A well known quantum theorem revisited

S T Kapellos, A T Tsatsas and A Mavridis

Department of Chemistry, University of Athens, 13A Navarinou Street, Athens 10680, Greece

Received 8 March 1989, in final form 25 September 1989

Abstract. The eigenvalue problem $\hat{A}|i\rangle = \alpha_i|i\rangle$ and the condition $[\hat{A}, \hat{B}] = 0$ imply that $\langle m|\hat{B}|n\rangle = 0$, under the restriction $\alpha_m \neq \alpha_n$. However, it is observed that even in cases where $[\hat{A}, \hat{B}] \neq 0$ and the commutator obeys a certain functional form, the simplest of which is $[\hat{A}, \hat{B}] = c$, then the off diagonal elements of $\hat{B}$ still vanish.

Abstrakt. Das Eigenwertproblem $\hat{A}|i\rangle = \alpha_i|i\rangle$ und die Bedingung $[\hat{A}, \hat{B}] = 0$ bedeuten, dass $\langle m|\hat{B}|n\rangle = 0$ gilt, unter der Einschränkung $\alpha_m \neq \alpha_n$. Trotz allem ist beobachtet worden, dass im Fall $[\hat{A}, \hat{B}] \neq 0$ und der Kommutator eine gewisse funktionelle Form befolgt, deren die einfachste $[\hat{A}, \hat{B}] = c$, dann verschwinden sogar hier die ausserdiagonalen Elemente von $\hat{B}$.

A well known theorem appearing in most standard textbooks on quantum chemistry states that, 'if $\hat{B}$ is an operator which commutes with an operator $\hat{A}$ (where both are Hermitian), and $|n\rangle$ and $|m\rangle$ are eigenfunctions of $\hat{A}$, then the matrix element $\langle n|\hat{B}|m\rangle$ vanishes unless $\alpha_n \neq \alpha_m$, where α_n, α_m are eigenvalues of $|n\rangle$, $|m\rangle$ respectively' (Eyring *et al* 1944). In symbols:

$$\hat{A}\,|\,i\rangle = \alpha_i|i\rangle \qquad i = n, m$$

$$\hat{A}^+ = \hat{A} \qquad \hat{B}^+ = \hat{B}$$

$$\alpha_n - \alpha_m \neq 0 \qquad \text{with } [\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$$

then

$$\langle n|\hat{B}|m\rangle = 0.$$

$\hat{A}^+$, $\hat{B}^+$ are the Hermitian adjoints of $\hat{A}$ and $\hat{B}$ respectively.

It appears (but *vide infra*) that the theorem can be easily extended to non-commuting operators of the general functional form:

$$[\hat{A}, \hat{B}] = \hat{B}F(\hat{A}) \tag{1}$$

where $F(\hat{A})$ is a well behaved function of the operator $\hat{A}$, by which it is meant that it may be expanded as a power series of $\hat{A}$. It is observed that it is sufficient for $\hat{A}$ to be normal†, whereas, no restrictions need be imposed on $\hat{B}$ (Pilar 1968). However, in what follows operator $\hat{A}$ is always to be considered as Hermitian.

Using the definition of the commutator $[\hat{A}, \hat{B}]$ and relation (1) we may write:

$$\langle n|\hat{A}\hat{B}|m\rangle = \langle n|\hat{B}F(\hat{A}) + \hat{B}\hat{A}|m\rangle$$
$$= F(\alpha_m)\langle n|\hat{B}|m\rangle + \alpha_m\langle n|\hat{B}|m\rangle. \tag{2}$$

It is also true that:

$$\langle n|\hat{A}\hat{B}|m\rangle = \alpha_n\langle n|\hat{B}|m\rangle. \tag{3}$$

By comparing (2) and (3) we obtain:

$$\{\alpha_n - \alpha_m - F(\alpha_m)\}\,\langle n|\hat{B}|m\rangle = 0. \tag{4}$$

Now if $\alpha_n - \alpha_m = F(\alpha_m)$, then $\langle n|\hat{B}|m\rangle$ need not be equal to zero. However, when $\alpha_n - \alpha_m \neq F(\alpha_m)$, then $\langle n|\hat{B}|m\rangle = 0$. In the diagonal case, (4) becomes:

$$F(\alpha_n)\langle n|\hat{B}|n\rangle = 0. \tag{5}$$

In (5), $F(\alpha_n)$ is either non-zero or zero. In the first case necessarily, $\langle n|\hat{B}|n\rangle = 0$, whereas in the latter case we are led back to the standard theorem.

