VIII. HYPERVIRIAL THEOREMS FOR 1D FINITE SYSTEMS. GENERAL BOUNDARY CONDITIONS

34. Reformulation of some theorems

The finite BC confront us with a problem no previously found in those cases studied in Part A. Let us suppose that ψ_i,ψ_j are two functions that obey the BC of the problem, so that they belong to D_H. If ω is an arbitrary linear operator, then in general, $\omega\psi_j$ does not belong to D_H. This fact makes the equality

$$<\psi_i|H\omega\psi_j> = <H\psi_i|\omega\psi_j>$$

no longer valid and it must be replaced by

$$<\psi_i|H\omega\psi_j> = <H\psi_i|\omega\psi_j> + S_{ij} \tag{1}$$

where S_{ij} arises from the divergence theorem

$$<\psi_i|\Delta\omega\psi_j> = <\Delta\psi_i|\omega\psi_j> + \int_S \{\psi_i^*\nabla(\omega\psi_j) - (\omega\psi_j)\nabla\psi_i^*\}.\vec{n}ds \quad . \tag{2}$$

If the dimensionless Hamiltonian for an N-coordinate system is written as

$$H = -\tfrac{1}{2}\Delta + V(\vec{r}) \quad ; \; \vec{r} = (x_1,...,x_N)$$

we deduce at once

$$S_{ij} = \tfrac{1}{2}\int_S \{(\omega\psi_j)\nabla\psi_i^* - \psi_i^*\nabla(\omega\psi_j)\}.\vec{n}ds \quad . \tag{3}$$

When ψ_i,ψ_j are H-eigenfunctions with eigenvalues E_i,E_j respectively, the HT has the form:

$$<\psi_i|[H,\omega]\psi_j> = \omega_{ij}<\psi_i|\omega\psi_j> + S_{ij} \quad . \tag{4}$$

If $\omega\psi_j \varepsilon D_H$, then $S_{ij}=0$ and the HT has the same expression as for infinite systems. The result due to Epstein [1] and given in section 33, is a particular case of (4) (when $\psi_i=\psi_j=\psi$ and $E_i=E_j=E$)

$$<\psi|[H,\omega]\psi> = S = \tfrac{1}{2}\int_S \{(\omega\psi)\nabla\psi^* - \psi^*\nabla(\omega\psi)\}.\vec{n}ds \quad . \tag{5}$$

Owing to this difference, we have to modify two theorems previously presented. The first one, given in section 2, is due to Hirschfelder [2].

Theorem I. The wave function is an H-eigenfunction iff fulfills (5) for any linear operator ω.

Proof: It is immediate because it follows the same scheme as shown in section 2 (Theorem I). It is only necessary to rearrange (5) as: $\langle H\psi|\omega\psi\rangle - \langle\psi|\omega H\psi\rangle = 0$.

When necessary, we will impose in addition the condition that ψ holds the BC of the problem.

The importance of this theorem rests upon the fact that it shows the advantage of using HO like $f(\vec{r})\nabla$ even though there exists finite BC (see the proof of Theorem I, section 2).

The next theorem [3-6] was previously discussed in depth (section 3 and section 21) and besides it was applied to problems with infinite BC.

Theorem II. If $H\psi_o = E\psi_o$ and ψ satisfies the NDHR

$$\langle\psi|[H,\omega_i]\psi_o\rangle = (E-E_o)\langle\psi|\omega_i\psi_o\rangle + \tfrac{1}{2}\int_S \{(\omega_i\psi_o)\nabla\psi^* - \psi^*\nabla(\omega_i\psi_o)\}.\vec{n}ds;\ i=1,2,... \qquad (6)$$

then

$$\langle(H-E)\psi|\omega_i\psi_o\rangle \ ;\ i=1,2,... \qquad (7)$$

Proof: Once again it is immediate if one takes into account that (6) can be rearranged as

$$\langle H\psi|\omega_i\psi_o\rangle - \langle\psi|\omega H\psi_o\rangle = (E-E_o)\langle\psi|\omega_i\psi_o\rangle \quad .$$

The essential difference between this theorem and that given in section 3 and section 21 is that D_H does not include $\overline{\{\omega_i\psi_o\}}$ which, in general, is not a subspace of the Hilbert space associated to the physical problem.

