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Evaluation of Upper and Lower Bounds to Energy Eigenvalues in Schonberg's Perturbation-Theory Ground State by Means of a Partitioning Technique

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Upper and lower bounds for the energy eigenvalues in Schönberg's perturbatiori-theory ground state are studied. After a review of the characteristic features of the partitiuning techniques the perturbative expansion proposed by Schönberg is generated from an exact operator equation. The upper and lower bounds for the ground state eigenvalue are derived by using reaction and wave operators concepts, the bracketing function and operator inequalities.

Apresenta-se um estudo de limites superior e inferior para os valores da energia do estado fundamental na teoria de perturbação desenvolvida por Schtlnberg. Após uma apresentação dos fatos característicos do método de partição, as expansões perturbativas propostas por Schtlnberg são obtidas de uma equação exata envolvendo operadores. Os limites superiores e inferior são determinados usando-se os conceitos de operadores de onda e de: reação, a função "bracketing" e desigualdade entre operadores.

1. INTRODLJCTION

In quantum theory, the energy values of the stationary states of a physical system are determined by the eigenvalues E of the time-independent Schrödinger equation

$$H\,|\psi\rangle = E\,|\psi\rangle \qquad (1.1)$$

where the Hamiltonian H is a self-adjoint operator ($H^{\dagger} = H$).

For the atomic and molecular systems, tha ground state and lower excited states correspond to a setof discrete energy leveis. The associated Hamiltonian is hence bounded from below, and the spectrum starts with a set of discrete eigenvalues. In addition to the closed stationary states, there may further be scattering ststes connected with a continuous part of the spectrum. In this paper we wi?l focus our interest on the discrete energy levels only.

In general, it is very difficult to solve the time-independent Schrödinger equation exactly. Perturbative treatment and variational methods are usually used for determining approximate solutions of Eq.(i.I!.

In the long history of the use of perturbation theory various different. perturbation expansions[1] have evolved, eãch oF which has its own particular advantages in solving particulãr physical problems. In atomic and molecular applications the commonly used perturbative expansions are those obtained from Brillouin[2] and Schrödinger[3] theories.

Some time ago, Schönberg proposed a modified perturbation theory[4]. In our opinion, this theory has not been sufficiently explored in its application yet. It has the advantage, over Brillouin and Schrödinger procedures, of permitting an immediate formulation of a dynamic treatment from stationary theory[5]. Furthermore, we foiind that it can be applied satisfactorily to the atomic and molecular systems.

The problem of finding convenient bounds in Schrödinger and Brillouin perturbation theories has been discussea by Löwdin in several papers[E-9] In order to make applications of the Schönberg theory andto compare its results (accuracy, rapidity of convergence) with those obtained by using Schrödinger and Brillouin expùnsions, it is important and necessary to know the expressions for upper and lower bounds of energy eigenvalues in tnis theory. This is the basic purpose of the present paper.

Ir! our study, we wili use the partitioninç technique developed by Löwdin[7,10,11]. From this method[8], a function

$$\varepsilon_1 = f(\varepsilon)$$

can De constructed, where both E, and ε are real variables. These variables have the property that at least orie true eigenvalue E of H should be contained in the interval $(\varepsilon,\varepsilon_1)$. Hence, it is possible to determine upper and lower bounds, and the main problem is to evaluate the quantities involved.

2. PARTITIONING TECHNIQUE

Tho partitioning technique for solving the Schrödinger equation (1.1) where $|\psi\rangle$ is subjected to certain boundary conditions (for closed states one will assume that the normalization integral $\langle\psi|\psi\rangle$ exists, whereas, for scatter-ing states one will assume that $|\psi\rangle$ itself stays finite at infinity) is based on the use of a normalized reference ket $|\phi\rangle$ in Hilbert space H, a variahle ε and a reduced resolvent T.

If $\Theta = |\phi\rangle\langle\phi|$ is the projection operator on the "reference space" H_1 and $E = 1-\Theta$ is the projection operator for the orthogonal complement H_2, one has, for the reduced resolvent T , the definition[R]

$$T = P\left[\alpha\Theta + P(\varepsilon - H)\,P\right]^{-1} P \tag{2.1}$$

where a is an arbitrary constant different from zero. The Hilbert space H is "partitioned" into two subspaces H: and H_2, i.e., it is the direct sum of H_1 and H_2.

