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On the upper bounds in Brillouin-Wigner perturbation theory

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Chimica teorica. — *On the upper bounds in Brillouin–Wigner perturbation theory* (*). Nota di GIORGIO ORLANDI, presentata (**) dal Socio G. SEMERANO.

RIASSUNTO. — Nella teoria perturbativa di Brillouin–Wigner, il principio viariazionale permette di ricavare i limiti superiori dell'energia, ma non quelli inferiori. Questi si ottengono attraverso la funzione racchiudente, mediante la tecnica della proiezione interna. In questa Nota si mostra che anche i limiti superiori dell'energia si possono ricavare con questa tecnica.

Upper bounds in Brillouin-Wigner perturbation theory have been derived following the variational principle [1, 2], but they may be obtained also by the bracketing function approach [3, 4].

In order to solve the Schroedinger equation $\mathcal{H}\psi_k = E_k \psi_k$ the Hamiltonian is written in the form $\mathcal{H} = \mathcal{H}_0 + V$ with $\mathcal{H}_0 \varphi_k = E_k^0 \varphi_k$. Introduction of the projection operators

$$O = | \varphi_0 \rangle \langle \varphi_0 | \qquad P = 1 - O \tag{1}$$

and of the reduced solvent

$$T(\varepsilon) = P(\varepsilon - \mathcal{H})^{-1} \tag{2}$$

leads to the bracketing function [3, 4]

$$\varepsilon_1 = E_0^0 + \langle \varphi_0 | t(\varepsilon) | \varphi_0 \rangle \tag{3}$$

where $t(\varepsilon)$, the reaction operator, can be written as

$$t(\varepsilon) = V - V(T(\varepsilon))V. \tag{4}$$

If ε is an upper bound to the ground state eigenvalue E_0, ε_1 is a lower bound to it, and viceversa [3, 4].

In the range where $-T(\varepsilon)$ is a positive definite operator inner projection may be applied to it. Given an arbitrary linear manifold $\boldsymbol{h} = (h_1, h_2, \cdots, h_m)$, we define the so-called Bazley projection of a positive definite operator A by [5]

$$A' = | \boldsymbol{h} \rangle \langle \boldsymbol{h} | A^{-1} | \boldsymbol{h} \rangle^{-1} \langle \boldsymbol{h} | \tag{5}$$

with $A \geq A'$, where the inverse is assumed to exist. Setting $A = -T(\varepsilon)$, $\boldsymbol{h} = (\varphi^{(1)}, \varphi^{(2)} \cdots \varphi^{(m)})$ and taking into account eq. (3) we get

$$\varepsilon_1' = E_0^0 + t_1 - \beta^+ \Delta^{-1} \beta \tag{6}$$

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(**) Nella seduta del 13 dicembre 1969.

where $\beta^{+} = (t_2, t_3 \cdots t_{m+1})$ is a row vector of order m and Δ is the $m \times m$ matrix with elements $\Delta_{kl} = t_{k+l+1} - t_{k+l}$. $\varphi^{(n)}$ and t_n have the usual meaning of n-order perturbation function and energy respectively.

Since $\varepsilon_1'(\varepsilon) > \varepsilon_1(\varepsilon)$, equation (6), for the properties of the bracketing function, renders an upper bound to E_0 for $\varepsilon \leq \varepsilon_1'$. Furthermore, for $T < 0$, it is identical to the variational result derived in Ref. 1 and 2.

A discussion about the condition $T < 0$, which has to be satisfied in order that eq. (6) is valid, together a more detailed derivation, is being published.

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