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Lower bounds of error for a trial wave function

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Chimica fisica. — *Lower bounds of error for a trial wave function.* Nota di PAOLA BONELLI e GIAN FRANCO MAJORINO, presentata (*) dal Corrisp. M. SIMONETTA (**) (***).

RIASSUNTO. — Si considera l'equazione di Schrödinger $H\psi = E\psi$. Partendo da una base di funzioni di prova $\varphi_1 \cdots \varphi_n$, e calcolati gli usuali integrali $\int \varphi_i H \varphi_j \, d\tau$ e $\int \varphi_i \varphi_j \, d\tau$, è possibile dedurre un limite inferiore per $\int \varphi_i H^2 \varphi_i \, d\tau$ e quindi anche per la « varianza » $\int [(H - E) \varphi_i]^2 \, d\tau$. Tali limiti sono stati calcolati con diverse funzioni di prova per l'atomo di Idrogeno e confrontati con i valori esatti.

1.—INTRODUCTION.

The research of lower bounds for the Schrödinger equation expectation values is actually carried out by expansion method or by projection method.

Investigating these two procedures, Bright Wilson jr. [1] points out that a great difficulty for the former one is the calculation of integrals of the type:

$$M = \int \varphi H^2 \varphi \, d\tau$$

where H is the hamiltonian operator and φ a trial wave function. A simple lower bound for M is given by the square of $\int \varphi H \varphi \, d\tau$: this one can be immediately derived by the demostration of Weinstein's formula (see [2], formulas 26–29).

But the bound obtained in this way is very poor in meaning: for example, it is impossible to calculate with it an effective bound for the energy variance function:

$$U^2 = \int [(H - E) \varphi]^2 \, d\tau.$$

In this work we demonstrate a simple approximation formula which gives a value between the square of $\int \varphi H \varphi \, d\tau$ and M. Then from such value it

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is possible to evaluate a lower bound for the variance U^2; the calculations reported in the last section are in good agreement with the exact values calculated for the hydrogen atom.

However, it is clear that the best advantages could be obtained by the knowledge of upper and lower bounds of M and U^2. Figures 1 and 2 seem to suggest interesting indications in this direction.

2.—APPROXIMATION FORMULA FOR M.

Given the Schrödinger equation for a stationary state:

$$H\psi = E\psi \tag{1}$$

we consider two real normalized trial functions φ_1, φ_2 with the usual integrals $S = \int \varphi_1 \varphi_2 \, d\tau$ and $H_{ij} = \int \varphi_i H\varphi_j \, d\tau$.

By Schwartz's inequality applied to a linear combination $\varphi_1 + a\varphi_2$ we obtain:

$$\left[\int (\varphi_1 + a\varphi_2) H\varphi_1 \, d\tau \right]^2 \leq \int (\varphi_1 + a\varphi_2)^2 \, d\tau \cdot \int (H\varphi_1)^2 \, d\tau \tag{2}$$

and by hermitian proprieties of H:

$$H_{11}^2 + a^2 H_{12}^2 + 2 a H_{11} H_{12} \leq (1 + a^2 + 2 aS) \cdot M.$$

This relation must be true for any value of the parameter a: with some manipulations (taking care that by normalization proprieties of φ_1 and φ_2 it follows that $1 - S^2 > 0$) this leads to:

$$M \geq H_{11}^2 + \frac{(SH_{11} - H_{12})^2}{1 - S^2} \geq H_{11}^2 . \tag{3}$$

About the meaning of this formula we can make the following remarks:

a) by Weinstein's formula:

$$H_{11} \geq E \geq H_{11} - \sqrt{M - H_{11}^2} \tag{4}$$

we can see that the difference between M and H_{11}^2 tends to zero when φ_1 tends to ψ; even more so (see (3)) the difference between M and its approximation:

$$T = H_{11}^2 + \frac{(SH_{11} - H_{12})^2}{1 - S^2} .$$

Qualitatively we can say that T is as much a better approximation for M as the trial function φ_1 is a good one for the exact eigenfunction.

b) The meaning of the error $M - T$ we make using inequality (3) can be made clear as follows: let us consider the $H\varphi_1$ function as linear com-

bination of φ_1 and φ_2:

$$H\varphi_1 = a\varphi_1 + b\varphi_2 + f_{ab}$$

where f_{ab} is a function different from zero unless $H\varphi_1$ can be exactly expanded in terms of φ_1 and φ_2.