It is shown[6] that the operator F satisfies the following algebraic relations

$$\Theta T = T\Theta = 0 \tag{2.2}$$

$$P(\varepsilon - H)T = P \tag{2.3}$$

$$\frac{\partial T}{\partial \alpha} \equiv 0, \quad \text{for } \alpha \neq 0 \tag{2.4}$$

$$\frac{\partial T}{\partial \varepsilon} = -T^2 \quad . \tag{2.5}$$

Using the reference ket $|\phi\rangle$ and the cperators H and T it is possible to define a trial ket $|\psi_E\rangle$ in the space H through the relation[6,7],

$$|\psi_\varepsilon\rangle = (I + TH)\,|\phi\rangle \quad . \tag{2.6}$$

It satisfies the intermediate normalization $\langle\phi\,|\,\psi_\varepsilon\rangle$, useful in all parts of the spectrum.

According to (2.3), it follows that

$$P(\varepsilon - H)\,|\psi_\varepsilon\rangle = 0 \ ,$$

and this implies that

$$\begin{aligned}(E-H)\,|\psi_\varepsilon\rangle &= (\Theta + P)\,(E-H)\,|\psi_\varepsilon\rangle \\ &= \Theta(\varepsilon - H)\,|\psi_\varepsilon\rangle \\ &= |\phi\rangle\langle\phi|\,(\varepsilon - H)\,|\psi_\varepsilon\rangle \\ &= (\varepsilon - \varepsilon_1)\,|\phi\rangle \end{aligned} \tag{2.7}$$

where we have introduced the notation $\varepsilon_1 = \langle\phi|H|\psi_\varepsilon\rangle$.

The relation (2.7) shows that the trial ket $|\psi_E\rangle$ satisfies an inhomogeneous Schrödinger equation, which reduces to the eigenvalues problem (1.1) only in the special case when $E_1 = E = E$.

The quantity ε_1 given by the relation

$$\begin{aligned}\varepsilon_1 &= \langle\phi|H|\psi_\varepsilon\rangle \\ &= \langle\phi|H + H\{P[\alpha\Theta + P(\varepsilon - H)P]^{-1}\,P\}H|\phi\rangle \\ &= f(\varepsilon) \end{aligned} \tag{2.8}$$

defines a function $\varepsilon_1 = f(\varepsilon)$ of the variable $\varepsilon\,(-\infty < E < \infty)$. This function will define the eigenvalues of H as solutions of the equation

$$E = f(E) \ .$$

From (2.7), with $E = f(E)$, we have $(H-E)\,|\psi_E\rangle = 0$.

From now on, we concentrate our interest to regions where the trial ket $|\psi_\varepsilon\rangle$ is normalized. One gets directly

$$\langle \psi_\varepsilon | \psi_\varepsilon \rangle = \langle \phi | \phi \rangle + \langle TH\phi | TH\phi \rangle$$

$$= 1 + \langle TH\phi | TH\phi \rangle \quad ,$$

and the quantity $\langle TH\phi | TH\phi \rangle$ measures essentially the contribution from the orthogonal complement to the trial ket. If $\langle TH\phi | TH\phi \rangle < 1$, one speaks of a "good" reference ket for the state under consideration.

For the derivative of the function (2.8) one obtains according to (2.5)

$$f'(\varepsilon) = - \langle \phi | HT^2 H | \phi \rangle = - \langle TH\phi | TH\phi \rangle \quad < 0$$

so that the derivative $f'(\varepsilon)$ is negative. The curve for $E_\nu = f(\varepsilon)$ is hence monotonically decreasing and, further, has a series of vertical asymptotes for as many E-values as eigenvalues of the operator $\bar{H} = PHP$.

