psi dq = - \int_{-\infty}^{\infty} \Psi^* \frac{d^2\Psi}{dq^2} dq + \int_{-\infty}^{\infty} q^2 \Psi^* \Psi dq$$

The Ψ 's are normalized so that $\int_{-\infty}^{\infty} |\Psi|^2 dq = 1$. If one integrates the first term by parts one obtains

$$\langle \epsilon \rangle = \Psi^* \left(-\frac{d}{dq} \Psi \right) \Big|_{-\infty}^{\infty} + \int_{-\infty}^{\infty} \left(\frac{d\Psi^*}{dq} \right) \left(\frac{d\Psi}{dq} \right) dq + \int_{-\infty}^{\infty} \Psi^* q^2 \Psi dq$$

The vanishing of the Ψ 's at boundary is a necessary condition for quadratic integrability over the range $-\infty \leq q \leq \infty$

$$\langle \epsilon \rangle = \int_{-\infty}^{\infty} \left| \frac{d\Psi}{dq} \right|^2 dq + \int_{-\infty}^{\infty} q^2 |\Psi|^2 dq$$

Since positive definite integrals are obtained then

$$\langle \epsilon \rangle = \int \left| \frac{d\Psi}{dq} \right|^2 dq + \int q^2 |\Psi|^2 dq \geq 0$$

or

$$\langle \epsilon \rangle \geq 0$$

There must be a lowest energy and an eigenfunction corresponding to the lowest energy. If the eigenfunction is denoted Ψ_0 , then consistency requires

$$(q + ip)\Psi_0 = 0$$

or

$$\left(\frac{\partial}{\partial q} + q \right) \Psi_0 = 0$$

Therefore, one finds that

$$\Psi_0 = c_0 \exp\left(\frac{-q^2}{2}\right), \quad \epsilon_0 = 1$$

In this way one finds that the energy of the oscillator is equal to

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right), \quad (n \geq 0)$$

and the corresponding eigenfunction may be determined by applying $q - d/dq$ to $\Psi_0 = \exp(-q^2/2)$ with the constant c_0 , one obtains

$$\begin{aligned} \left(q - \frac{d}{dq} \right) \Psi_0 &= (-1) \exp\left(\frac{q^2}{2}\right) \frac{d}{dq} \exp\left(-\frac{q^2}{2}\right) \Psi_0 \\ &= 2q \exp\left(-\frac{q^2}{2}\right) \end{aligned}$$

also

$$\begin{aligned} \left(q - \frac{d}{dq} \right)^2 \Psi_0 &= \left(q - \frac{d}{dq} \right) \left(q - \frac{d}{dq} \right) \Psi_0 \\ &= (-1)^2 \exp\left(\frac{q^2}{2}\right) \frac{d}{dq} \exp\left(-\frac{q^2}{2}\right) \\ &\quad \exp\left(\frac{q^2}{2}\right) \frac{d}{dq} \left(\exp\left(-\frac{q^2}{2}\right) \right) \Psi_0 \\ &= (-1)^2 \exp\left(\frac{q^2}{2}\right) \frac{d^2}{dq^2} \left(\exp\left(-\frac{q^2}{2}\right) \right) \Psi_0, \end{aligned}$$

and generally,

$$\left(q - \frac{d}{dq} \right)^n \Psi_0 = (-1)^n \exp\left(\frac{q^2}{2}\right) \left(\frac{d}{dq} \right)^n \left(\exp\left(-\frac{q^2}{2}\right) \right) \Psi_0$$

which gives

$$\psi_n = A \exp\left(-\frac{q^2}{2}\right) \left(\frac{d}{dq} \right)^n \exp(-q^2)$$

where A is the normalization constant.

Comments

We have by these notes attempted to remove some of the abstractness from the factorization technique. The original second-order differential equation is not of central importance. The second-order differential equation is replaced by a pair of first-order equations.

The first-order equations are chosen in such a manner that one is led to consider only those solutions which are quadratically integrable. The quadratic integrability of a solution depends entirely on the behavior of the solutions near the end points and so the condition of quadratic integrability is essentially a boundary condition. Once the boundary conditions hold, then the operators are chosen to preserve not only quadratic but normalization of the eigenfunctions.⁴

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