Both theorems are totally general and they are valid for any system whose potential depends only on the coordinates, because no reference was made respect the nature of the variables, to the frontier shape nor the class of BC. They are even valid for non bound states (section 6). When the frontier S is at infinity (so that $\psi, \nabla\psi$ are zero on S), these theorems reduce to those presented in Part A, so that they can be considered as a generalization of those given formerly.

35. Hypervirial theorems for 1D systems under general BC

Now we will develop the HT for those quantum 1D systems

$$H\psi_i = E_i\psi_i \; ; \quad H = -\tfrac{1}{2}D^2 + V(x) \tag{8}$$

satisfying the general boundary conditions (GBC)

$$\begin{aligned} \psi(a) &= A\psi'(a) \\ \psi(b) &= B\psi'(b) \end{aligned} \tag{9}$$

with A,B being real numbers and a<b.

First of all, we must prove that H is Hermitian. If χ_1, χ_2 obey (9), then

$$\langle\chi_1|H\chi_2\rangle = \langle H\chi_1|\chi_2\rangle + \tfrac{1}{2}\{|\chi_1'^*\chi_2|_a^b - |\chi_1^*\chi_2'|_a^b\} = \langle H\chi_1|\chi_2\rangle +$$

$$+ \tfrac{1}{2}\{B\chi_1^*(b)\chi_2(b) - A\chi_1^*(a)\chi_2(a) - \chi_1^*(b)B\chi_2(b) + \chi_1^*(a)A\chi_2(a)\} =$$

$$= \langle H\chi_1|\chi_2\rangle \quad . \tag{10}$$

Hereinafter we will consider only real functions and real operators, so it will be not necessary to add the term c.c.

When ψ_i, ψ_j are H-eigenfunctions with eigenvalues E_i and E_j, respectively, Eqs. (3)-(5) assure us that

$$\langle\psi_i|[H,\omega]\psi_j\rangle = \omega_{ij}\langle\psi_i|\omega\psi_j\rangle + S_{ij} \tag{11}$$

$$S_{ij} = \tfrac{1}{2}\{|(\omega\psi_j)\psi_i'|_a^b - |\psi_i(\omega\psi_j)'|_a^b\} \tag{12}$$

$$\langle\psi|[H,\omega]\psi\rangle = S = \tfrac{1}{2}\{|(\omega\psi)\psi'|_a^b - |\psi(\omega\psi)'|_a^b\} \quad . \tag{13}$$

In order to determine the variation of the eigenvalues with the extreme points of the interval (a,b), it is just necessary to differentiate (8) and then to apply the function $<\psi|$ (we omit lower indices).

For example, for b we get

$$<\psi|H\frac{\partial\psi}{\partial b}> = \frac{\partial E}{\partial b}\,\Gamma + E<\psi|\frac{\partial\psi}{\partial b}> \quad ; \quad \Gamma = <\psi|\psi> \quad . \tag{14}$$

The use of (2) enables us to transform the last equation in

$$\frac{\partial E}{\partial b}\,\Gamma = \tfrac{1}{2}\{|\psi' \,\frac{\partial\psi}{\partial b}|_a^b - |\psi\frac{\partial\psi'}{\partial b}|_a^b\} \quad . \tag{15}$$

Since, in general $\partial\psi/\partial b$ does not satisfy the same BC as ψ does, the r.h.s. in (15) is not zero and $\partial E/\partial b \neq 0$. This result is entirely logic because the eigenvalues depend on a and b.

For the other extreme point it follows a similar expression:

$$\frac{\partial E}{\partial a}\,\Gamma = \tfrac{1}{2}\{|\psi' \,\frac{\partial\psi}{\partial a}|_a^b - |\psi\frac{\partial\psi'}{\partial a}|_a^b\} \quad . \tag{16}$$

Since ψ holds (9), it depends on a and b, i.e. $\psi=\psi(a,b,x)$. When the GBC (9) are valid for any b value (in general, for any b value within a given interval)

$$\psi(a,b,b) = B\psi'(a,b,b) \tag{17}$$

$$\psi(a,b,a) = A\psi'(a,b,a) \tag{18}$$

it is possible to obtain a useful relationship just differentiating (17)-(18) with respect to b:

$$\frac{\partial\psi}{\partial b}(b) + \psi'(b) = B\{\frac{\partial\psi'}{\partial b}(b) + \psi''(b)\}$$
$$\frac{\partial\psi}{\partial b}(a) = A\,\frac{\partial\psi'}{\partial b}(a) \quad . \tag{19}$$