Let us now consider a continuous part of the curve $E_\nu = f(\varepsilon)$ associated with the eigenvalue E. Putting $E = E + 6$, $\varepsilon_1 = E + \beta_1$, and using the Lagrange mean value theorem, one obtains from (2.8)

$$E + \beta_1 = f(E + \beta) = f(E) + \beta . f'(E + \delta\beta)$$

i.e.

$$\beta_1 = \beta . f' (E + \delta\beta) \quad , \quad 0 < \delta < 1.$$

Since f' is negative, this result implies that β and β_1 have different signs, and that the numbers E and ε_1 bracket at least one true eigenvalue E. Because of this bracketing property, the function $E_\nu = f(E)$ is often called the "bracketing function". If E is an upper bound to E, the quantity E_ν will provide a lower bound, and vice versa. In our discussion of the bounds to energy eigenvalues in Schönberg perturbation theory we will use this property of the function $\varepsilon_1 = f(\varepsilon)$.

3. PARTITIONING TECHNIQUE AND PERTURBATION THEORY

We will denote the eigenvalues (eigenkets) of H and H_0 by E_ℓ ($|\psi_\ell\rangle$) and $E_\ell^{(0)}$ ($|\phi_\ell^{(0)}\rangle$), respecrively, i.e.

$$H|\psi_\ell> = E_\ell|\psi_\ell> \quad , \quad H_0|\psi_\ell^{(0)}> = E_\ell^{(0)}|\phi_\ell{}^0> \ , \ \ell = 0, 1, 2,... \quad (3.1)$$

In perturbation theory one starts from the general assumption that tiie Hamiltonian has the form

$$H = H_0 + V \quad (3.2)$$

where the first term H_0 is referred to às the "unperturbed Hamiltonian" and the second term V is called the "perturbation"

In the conventional approach, one considers often the Hamiltonian $H_\lambda = H_0 + \lambda V$ where A is a variable parameter, and one tries to expand the eigenfunctions and eigenvalues of H_λ into power series in λ. In Schönberg's perturbation procedure one considers $H = R + V \equiv J + I$, where J is such that $J|\phi_\ell^{(0)}> = E_0|\phi_\ell^{(0)}>$. The expansions are given in powers of I.

In order to obtain Schönberg's expansion by means of the partitioning techiiiaue, we will consider the Hamiltonian written as the sum of two terms

$$H = H_i + H_p \quad (3.3)$$

where

$$H_i|\phi_\ell^{(0)}> = h_\ell|\phi_\ell^{(0)}> \quad (3.4)$$

with

$$\lim_{H\to H_0} h_\ell = E_\ell^{(0)} \quad (3.5)$$

Let us assume that the reference ket $|\phi>$ is $|\phi_\ell^{(0)}$, a normalized eigenket of H_0 associated with the eigenvalue $E_R^{(0)}$. Then, one gets For Θ and P

$$\Theta = |\phi_\ell^{(0)}><\phi_\ell{}^{(0)}| \ ,$$

and

$$P = \sum_{\ell'\neq\ell} |\phi_{\ell'}^{(0)}><\phi_{\ell'}^{(0)}| \ . \quad (3.6)$$

Acccrding to (2.6) and (2.7), one obtains

$$|\psi_\varepsilon> = (1 + TH_p)|\phi_\ell^{(0)} \tag{3.7}$$

and

$$\varepsilon_1 = h_\ell + <\phi_\ell^{(0)}|H_p + H_p T H_p|\phi_\ell^{(0)}> \tag{3.8}$$

Introducing the reaction operator t and the wave operator w by

$$t = H_p + H_p T H_p \tag{3.9}$$

and

$$w = 1 + T H_p , \tag{3.10}$$

we have from (3.7) and (3.8)

$$|\psi_\varepsilon> = w|\phi_\ell^{(0)}> \tag{3.11}$$

$$\varepsilon_1 = h_\ell + <\phi_\ell^{(0)}|t|\phi_\ell^{(0)}> \tag{3.12}$$

The operators w and t will here be considered as functions of the parameters ε.

The operator T is essentially an inverse operator and, in this connection, we note the operator identities

$$(A - B)^{-1} \equiv A^{-1} + A^{-1}B\,(A - B)^{-1} \tag{3.13}$$

$$(A - B)^{-1} \equiv A^{-1} + (A - B)^{-1}BA^{-1} \tag{3.14}$$

which are valid provided that the inverse operators involved exist.