More interesting than the general case (1) is the situation where the commutator is of the type

$$[\hat{A}, \hat{B}] = F(\hat{A}). \tag{6}$$

Following exactly the previous procedure and taking into account the orthogonality of the eigenfunctions of $\hat{A}$, $\langle n|m\rangle = \delta_{nm}$, equation (7) is obtained instead of equation (4):

$$(\alpha_n - \alpha_m)\langle n|\hat{B}|m\rangle = F(\alpha_m)\delta_{nm}. \tag{7}$$

Consider the following two possible distinct cases.

(i) If $n \neq m$ then, clearly, $\langle n|\hat{B}|m\rangle = 0$.

(ii) If $n = m$ (diagonal case), then

$$0 \cdot \langle n|\hat{B}|n\rangle = F(\alpha_n).$$

† An operator, $\hat{\Omega}$, is defined as normal when it commutes with its Hermitian adjoint, $\hat{\Omega}^+$, $[\hat{\Omega}^+, \hat{\Omega}] = 0$.

0143-0807/90/030152 + 03 $03.50

In this case if, accidentally, $F(\alpha_n) = 0$ then $\langle n|\hat{B}|n\rangle$ can be non-zero. However, in general, $F(\alpha_n) \neq 0$ and the matrix element $\langle n|\hat{B}|n\rangle$ is ill defined. Before we comment upon this result let us examine the simplest possible case of non-commuting operators, so instead of relation (1) assume that:

$$[\hat{A}', \hat{B}'] = c \tag{9}$$

where c is a constant. Or, redefining the operators $\hat{A}'$, $\hat{B}'$ in an obvious way equation (9) can be written

$$[\hat{A}, \hat{B}] = 1. \tag{9a}$$

Direct application of (7) yields $\langle n|\hat{B}|m\rangle = 0$ when $n \neq m$. In the diagonal case, again, $\langle n|\hat{B}|n\rangle$ behaves pathologically. This pathological behaviour of $\langle n|\hat{B}|n\rangle$ as in the previous situation, is consistent with the statement that 'two (Hermitian) operators cannot be simultaneously diagonalised if they do not commute'.

The previous findings concerning the commutator cases (6) or (9a) suggest that the matrix B of $\hat{B}$ with respect to the set $|i\rangle$ of the (discrete) eigenvalues of $\hat{A}$ is ill defined: the off diagonal elements of $\hat{B}$ are all zero but the diagonal elements diverge. This in turn, could suggest for the physics and/or the chemistry of the problem defined by the operator $\hat{A}$, that if an operator $\hat{B}$ obeys relation (6) or even (9a), then $\hat{B}$ is not a 'useful' operator for the particular problem at hand. Or in other words, no information concerning $\hat{B}$ can be obtained using the set of functions $|i\rangle$, i.e. the eigenfunctions of $\hat{A}$. This problem, in a natural way, does not arise on the more general case of the operator equation (1).

Three examples of the aforementioned results are presented. Examples 1 and 2 are along similar lines and conform to the operator equation (1), but with $F(\hat{A})$ replaced by a constant. Example 3 conforms to equation (9), but with the eigenvalue spectrum of $\hat{A}$ running into the continuum. Admittedly the examples presented are not very inspiring, yet they illustrate the points made.

Example 1

$$[\hat{J}_z, \hat{J}_+] = \hbar \hat{J}_+ \tag{10}$$

where $\hat{J}_z$ is the z component of the angular momentum operator, and $\hat{J}_+$ is the usual raising operator, $\hat{J}_+ = \hat{J}_x + \mathrm{i}\hat{J}_y$. Equation (10) pertains to (1) where $\hat{J}_z$ is identified with $\hat{A}$, $\hat{J}_+$ with $\hat{B}$ and $F(\hat{A})$ with $\hbar$. Notice that, although $\hat{J}_z$ is Hermitian, $\hat{J}_+$ is neither Hermitian nor even normal.

Using the spectrum of $\hat{J}_z$, $\hat{J}_z|jm_j\rangle = m_j\hbar|jm_j\rangle$, we obtain directly from (4)

$$(m_j' - m_j - 1)\langle jm_j'|\hat{J}_+|jm_j\rangle = 0.$$

If $m_j' - m_j = \Delta m_j \neq 1$, then $\langle jm_j'|\hat{J}_+|jm_j\rangle = 0$, in agreement with results obtained from (4) and which are obvious from the properties of raising operators. *Mutatis mutandis*, having used the lowering operator $\hat{J}_-$ we would have obtained $\langle jm_j'|\hat{J}_-|jm_j\rangle = 0$, if $\Delta m_j \neq -1$.