Squaring and integrating we obtain:

$$\int f_{ab}^2 \, d\tau = a^2 + b^2 + 2\,abS - 2\,aH_{11} - 2\,bH_{12} + M. \tag{5}$$

The minimum of the norm of f_{ab} with respect to the a, b parameters is for:

$$a = \frac{H_{11} - SH_{12}}{1 - S^2} \quad ; \quad b = \frac{H_{12} - SH_{11}}{1 - S^2}.$$

Substituting these parameter values into (5) we have at last:

$$\mathrm{Min} \int f_{ab}^2 \, d\tau = M - T.$$

Then, the best φ_2 functions we can use into (3) are such that φ_1 and φ_2 are an expansion basis for $H\varphi_1$.

c) We can take φ_2 as linear combination of n given functions $g_1 \cdots g_n$. The coefficients can be optimized with the two conditions (i) T maximum, (ii) φ_2 normalized.

Otherwise, we can repeat the previous procedure starting from an obvious generalisation of (2):

$$\left[\int \Sigma a_i \, g_i \, H\varphi_1 \, d\tau \right]^2 \leq \int \Sigma a_i \, a_j \, g_i \, g_j \, d\tau \cdot \int (H\varphi_1)^2 \, d\tau.$$

3.—Approximation formula for U^2.

Goodness evaluation for a trial wave function φ_1 is given usually by the energy variance function [3], [4]:

$$U^2 = \int [(H - E)\,\varphi_1]^2 \, d\tau$$

or alternatively by the remaining variance [5]:

$$\sigma^2 = \int [(H - H_{11})\,\varphi_1]^2 \, d\tau.$$

The graphs of the functions:

$$f(\lambda) = \int [(H - \lambda)\,\varphi_1]^2 \, d\tau = M - 2\,\lambda H_{11} + \lambda^2$$

are given in fig. 1, with exact value for M and with M approximated by T.

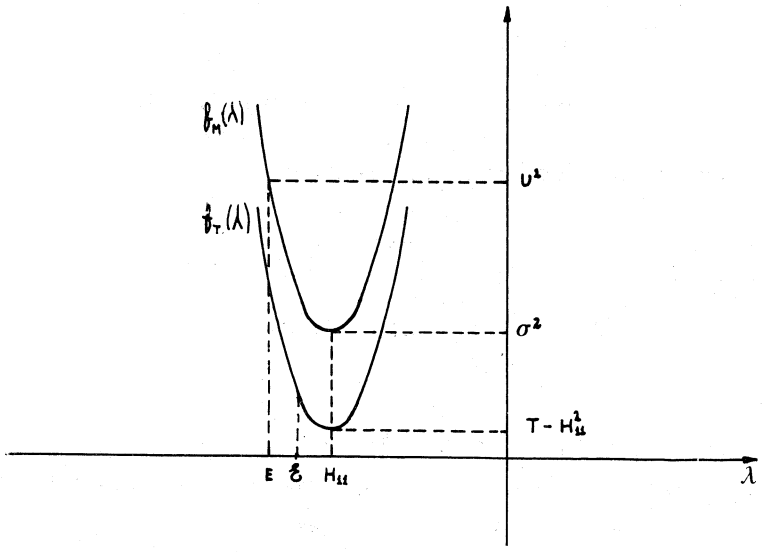


Fig. 1. – Graphs of the functions: $f_M(\lambda) = M - 2\lambda H_{11} + \lambda^2$ and $f_T(\lambda) = T - 2\lambda H_{11} + \lambda^2$.

With obvious considerations such analysis can be generalized by the following inequalities:

$$U^2 \geq \sigma^2 = M - H_{11}^2 \geq T - H_{11}^2 \tag{6}$$

$$U^2 \geq T - 2\,\mathcal{E}H_{11} + \mathcal{E}^2 \tag{7}$$

where $\mathcal{E}$ represents any approximation for E that is better than H_{11}. For instance, having φ_1 and φ_2 we can calculate $\mathcal{E}$ with the ordinary Ritz variation method.

Further improvement in this direction could be made considering the graph of E bounds by Weinstein's formula (4), reported in fig. 2.

This graph is very expressive about the rôle played by the different approximations of M.