In order to obtain perturbative expansions it should be observed that one has for T the transforrnation

$$\begin{aligned} T &= P\,[\alpha\Theta + P(\varepsilon - H_i)P - P\,H_p\,P]^{-1}\,P \\ &= P\,[\alpha\Theta + P(\varepsilon + \Lambda - H_i)P - P(H_p+\Lambda)P]^{-1}P, \end{aligned} \tag{3.15}$$

where Λ is a real variable.

Thus, if one applies the identities (3.13) and (3.14) to the operator T with $A = \alpha\Theta + P(\varepsilon - \Lambda - H_i)P$ and $B = P(H_p + h)\,P$ one obtains

$$T = T_{\Lambda i} + T_{\Lambda i}\, H_p'\, T \tag{3.16}$$

or

$$T = T_{\Lambda i} + T\, H_p'\, T_{\Lambda i} \quad , \tag{3.17}$$

where

$$T_{\Lambda i} = P\left[\alpha\Theta + P(\varepsilon + \Lambda - H_i)P\right]^{-1} P \tag{3.18}$$

and

$$H_p' = H_p + \Lambda. \tag{3.19}$$

Repeated use of (3.16) leads to the infinite expansion

$$T = \sum_{n=0}^{\infty} (T_{\Lambda i}\, H_p')^n\, T_{\Lambda i}. \tag{3.20}$$

Using the definitions (3.9), (3.10) and the expansion (3.20), we have

$$w = 1 + \sum_{n=0}^{\infty} (T_{\Lambda i}\, H_p')^n\, T_{\Lambda i}\, H_p \tag{3.21}$$

$$t = H_p\,(1 + \sum_{n=0}^{\infty} (T_{\Lambda i}\, H_p')^n\, T_{\Lambda i}\, H_p)\ . \tag{3.22}$$

Substituting expansion (3.21) into (3.11), and (3.22) into (3.12), we obtain the fundamental formulas

$$|\psi_\varepsilon\rangle = \left[1 + \sum_{n=0}^{\infty} (T_{\Lambda i}\, H_p')^n\, T_{\Lambda i}\, H_p\right] |\phi_\ell^{(0)}\rangle \tag{3.23}$$

$$\varepsilon_1 = h_\ell + \langle\phi_\ell^{(0)}|H_p\,|1 + \sum_{n=0}^{\infty} (T_{\Lambda i}\, H_p')^n\, T_{\Lambda i}\, H_p\,||\phi_\ell^{(0)}\rangle\ . \tag{3.24}$$

These relations are the perturbative expansions obtained when we consider $H = H_i + H_p$, where H_i is sush that $H_i\,|\phi_\ell^{(0)}\rangle = h_\ell\,|\phi_\ell^{(0)}\rangle$ and $|\phi_\ell^{(0)}\rangle$ are eigenkets of H_0 associated with the eigenvalues $h_\ell^{(0)}$

The usefulness of the relations *(3.23)* and *(3.24)* is that they allow to obtain the Brillouin, Schrlldinger and Schblnberg-type expansions by using convenient choice of the parameter A and the operator H_i. In fact, if we take $\Lambda = 0$ and $H_i = H$, , we have $h_\ell = E_\ell^{(0)}$, $H'_p = H_P \equiv V$ and the formúlae *(3.23)* and *(3.24)* give the Brillouin expansion. If we take $\Lambda = -\Delta E_\ell = (E_\ell^{(0)} - E)$ and $H_i = H$,, one obtains $h_\ell = E_R^{(0)}$. $H'_p = H_p - \Delta E = V - \Delta E_R \equiv V'$, and we have the Schrlldinger-type perturbation theory.

