THEORETICA CHIMICA ACTA

Theoret. Chim. Acta (Berl.) 56, 183–189 (1980)

Variance Minimization. A Variational Principle for Accurate Lower and Upper Bounds of the Eigenvalues of a Selfadjoint Operator, Bounded Below

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In connection with Temple's formula variance minimization yields accurate values especially for groundstate energies of Schrödinger operators with a discrete spectrum.

The result in a.u. for the groundstate E_0 of the He-atom in the infinite nuclear mass approximation is

$$-2.9037243865_5 \leq E_0 \leq -2.9037243769_6$$

i.e. E_0 is determined with an absolute error smaller than 0.0022 cm^{-1}.

Key words: Eigenvalue problems.

1. Introduction

The determination of eigenvalues of the nonrelativistic Schrödinger operator with spectroscopic accuracy, that is within an error of approximately 0.005 cm^{-1} is even for the groundstate of the He-atom a hard problem as shown by Kinoshita [1], Pekeris [2], Gay [3] and others.

The main method used to get upper bounds is the Rayleigh–Ritz principle. Among others the method of Bazley and Fox [4] and its generalization by Hill [5] are available for lower bounds. An effective accurate lower bound of the groundstate E_0 is obtained by Temple's formula [6], which could be used too for the excited states E_i with suitable ρ. In the following the discussion is limited to the

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0040-5744/80/0056/0183/$01.40

evaluation of the groundstate E_0, the necessary extension needed for the calculation of E_i could be done analogously.

For a selfadjoint operator H, bounded below, with a discrete spectrum $\sigma_d = \{E_i | E_0 < E_1 < \cdots\}$ below the bottom of the continuum Temple's formula yields

$$E_0 \geq (Hu, u) - \frac{\|Hu\|^2 - (Hu, u)^2}{\rho - (Hu, u)}, \qquad u \in D_H, \qquad \|u\| = 1$$

with D_H as the domain of H and $E_0 < \rho < E_1$. As can be seen from Temple's formula the knowledge of a "good" value for ρ, i.e. a sharp lower bound for E_1 is not very effective for a better value of a lower bound of E_0. Much more essential for a good lower bound is a small value of the variance

$$F[u] = \|Hu\|^2 - (Hu, u)^2.$$

This idea leads to the method of variance minimization [7].

2. The Method of Variance Minimization

Let H be a selfadjoint operator in the Hilbert-space L^2, where $\|\cdot\|$ and $(\cdot, \cdot)$ denote the usual L^2-norm and inner product, respectively. Furthermore let D_H be the domain of H, $\sigma(H)$ the spectrum and $\rho(H)$ the resolvent set of H. From the spectral theorem of selfadjoint operators for each $v \in L^2$ and $u \in D_A$ with $A = f(H)$ and continuous f follows

$$(v, f(H)u) = \int_{-\infty}^{\infty} f(\lambda)\, d(v, E_\lambda u) \tag{1}$$

with $\{E_\lambda\}$ as a spectral family of H. Let λ^* be an arbitrary real number and r the distance between λ^* and $\sigma(H)$, i.e.

$$r = \inf_{\lambda \in \sigma(H)} |\lambda - \lambda^*|$$

It follows for every $u \in D_H$ from (1)

$$r^2 \|u\|^2 = \int_{-\infty}^{\infty} r^2\, d\|E_\lambda u\|^2 \leq \int_{-\infty}^{\infty} |\lambda - \lambda^*|^2\, d\|E_\lambda u\|^2$$
$$= \|(H - \lambda^*)u\|^2$$

taking into account $E_\lambda u$ being a constant function on $\rho(H)$ with respect to λ and $r^2 \leq |\lambda - \lambda^*|^2$ for all $\lambda \in \sigma(H)$. The obtained inequality

$$\inf_{\lambda \in \sigma(H)} |\lambda - \lambda^*| \leq \|(H - \lambda^*)u\|, \qquad u \in D_H, \qquad \|u\| = 1$$

leads for a n-dimensional subspace $V_n \subset D_H$ to the principle of variance minimization as stated in [7]:

Minimization of the non-negative functional

$$F[u] = \|Hu\|^2 - (Hu, u)^2, \qquad \|u\| = 1$$

i.e. the determination of

$$F_0^* = \inf_{u \in V_n} F[u] = F[u_0^*]$$

gives an $u_0^* \in V_n$ and further a $\lambda_0^* = (Hu_0^*, u_0^*)$ with

$$\inf_{\lambda \in \sigma(H)} |\lambda - \lambda_0^*|^2 \leq F_0^*.$$

Because $\sigma(H)$ is a closed set on the real line considered as a metric space, there is at least one point $\lambda_0 \in \sigma(H)$ for which the infimum is achieved. Therefore

$$|\lambda_0 - \lambda_0^*|^2 \leq F_0^*$$

and λ_0^* is an approximate value for λ_0 with the error $\sqrt{F_0^*}$.