In what follows, we will assume the existence and continuity of the derivatives $\partial E/\partial b$; $\partial E/\partial a$; $\partial\psi/\partial b$; $\partial\psi/\partial a$; $\partial^2\psi/\partial b\partial x = \partial^2\psi/\partial x\partial b$; etc., so that, substituting (19) in (15) we have

$$\frac{\partial E}{\partial b}\Gamma = \tfrac{1}{2}\{\psi'(b)\frac{\partial\psi}{\partial b}(b) - \psi(b)\frac{\partial\psi'}{\partial b}(b)\} = \tfrac{1}{2}\{\frac{\partial\psi}{\partial b}(b) - B\,\frac{\partial\psi'}{\partial b}(b)\}\psi'(b) = \tfrac{1}{2}\{B\psi''(b) - \psi'(b)\}\psi'(b) =$$
$$= \tfrac{1}{2}\{2B\{V(b) - E\}\psi(b) - \psi'(b)\}\psi'(b) = \{B^2[V(b) - E] - \tfrac{1}{2}\}\psi'(b)^2 \quad . \tag{20}$$

Analogously, for the other extreme point

$$\partial E/\partial a \ \Gamma = \{\tfrac{1}{2} - A^2[V(a) - E]\}\psi'(a)^2 \quad . \qquad (21)$$

The same result is obtained when one applies the Gonda and Gray's procedure [7].

These two last formulas will be useful to deduce the analytical expressions for the HT.

We have used in Part A basically two kinds of HO: $\omega = f(x)$ and $\omega = f(x)D$. The second HO is really important, as stated in Theorem I, section 2 and Theorem I, this section. The replacement $\omega = f(x)$ in (13) gives

$$\langle\psi|[H,f]\psi\rangle = \tfrac{1}{2}\{|f\psi\psi'|_a^b - |f\psi\psi'|_a^b - |f'\psi^2|_a^b\} =$$

$$= \tfrac{1}{2}\{-f'(b)\psi^2(b) + f'(a)\psi^2(a)\} =$$

$$= \tfrac{1}{2}\{A^2f'(a)\psi'(a)^2 - B^2f'(b)\psi'(b)^2\} \quad . \qquad (22)$$

Substituting (20) and (21) in (22) we get:

$$\langle\psi|[H,f]\psi\rangle = \{\frac{A^2f'(a)}{1 - 2A^2[V(a)-E]}\frac{\partial E}{\partial a} + \frac{B^2f'(b)}{1 - 2B^2[V(b)-E]}\frac{\partial E}{\partial b}\}\Gamma \quad . \qquad (23)$$

Working along the same lines with the other operator ($\omega = f(x)D$) we obtain

$$\langle\psi|[H,fD]\psi\rangle = \tfrac{1}{2}\{|f\psi'^2|_a^b - |f\psi\psi''|_a^b - |f'\psi\psi'|_a^b\} =$$

$$= \tfrac{1}{2}\{f(b)\psi'(b)^2 - f(a)\psi'(a)^2 - 2f(b)\psi(b)[V(b)-E]\psi(b) + 2f(a)\psi(a)[V(a) -$$

$$- E]\psi(a) - f'(b)\psi(b)\psi'(b) + f'(a)\psi(a)\psi'(a)\} =$$

$$= \tfrac{1}{2}\{f(b) - 2B^2f(b)[V(b)-E] - Bf'(b)\}\psi'(b)^2 + \tfrac{1}{2}\{-f(a) + 2A^2f(a)[V(a) -$$

$$- E] + Af'(a)\}\psi'(a)^2 = -\{f(b) + \frac{Bf'(b)}{2B^2[V(b)-E]-1}\} - \{f(a) +$$

$$+ \frac{Af'(a)}{2A^2[V(a)-E]-1}\}\frac{\partial E}{\partial a}\Gamma \quad . \qquad (24)$$

Owing to their general character, Eqs. (23)-(24) represent the starting point for all the following derivations. Multiplying (23) and (24) by Γ^{-1} we normalize the function:

$$<[H,f]> = \left\{\frac{A^2 f'(a)}{1-2A^2[V(a)-E]} \frac{\partial E}{\partial a} + \frac{B^2 f'(b)}{1-2B^2[V(b)-E]} \frac{\partial E}{\partial b}\right\} \tag{25}$$

$$<[H,fD]> = -\left\{f(b) + \frac{Bf'(b)}{2B^2[V(b)-E]-1}\right\} \frac{\partial E}{\partial b} - \left\{f(a) + \frac{Af'(a)}{2A^2[V(a)-E]-1}\right\} \frac{\partial E}{\partial a} \quad . \tag{26}$$

It is interesting to point out that the HT involving operators dependent only on the coordinates are trivial when $f\psi \varepsilon D_H$ because Eq. (25) shows a dependence with respect to the potential function as well as regarding the extremes of the interval.