4. SCHÖNBERG PERTURBATION THEORY

If we consider $\Lambda=0$ and $H_i|\phi_\ell^{(0)}> = E_\ell|\phi_\ell^{(0)}>$, we have, using the Schönberg's notation,

$$H_i \equiv J \ , \quad H' = H_P \equiv I \quad ,$$

and the reduced resolvent $T_{\Lambda i}$ will be

$$T_{\Lambda i} = P|\alpha\Theta + P(\varepsilon - J)P|^{-1} P \equiv K_\varepsilon$$

with

$$\Theta = |\phi_\ell^{(0)}><\phi_\ell^{(0)}| \ ; \quad P = 1 - |\phi_\ell^{(0)}><\phi_\ell^{(0)}|$$

l'hen, from *(3.23)* and (3.24), it follows that

$$|\psi_\varepsilon> = \sum_{n=0}^{\infty} (K_\varepsilon I)^n \, |\phi_\ell^{(0)}> \tag{4.1}$$

$$\varepsilon_1 = E_\ell + <\phi_\ell^{(0)}| \, I \sum_{n=0}^{\infty} (K_\varepsilon I)^n |\phi_\ell^{(0)}> \ . \tag{4.2}$$

If one uses the relations *(3.2)* and *(3.3)* with $H_i = J$ and $H_P = I$, one obtains

$$I = H - J = H_0 + V - J \ , \tag{4.3}$$

and from (4.1) and *(4.2)* one has

$$|\psi_\varepsilon> = \sum_{n=0}^{\infty} (K_\varepsilon I)^n |\phi_\ell^{(0)}> \tag{4.4}$$

$$\varepsilon_1 = E_\ell^{(0)} + <\phi_\ell^{(0)}| V \sum_{n=0}^{\infty} (K_\varepsilon I)^n |\phi_\ell^{(0)}> \tag{4.5}$$

We note that we are here dealing with a Schönberg-type perturbation theory which contains a variable parameter ε and a bracketing function $\varepsilon_1 = f(\varepsilon)$ such that the interval $(\varepsilon,\varepsilon_1)$ contains a true eigenvalue E. The expansions obtained by Schönberg are limited to the point $\varepsilon_1 = \varepsilon = E$. They coincide with (4.4) and (4.5) in the point $\varepsilon_1 = \varepsilon = E_\ell$.

From (3.9) and (3.10) we note that in Schönberg-type perturbation theory the wave and reaction operators sre defined, respectively, by

$$w = 1 + I\,T \tag{4.6}$$

and

$$t = I + I\,T\,I. \tag{4.7}$$

According to (4.2), this means that in the point $\varepsilon_1 = \varepsilon = E_\ell$ we have $<\phi_\ell^{(0)}|t|\phi_\ell^{(0)}> = 0$. This result implies that in the evaluation of bounds to energy eigenvalues the relations involving the inverse operator t^{-1} cannot Le used. In the Schrödinger and Brillouin perturbation theories $<\phi_\ell^{(0)}|t|\phi_\ell^{(0)}> \neq 0$ and the relations involving t^{-1} are then the starting point for the treatment of lower and upper bounds for E_ℓ [8].

5. UPPER AND LOWER BOUNDS TO GROUND STATE ENERGY EIGENVALUE

We will here use cperator inequalities as our main tool [8], i.e. if A and B are two self-adjoint operators, we will write $A \geq B$, if one has the relation

$$<\psi|A|\psi> \geq <\psi|B|\psi> \tag{5.1}$$

for all $|\psi>$ on the common domain of A and B.

If C is an arbitrary linear operator, the transformation $|\psi> =$

$= \sim |\psi'\rangle$ leads to the new inequality

$$C^{\dagger} A\, C > C^{\dagger}\, B\, C. \tag{5.2}$$

A negative definite operator A satisfies hence the inequality $A < 0$, and if the inverse exists, one has further $A^{-1} < 0$, i.e.

$$A < 0 \rightarrow A^{-1} < 0 \tag{5.3}$$

In the Schönberg-type perturbation theory we have from (4.2) and (3.16) that, for the ground state,

$$\varepsilon_1 = E_0 + \langle \phi_0^{(0)} | t | \phi_0^{(0)} \rangle , \tag{5.4}$$

$$T = K_{\varepsilon} + T\, I\, K_{\varepsilon} \tag{5.5}$$

where

$$t = \sum_{n=0}^{\infty} I\, (K_{\varepsilon} I)^n , \tag{5.6}$$

and the operator K_{ε} has the spectral resolution

$$K_{\varepsilon} = \sum_{\ell \neq 0}^{\infty} (\varepsilon - E_{\ell})^{-1} |\phi_{\ell}^{(0)}\rangle \langle \phi_{\ell}^{(0)}| . \tag{5.7}$$