For a selfadjoint operator H, bounded below, with a discrete spectrum $\sigma_d = \{E_i | E_0 < E_1 < \cdots\}$ below the bottom of the continuum the lower bound $\lambda_0^* - \sqrt{F_0^*}$ for the lowest eigenvalue $\lambda_0 = E_0$ can be essentially sharpened by Temple's formula, because in this formula F_0^* is used instead of $\sqrt{F_0^*}$. With

$$\lambda_0^* = (Hu_0^*, u_0^*) \quad \text{and} \quad F_0^* = F[u_0^*]$$

one obtains a lower bound E_0^* for E_0 with

$$E_0 \geq E_0^* = \lambda_0^* - \frac{F_0^*}{\rho - \lambda_0^*} \tag{2}$$

if a suitable value for ρ is available. But the method of variance minimization gives automatically a good value for ρ with $\rho = \lambda_1^* - \sqrt{F_1^*}$, if it is ensured that $\lambda_1^* - \sqrt{F_1^*}$ is a lower bound for E_1.

As is shown in [7] for an upper bound we have

$$E_0 \leq \lambda_0^r \leq \lambda_0^*$$

where λ_0^r is the Ritz value, i.e.

$$\lambda_0^r = \inf_{u \in V_n} (Hu, u) = (Hu_0^r, u_0^r), \qquad \|u\| = 1$$

Because $\lambda_0^* \geq \lambda_0^r$, but $F[u_0^*] \leq F[u_0^r] = F_0^r$ [8] the lower bound E_0^* is sharpened by both terms against the lower bound E_0^r with

$$E_0 \geq E_0^r = \lambda_0^r - \frac{F_0^r}{\rho - \lambda_0^r} \tag{3}$$

obtained from Temple's formula with the Ritz values λ_0^r and F_0^r, apart from the fact that a lower bound for E_1, i.e. a value for ρ has to be estimated in another way.

3. The Comparison of E_0^* and E_0^r for the He-Groundstate with Infinite Nuclear Mass

For the He-atom values of λ^* and F^* for the groundstate E_0 and the first excited singlet state E_1 were calculated with the linearized method of variance

minimization [9]. To compare the lower bounds which could be obtained from formula (2) and (3) the corresponding Ritz values λ_0^r and F_0^r were calculated additionally. The Schrödinger operator used for the S-states of the He-atom was

$$H = T + V$$

$$T = -\left\{\frac{\partial^2}{\partial x^2}+\frac{1}{2}\frac{\partial^2}{\partial y^2}+\frac{1}{2}\frac{\partial^2}{\partial z^2}\right.$$
$$+\frac{1}{2}\frac{x^2+y^2-z^2}{xy}\frac{\partial^2}{\partial x\partial y}+\frac{1}{2}\frac{x^2+z^2-y^2}{xz}\frac{\partial^2}{\partial x\partial z}$$
$$\left.+\frac{2}{x}\frac{\partial}{\partial x}+\frac{1}{y}\frac{\partial}{\partial y}+\frac{1}{z}\frac{\partial}{\partial z}\right\} \tag{4}$$

$$V = \frac{1}{x}-\frac{2}{y}-\frac{2}{z}$$

and the test functions were linear combinations of basic functions

$$\psi_{\mathrm{prs}} = x^p y^r z^s \, \mathrm{e}^{-\alpha(y+z)}, \qquad \alpha = \alpha_{\mathrm{prs}} > 0 \tag{5}$$

with the notation as in [10].

The results of the calculations of the λ-values with the corresponding errors F as a function of the dimension of the vectorspace V_n spanned by the ψ_{prs} with $\alpha_{\mathrm{prs}} = 1.8$ for all indices are shown in Table 1.

Table 2 allows the comparison of the lower bounds E_0^* and E_0^r of the groundstate E_0 where the same ρ with $\rho = \lambda_1^* - \sqrt{F_1^*}$ was used in both formulas (2) and (3). The difference $\Delta = E_0^* - E_0^r$ given in cm^{-1} is relatively large even in the case of an extended basis.

The calculations were performed on a CDC Cyber 76 in double precision, i.e. with 26 digits. The dimension of the vector space was limited to 444 basic functions in first order, because the matrix diagonalization by Householder's method for still larger matrices failed. Two reasons were responsible for the instability: first the overcompleteness of the basis ψ_{prs} which yields an overlap matrix containing extremely small eigenvalues, and second the fact that the small value F_0^* is

Table 1. The λ- and F-values for E_0 and E_1 of the He-atom in a.u.

dim V_n	λ_0^r	$F_0^r \cdot 10^3$	λ_0^*	$F_0^* \cdot 10^3$	λ_1^*	$F_1^* \cdot 10^3$
7	-2.903423172_7	12.58548	-2.903030128_0	7.34200	−1.6617494	478.11400
34	-2.903716217_6	0.73267	-2.903700774_4	0.36775	−2.1039081	10.11826
95	-2.903723731_3	0.11141	-2.903721926_7	0.05198	−2.1409714	0.75060
161	-2.903724203_7	0.04188	-2.903723619_0	0.01896	−2.1449452	0.14799
203	-2.903724280_1	0.02716	-2.903723926_0	0.01215	−2.1455413	0.06415
252	-2.903724320_6	0.01816	-2.903724093_1	0.00804	−2.1457960	0.02766
444	-2.903724363_5	0.00627	-2.903724296_2	0.00271	−2.1459644	0.00196