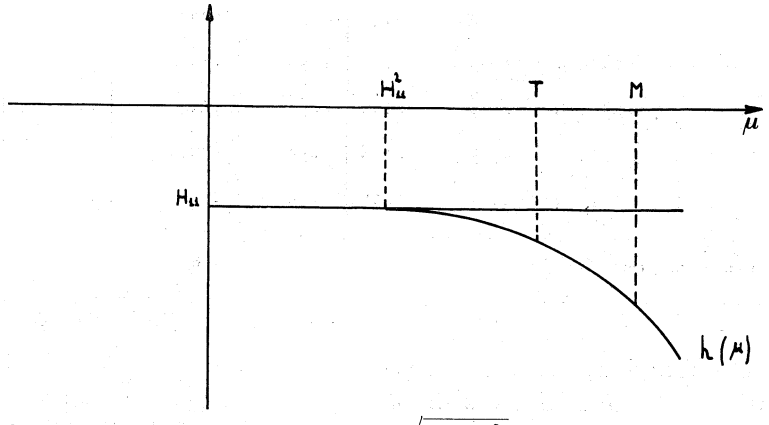


Fig. 2. – Graph of the function: $h(\mu) = H_{11} - \sqrt{\mu - H_{11}^2}$. For $\mu = M$ we have the energy bounds as by Weinstein's inequality (4).

4.—Numerical results.

Approximated values furnished by (3), (6), (7) have been compared with exact values for the hydrogen atom. In Table I we report the results obtained from three different φ_1 functions.

Table I.

δ_1	δ_2	δ_3	M	T	H_{11}^2	U^2	$T+\mathcal{E}^2-2\mathcal{E}H_{11}$	σ^2	$T-H_{11}^2$
.50	.6	.9	.2031	.1801	.1406	.0781	.0521	.0625	.0395
.50	.6	3.	.2031	.1949	.1406	.0781	.0552	.0625	.0542
.50	.6	15.	.2031	.1871	.1406	.0781	.0465	.0625	.0465
.50	2.	.9	.2031	.1906	.1406	.0781	.0533	.0625	.0500
.50	2.	3.	.2031	.1932	.1406	.0781	.0534	.0625	.0525
.50	2.	15.	.2031	.2007	.1406	.0781	.0601	.0625	.0601
.85	.6	.9	.2551	.2463	.2389	.0164	.0075	.0163	.0074
.85	.6	3.	.2551	.2514	.2389	.0164	.0126	.0163	.0126
.85	.6	15.	.2551	.2510	.2389	.0164	.0121	.0163	.0121
.85	2.	.9	.2551	.2499	.2389	.0164	.0111	.0163	.0111
.85	2.	3.	.2551	.2516	.2389	.0164	.0128	.0163	.0128
.85	2.	15.	.2551	.2542	.2389	.0164	.0153	.0163	.0153
.95	.6	.9	.2510	.2497	.2488	.2258 (*)	.0940 (*)	.2256 (*)	.0938 (*)
.95	.6	3.	.2510	.2504	.2488	.2258	.1682	.2256	.1682
.95	.6	15.	.2510	.2505	.2488	.2258	.1701	.2256	.1701
.95	2.	.9	.2510	.2502	.2488	.2258	.1464	.2256	.1463
.95	2.	3.	.2510	.2505	.2488	.2258	.1728	.2256	.1727
.95	2.	15.	.2510	.2509	.2488	.2258	.2112	.2256	.2112

(*) We have multiplied by 10^2 the values of the last 4 columns relative to $\delta_1 = .95$.

All our functions are 1s Slater-type orbitals.

In the first column there is the δ_1 exponent of φ_1. We chose the numerical values: $\delta_1 = .50$; .85; .95; to represent respectively a bad, a mediocre and a good trial function.

Then we have constructed φ_2 as linear combination of two 1s orbitals:

$$\varphi_2 = N(g_2 + ag_3)$$

optimizing the parameter a by the procedure shown in section 2, *c*).

The exponents of g_2 and g_3 are reported in the second and third columns. In order to examine a significatively extended set of φ_2 functions, we have chosen the numerical values .60 and 2.00 for δ_2, and the numerical values .90; 3.00; 15.00 for δ_3.

The T approximation is the less sensitive to φ_2 variations the more φ_1 is a good function.

REFERENCES.

[1] E. BRIGHT WILSON, JR., *Lower bounds for eingenvalues*, « J. Chem. Phys. », *43*, S172 (1965).

[2] PAULING–WILSON, *Introduction to Quantum Mechanics*, Mc Graw–Hill Book Company, New York 1935.

[3] JAMES–COOLIDGE, *Criteria of Goodness for approximate Wave Functions*, « Phys. Rev. », *51*, 860 (1937).

[4] CONROY, *Properties of the Energy Variance Functions: the estimation of Energy Eingenvalues*, « J. Chem. Phys. », *47*, 930 (1967).

[5] FRÖMAN–HALL, *The Accuracy of Atomic Wave Functions and their Scale*, « J. Mol. Spec. », *7*, 410 (1961).