We will assume that the variable E is such that

$$\varepsilon < E_1 < E_2 < E_3 < \ldots \tag{5.8}$$

According to (5.7), the condition (5.8) implies that

$$K_{\varepsilon} < 0 \tag{5.9}$$

that is, the operator K_{ε} is negative definite.

For the operator T (see (3.15)) one may obtain the following spectral resolution

$$T = \sum_{k=1}^{\infty} (\varepsilon - \bar{E}_k)\, |\bar{\psi}_k\rangle \langle \bar{\psi}_k| , \tag{5.10}$$

where $\bar{E}_k$ and $|\bar{\psi}_k\rangle$ denote the eigenvalues and eigenkets to $\bar{H} = PHP$, respectively.

Using the result[8,12] that the eigenvalues to $\bar{H} = P H P$, $\bar{E}_k$, are such that

$$E_{k-1} \leq \bar{E}_k \leq E_k , \quad k = 1, 2, \ldots$$

it follows from (5.10) that the operator T is negative definite when $\varepsilon < \bar{E}_1$. We will consider this case.

According to (5.5) the operator T may be expressed in the form

$$T = (1 - K_\varepsilon I)^{-1} K_\varepsilon .$$

Hence one has

$$T^{-1} = K_\varepsilon^{-1} - I . \tag{5.11}$$

From the relations (5.9) and (5.3) we have $K_\varepsilon^{-1} < 0$. This implies, according to (5.11), that

$$T^{-1} < -I ,$$

or if we consider I positive definite

$$T > -I^{-1} . \tag{5.12}$$

For the operator T, one has consequently

$$0 > T > -I^{-1} , \quad \varepsilon < \bar{E}_1 < E_1$$

A still better bound for T is rendered if we consider the expansion

$$T = \sum_{i=0}^{2n-1} K_\varepsilon (IK_\varepsilon)^i + (K_\varepsilon I)^n T (IK_\varepsilon)^n , \tag{5.13}$$

obtained from the relation (5.5). In fact, with T < 0 we obtain

$$(K_\varepsilon I)^n T (IK_\varepsilon)^n < 0 , \tag{5.14}$$

and from $T > -I^{-1}$. it follows that

$$(K_\varepsilon I)^n T (IK_\varepsilon)^n > -(K_\varepsilon I)^n I^{-1} (IK_\varepsilon)^n . \quad (5.15)$$

tience one obtains from (5.13)

$$T < \sum_{i=0}^{2n-1} K_\varepsilon (IK_\varepsilon)^i \quad (5.16)$$

and

$$T > \sum_{i=0}^{2n-1} K_\varepsilon (IK_\varepsilon)^i - (K_\varepsilon I)^n I^{-1} (IK_\varepsilon)^n . \quad (5.17)$$

The connection between the operator T and the reaction operator t is expressed in the definition (4.7). Substitution of the bounds (5.16) and (5.17) into (4.7) gives

$$t < \sum_{i=0}^{2n} I(K_\varepsilon I)^i \quad (5.18)$$

and

$$t > \sum_{i=0}^{2n-1} I(K_\varepsilon I)^i . \quad (5.19)$$

Substituting the estimates (5.18) and (5.19) into the relation (5.4), it follows that

$$\varepsilon_1 < E_0 + \langle \phi_0^{(0)} | \sum_{i=0}^{2n} I(K_\varepsilon I)^i | \phi_0^{(0)} \rangle \quad (5.20)$$

and

$$\varepsilon_1 > E_0 + \langle \phi_0^{(0)} | \sum_{i=0}^{2n-1} I(K_\varepsilon I)^i | \phi_0^{(0)} \rangle \quad (5.21)$$