Table 2. The comparison of the lower bounds E_0^r and E_0^* in a.u., $\Delta = E_0^* - E_0^r$ in cm^{-1}

dim V_n	$\rho = \lambda_1^* - \sqrt{F_1^*}$	E_0^r	E_0^*	Δ
7	−2.35320	−2.926296582	−2.916383343	2175.00
34	−2.20449	−2.904764047	−2.904226724	117.92
95	−2.16836	−2.903875234	−2.903792612	18.13
161	−2.15711	−2.903780296	−2.903749015	6.86
203	−2.15355	−2.903760485	−2.903740122	4.47
252	−2.15105	−2.903748447	−2.903734775	3.00
444	−2.14736	−2.903732653	−2.903727879	1.05

determined as the lowest eigenvalue of a positive definite matrix, which becomes singular as a consequence of rounding errors.

4. Accurate Lower and Upper Bounds for the Groundstate E_0 of the He-Atom with Infinite Nuclear Mass

To get a more accurate value of E_0 than obtained up to now, a better basis must be used or, respectively, a stable method has to be found to solve the generalized eigenvalue problem

$$Ax = \lambda Bx \tag{6}$$

with large matrices A and B. No general rules are known which guarantee the construction of a "good small" basis a priori. Various choices of the nonlinear parameters α_{prs} in (5) did not yield any decisive improvement. A somewhat better result was obtained with symmetry adapted coordinates

$$u = y + z, \qquad v = y - z$$

and a corresponding basis analog to (5), but also in this case larger basic sets could not be avoided.

Therefore, three iterative methods for solving the generalized eigenvalue problem (6) with large matrices were tested: The methods of Nesbeth [11] and Falk [12] were inefficient for computer technical reasons, because of the slow convergence already for relatively small matrices and memory problems for big matrices the rows of which have to be stored and processed sequentially. In contrast the Wieland iteration [13] proved to be very fast and computer suitable for the determination of the absolutely lowest eigenvalue which for positively defined A is also the lowest.

The application of the Wieland iteration was performed in such a way that starting from a suitable value for x, this value was replaced by $A^{-1}Bx$ until the Rayleigh quotient x^TAx/x^TBx barely changed. The operation A^{-1} was produced by the multiplication of two matrices which arise from a Lower–Upper-decomposition of A by Gauß algorithm. It was possible to master the decomposition and all

Table 3. Upper and lower bounds of E_0 in a.u. by Wieland iteration, $\delta = \lambda_0^* - E_0^*$ in cm^{-1}

dim V_n	λ_0^*	$F_0^* \cdot 10^8$	E_0^*	$\delta \cdot 10^3$
444	-2.903724367202_3	7.11831	-2.9037244613_2	20.6
525	-2.903724374960_5	4.15537	-2.9037244299_0	12.1
615	-2.903724376166_3	2.84863	-2.9037244138_3	8.3
715	-2.903724376746_5	2.06778	-2.9037244040_9	6.0
825	-2.903724376811_3	1.56066	-2.9037243974_5	4.5
946	-2.903724376903_6	1.11917	-2.9037243917_1	3.3
1078	-2.903724376927_9	0.95602	-2.9037243895_7	2.8
1222	-2.903724376958_5	0.72500	-2.9037243865_5	2.2

multiplications by processing the upper triangle column by column, which yields a very effective method for the calculation of the absolutely lowest eigenvalue.

With a little trick every isolated eigenvalue λ_i could be made the absolutely smallest eigenvalue by considering the modified problem

$$(A - \lambda_i^* B) = \mu_i B x \tag{7}$$

with an approximated λ_i^*, which is closer to this eigenvalue than any other. The solution of (7) leads to a

$$\mu_i = \lambda_i - \lambda_i^*$$

which for this problem is indeed the absolutely smallest eigenvalue with the same eigenvector as for the former λ_i. The identity of λ_i and λ_i^* is shown by the failure of the Lower–Upper-decomposition. With the knowledge of λ_i the eigenvector could be estimated now, if necessary by using a λ_i^* slightly different from λ_i.

Table 3 gives the result of the Wieland iteration as a function of the dimension of the basis. The value of ρ, e.g. $\rho = -2.14736$ was taken from the formerly performed calculations with 444 basic functions. As mentioned above new coordinates and a new basis with $\alpha = 3.5$ were used, i.e.

$$\Psi = \sum c_{prs} x^p u^r v^s \, e^{-\alpha u}$$

with

$$u = y + z, \qquad v = y - z$$

and the Schrödinger operator (4) was transformed into the new coordinates.

The precision of this calculation is almost better than the values of the fundamental constants, e and h, are known; latter are necessary to calculate via the Bohr radius $a_0 = 219474.62\ cm^{-1}$ [14] the energy values in cm^{-1} in order to compare with the experimental result.

Acknowledgement. We appreciate the assistance of Dr. G. Petermann, Institut für Physikalische Chemie, Universität Düsseldorf, in translating this paper.

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Received February 18, 1980