Example 2

Consider the Hamiltonian operator of the one-dimensional harmonic oscillator

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \tfrac{1}{2}k\hat{x}^2 \tag{11}$$

where $k = \omega^2 m$ and ω is the frequency. We define the operators

$$\hat{\beta} = \frac{1}{(2\hbar\omega)^{1/2}}\left(\frac{\hat{p}_x}{m^{1/2}} - \mathrm{i}\sqrt{k}\,\hat{x}\right)$$

and

$$\hat{\beta}^+ = \frac{1}{(2\hbar\omega)^{1/2}}\left(\frac{\hat{p}_x}{m^{1/2}} + \mathrm{i}\sqrt{k}\,\hat{x}\right) \tag{12}$$

(see, for example, Ziman 1969).

Using the fundamental commuator $[\hat{x}, \hat{p}_x] = \mathrm{i}\hbar$ it follows that

$$[\hat{\beta}, \hat{\beta}^+] = 1. \tag{13}$$

By using equation (12), (11) can be factorised to the well known form

$$\hat{H} = \tfrac{1}{2}\hbar\omega(\hat{\beta}\hat{\beta}^+ + \hat{\beta}^+\hat{\beta}). \tag{14}$$

Notice that although $\hat{\beta}$ and $\hat{\beta}^+$ are not Hermitian the symmetrical combination $\hat{\beta}\hat{\beta}^+ + \hat{\beta}^+\hat{\beta}$ is as it should be. If now $|n\rangle$ are the eigenfunctions of $\hat{H}$ the following relations hold:

$$\hat{H}|n\rangle = E_n|n\rangle \tag{15}$$

with

$$\left.\begin{aligned} &\hat{\beta}|n\rangle = n^{1/2}|n-1\rangle \\ \text{and}\quad &\hat{\beta}^+|n\rangle = (n+1)^{1/2}|n+1\rangle \end{aligned}\right\}. \tag{16}$$

Combining now (13) and (14) it is easily proved that

$$[\hat{H}, \hat{\beta}] = -\hbar\omega\hat{\beta} \tag{17}$$

and

$$[\hat{H}, \hat{\beta}^+] = +\hbar\omega\hat{\beta}^+. \tag{18}$$

Equations (17) and (18) conform to the general commutator relation (1), and therefore applying (4) directly, one obtains

$$[(n + \tfrac{1}{2})\hbar\omega - (m + \tfrac{1}{2})\hbar\omega - (-\hbar\omega)]\langle n|\beta m\rangle = 0$$

or

$$(n - m + 1)\langle n|\hat{\beta}|m\rangle = 0. \tag{19}$$

From the above it immediately follows that if $n - m + 1 \neq 0$ or $n - m \neq -1$, then $\langle n|\hat{\beta}|m\rangle = 0$; and if $n - m - 1 \neq 0$ or $n - m \neq +1$, then $\langle n|\hat{\beta}^+|m\rangle = 0$. Of course the diagonal elements of both $\hat{\beta}$ and $\hat{\beta}^+$ are zero. That this is indeed the case follows by employing (16)

$$\langle n|\hat{\beta}|m\rangle = m^{1/2}\langle n|m-1\rangle = m^{1/2}\delta_{nm-1}$$

and

$$\langle n|\hat{\beta}^{+}|m\rangle = (m+1)^{1/2}\langle n|m+1\rangle = (m+1)^{1/2}\delta_{nm+1}$$

by virtue of the orthogonality of $|n\rangle$.

Example 3
Here we identify $\hat{A}$ with $\hat{x}$, the translational operator and $\hat{B}$ with $\hat{p}_x$, the momentum operator; the commutator is $[\hat{x},\hat{p}_x] = \mathrm{i}\hbar$ which conforms with relation (9). We write:

$$\hat{x}|x\rangle = x|x\rangle.$$

Therefore

$$\begin{aligned}\langle x'|\hat{B}|x''\rangle &= \langle x'|\hat{p}_x|x''\rangle = \int \mathrm{d}p\langle x'|\hat{p}_x|p_x\rangle\langle p_x|x''\rangle \\ &= \int \mathrm{d}p\, p_x\langle x'|p_x\rangle\langle p_x|x''\rangle \\ &= \int \mathrm{d}p\, p_x \exp[\mathrm{i}\, p_x(x'-x'')/\hbar] = (\hbar/\mathrm{i})\,\delta'(x'-x'').\end{aligned}$$

When $x' \neq x''$ the derivative of the delta function δ' can be 'considered' zero, while, as expected, the diagonal elements ($x' = x''$) are ill behaved.

References

Eyring H, Walter J and Kimball G E 1944 *Quantum Chemistry* (New York: Wiley) p 37

Pilar F L 1968 *Elementary Quantum Chemistry* (New York: McGraw-Hill) p 83

Ziman M J 1969 *Elements of Advanced Quantum Theory* (Cambridge: Cambridge University Press) pp 1–4