Using (4.3) one has

$$\varepsilon_1 < E_0^{(0)} + \langle \phi_0^{(0)} | \sum_{i=0}^{2n} V(K_\varepsilon I)^i | \phi_0^{(0)} \rangle \quad (5.22)$$

and

$$\varepsilon_1 > E_0^{(0)} + \langle \phi_0^{(0)} | \sum_{i=0}^{2n-1} V(K_\varepsilon I)^i | \phi_0^{(0)} \rangle \qquad (5.23)$$

From the bracketing property of the functicn $E_1 = f(\varepsilon)$ one obtains finally

i) if $a < E_0$, then $\varepsilon_1 > E_1$, and from (5.22) we have

$$E_0 < E_0^{(0)} + \sum_{i=0}^{2n} \langle \phi_0^{(0)} | V (K_\varepsilon I)^i | \phi_0^{(0)} \qquad n = 1,2... \qquad (5.24)$$

ii) if $\varepsilon > E_0$, then $\varepsilon_1 < E_0$ and from (5.23) we have

$$E_0 > E_0^{(0)} + \sum_{i=0}^{2n-1} \langle \phi_0^{(0)} | V (K_\varepsilon I)^i | \phi_0^{(0)} \quad , n=1,2... \qquad (5.25)$$

The partial sums of even (odd) orders in I form hence a set of upper (lower) bounds to the true eigenvalue E in the Schönberg-type perturbation theory.

We conclude this section by noting that the case $I < 0$ does not occur in the Schdnberg perturbation theory because one has

$$\langle \phi_0^{(0)} | I | \phi_0^{(0)} \rangle = \langle \phi_0^{(0)} | H | \phi_0^{(0)} \rangle - E_0 < 0 ,$$

and this result is contrary to the variation principle[13].

7. CONCLUSIONS

The bracketing function in the partitioning technique has been used in the evaluation of the lower and upper bnunds to ground state energy eigenvalue in Schdnberg perturbation theory.

The expressions obtained from the partitioning technique for the upper and lower bounds in Schrtldinger and Brillouin theories are essentially confined to the case of a positive definite perturbation. This fact could be a disadvantage of these theories if we wanttoobtain numerical results. A simple physical example we can quote for a non-positive perturbation is the Stark-effect. In the Schönberg's procedure,

the perturbed Hamiltonian is written as $H = J + \lambda I$ (J is such that $J|\phi_q^{(0)}> = E_q|\phi_q^{(0)}>$) and the expansions are given in powers of λ, where I is necessarily positive definite. Our results are true for all I which can occur in the theory, and this includes the cases which can not be studied by Schrödinger and Brillouin bounds. The only condition we have to impose is $\varepsilon < \bar{E}_1 < E_1$. This implies that it is necessary to know a rough lower bound of the lowest eigenvalue $\bar{E}_1$ of the operator $\bar{H} = PHP$. In Schrddinger and Brillouin theories, for $V > 0$, a such condition isnot imposed because we can use the relations involving the inverse operator t^{-1} as starting point for the study of bounds. In the modified perturbation theory proposed by Schdnberg the corresponding inverse operator t^{-1} does not exist.

In order to study the relative utility of Schrddinger, Brillouin and Schdnherg bounds in determining the exact eigenvalue E_n, applications of our results to the atomic and molecular systems were initiated. We hope to report these results in a forthcoming paper.

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12. In the reference (8) the lowest eigenvalues to H and $\bar{H}$ are dcsigned by E, and $\bar{E}_1$, respectively. Hence, one has $E_k \leq \bar{E}_k$. In our paper, the lowest eigenvalue to H is designed by E, while to $\bar{H}$ is $\bar{E}_1$. Thus we have $E_{k-1} \leq \bar{E}_k \leq E_k$, k = 1,2,... .

13. The variation principle says that the expectation value

$$\langle H \rangle_{av} = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}$$

gives an upper bound to E_0, eigenvalue of H , for arbitrary kets $|\phi\rangle$. In particular it is true that $\langle H \rangle_{av} \geq E$, if $|\phi\rangle$ i $|\phi_0^{(0)}\rangle$, where $|\phi_0^{(0)}\rangle$ is eigenket of H, associated to eigenvalue $E_0^{(0)}$.