Now we present some important results that follow when f(x) adopts particular expressions:

1) Substituting f(x) = x in (26) we deduce the VT in a very general formulation

$$2<T> - <(vV)> = -\left\{b + \frac{B}{2B^2[V(b)-E]-1}\right\} \frac{\partial E}{\partial b} - \left\{a + \frac{A}{2A^2[V(a)-E]-1}\right\} \frac{\partial E}{\partial a} \quad . \tag{27}$$

2) Eq. (26) with f(x) = 1 gives

$$<V'> = \partial E/\partial a + \partial E/\partial b \quad . \tag{28}$$

Eq. (28) admits a simple and interesting enough interpretation:

Let us suppose that we write the ends of the interval as $a = -\frac{L}{2} + x^\circ$; $b = \frac{L}{2} + x^\circ$. The change of variable $y = x - x^\circ$ allows us to express the energy formula as:

$$E = \int_{-L/2+x^\circ}^{L/2+x^\circ} \psi(x)H(x)\psi(x)dx = \int_{-L/2}^{L/2} \psi(y+x^\circ)H(y+x^\circ)\psi(y+x^\circ)dy \quad . \tag{29}$$

Since $\psi(y+x^\circ)$ satisfies the GBC when $y = \pm L/2$ for any x° value, obviously $\partial\psi/\partial x^\circ$ will satisfy the same BC, so that the HFT holds

$$\frac{\partial E}{\partial x^\circ} = \frac{\partial E}{\partial a} + \frac{\partial E}{\partial b} = <\frac{\partial V}{\partial x^\circ}> = <V'> \quad . \tag{30}$$

One realizes at once that Eq. (28) is the HFT. The change of variable used here to demonstrate (30) is a particular case of the more general transformation proposed by Brillouin [8].

3) Substituting $f(x) = x$ in (25) we obtain an expression for the momentum average value

$$<D> = -\left\{\frac{A^2}{1-2A^2[V(a)-E]}\frac{\partial E}{\partial a} + \frac{B^2}{1-2B^2[V(b)-E]}\frac{\partial E}{\partial a}\right\} \quad . \tag{31}$$

4) When the problem has a maximum symmetry, i.e. when $V(x)$ is even $b=-a$ and $A=B$, then Eqs. (25)-(26) are simplified up to a large extent (it is important to take into account that in this case, $(\partial E/\partial b)\Gamma = \{2B^2[V(b)-E]-1\}\psi'(b)^2$).

$$<[H,f]> = \frac{B^2 f'(b)}{1-2B^2[V(b)-E]}\frac{\partial E}{\partial b} \quad ; \quad f(-x) = f(x) \tag{32}$$

$$<[H,fD]> = -f(b)\partial E/\partial b \quad ; \quad f(-x) = -f(x) \quad . \tag{33}$$

Eqs. (32)-(33) are identically null when the parity of $f(x)$ is the opposed to that indicated there. As a particular case, we can verify the validity of the VT in its usual form

$$2<T> - <(vV)> = -b\partial E/\partial b \quad . \tag{34}$$

5) When the Hamiltonian operator depends on a parameter λ, its eigenfunctions must satisfy (9) for any λ-value and $\partial\psi/\partial\lambda$ has to satisfy (9) too, so that it assures us the fulfillment of the HFT

$$\partial E/\partial\lambda = <\partial H/\partial\lambda> \quad . \tag{35}$$

6) When $a=\infty$, the solutions (8) must meet the condition $\psi(\infty)=\psi'(\infty)=0$ (it is understood that we are considering only bound states) and the solutions (25)-(26) change to $(\partial E/\partial a=0)$

$$<[H,f]> = \frac{B^2 f'(b)}{1-2B^2[V(b)-E]}\frac{\partial E}{\partial b} \tag{36}$$

$$<[H,fD]> = -\left\{f(b) + \frac{Bf'(b)}{2B^2[V(b)-E]-1}\right\}\frac{\partial E}{\partial b} \quad . \tag{37}$$

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