Theoret. chim. Acta (Berl.) 13, 155—158 (1969)

A Procedure for Obtaining Lower Bounds for Ground State Energies of Atoms and Molecules

M. BERSOHN, M. GLICKSOHN, and J. STEWART
Chemistry Department, University of Toronto

Received November 26, 1968

Using Löwdin's partition method we have re-derived the D. Weinstein lower bound, $E > H_{11} - \sigma$. By the same method, plus the assumption that the calculated first excited state energy is lower than a certain weighted average of approximate energies of all the excited states, we have derived a moderately better lower bound.

There exist two useful methods for obtaining lower bounds to ground state energies. One method [1, 2, 3] starts by separating the Hamiltonian of the problem into two parts, i.e. $H = H_0 + H_1$. H_0 is a part which has eigenfunctions that can be obtained exactly. This requirement seems to restrict this method to atoms.

In the other practical method, one uses the theorem of D. Weinstein [4] which guarantees that the difference between $\langle\varphi|H|\varphi\rangle$ and the nearest eigenvalue of H is less than one standard deviation, σ. The standard deviation is defined by

$$\sigma^2 = \langle\varphi|\,(H - \langle\varphi|H|\varphi\rangle)^2\,|\varphi\rangle\,.$$

Let E_2 be the energy of the first excited state. If we assume

$$\tfrac{1}{2}(E_1 + E_2) > \langle\varphi|H|\varphi\rangle \tag{1}$$

i.e., that the approximate value obtained is closer to the ground state than to the first excited state, then D. Weinstein's theorem leads to the lower bound for E_1 (also referred to as E).

$$E > \langle\varphi|H|\varphi\rangle - \sigma\,. \tag{2}$$

This method is largely inelegant because it is in essence only the quantification of assumption (1). On the other hand, with present-day computers, in practice it is quite usual in a serious *a priori* calculation to get an approximate value for the energy which is much closer to E_1 than to E_2. Consequently the assumption made is not very arbitrary; actually it is a highly likely one. It is to be noted that this method can be used for both atomic and molecular calculations.

The present paper presents a lower bound formula of the type of (2). This new lower bound is higher than that of (2). The derivation of this lower bound also utilizes an assumption, highly likely to be the case. In passing we will derive inequality (2) from another starting point.

We choose any complete, discrete and orthonormal basis. In general it will be of infinite dimension. In this basis the Schrödinger eigenvalue equation appears

as follows:

$$HC = EC\,. \tag{3}$$

The eigenvalue is represented as a column vector C. We can write the basis as $(u_1, u_2, \ldots, u_n, \ldots)$.

As is usual in solving such problems, we obtain the eigenvectors of the matrix KHK, where K is

$$\begin{pmatrix} 1_{nn} & 0 \\ 0 & 0 \end{pmatrix}.$$

The matrix K is the projection operator for the space of the first n functions out of the complete set. Next, in place of the original first n basis functions let us take the n linear combinations of them which diagonalize the KHK matrix. Let φ_1 be the eigenvector of KHK which has the lowest eigenvalue. Our new basis is $(\varphi_1, \varphi_2, \ldots, \varphi_n, u_{n+1}, u_{n+2}, \ldots)$. We have simply scrambled the first n functions; the succeeding functions from the $(n+1)$'th function on are unchanged. It will be convenient for notational clarity to rename the whole basis set as

$$(\varphi_i) = (\varphi_1, \varphi_2, \ldots, \varphi_n, \varphi_{n+1}, \varphi_{n+2}, \ldots)\,.$$

At this point we partition the basis in the manner of Löwdin [5, 6]. We divide the basis into two subspaces. The first subspace is φ_1 and the second subspace is all the other functions, i.e. the set of all functions orthogonal to φ_1. The latter set will be called the b space. Then

$$C = \begin{pmatrix} c_1 \\ C_b \end{pmatrix}.$$

Equation (3) is now written as

$$\begin{vmatrix} H_{11} & H_{1b} \\ H_{b1} & H_{bb} \end{vmatrix} \begin{vmatrix} c_1 \\ C_b \end{vmatrix} = E \begin{vmatrix} c_1 \\ C_b \end{vmatrix}, \tag{4}$$

φ_1 is our trial wave function. $H_{11} = \langle \varphi_1 | H | \varphi_1 \rangle$ is our closest approximate value for the ground state energy. H_{1b} and H_{b1} are infinite dimensional row and column vectors respectively. H_{bb} is a square matrix. The subscript b here is not an index, to be summed over; it merely indicates the b space.

At this point we diagonalize the H_{bb} matrix by a unitary transformation. The new basis functions $f_2, f_3, \ldots, f_p, \ldots$, which diagonalize H_{bb}, are used instead of $\varphi_2, \varphi_3, \ldots, \varphi_p, \ldots$ etc. We rename φ_1 as f_1. From Löwdin's equation (33) of Ref. [6] we get

$$E = H_{11} + \sum_{p=2} |H_{1p}|^2 (E - E_p)^{-1}\,, \tag{5}$$

where H_{1p} is $\langle f_1 | H | f_p \rangle$.

There must exist an average E_p, which we can call $\bar{E}$, such that

$$\sum_{p=2} |H_{1p}|^2 (E - E_p)^{-1} = \sum_{p=2} |H_{1p}|^2 (E - \bar{E})^{-1}\,.$$

Note that the quantity $\sum_{p=2} |H_{1p}|^2$ is precisely σ^2, the variance of the expectation

value of the Hamiltonian.

$$\sigma^2 = \langle f_1 | (H - H_{11})^2 | f_1 \rangle = \langle H f_1 | H f_1 \rangle - \langle f_1 | H | f_1 \rangle^2 .$$

Since the basis $\{f_p\}$ is complete, we can expand the vector $H f_1$ in this basis:

$$\sigma^2 = \sum_p \langle \varphi_p | H \varphi_1 \rangle \varphi_p | \sum_k \langle \varphi_k | H \varphi_1 \rangle \varphi_k \rangle - H_{11}^2$$

$$= \sum_{p=1}^{\infty} |H_{1p}|^2 - H_{11}^2 = H_{11}^2 + \sum_{p=2}^{\infty} |H_{1p}|^2 - H_{11}^2 .$$

Equation (5) thus simplifies to

$$(E - H_{11})(E - \bar{E}) = \sigma^2 . \tag{6}$$

$\bar{E}$ is a certain weighted average of the eigenvalues of the b space. At this point the selection of a substitute value for $\bar{E}$ (of which we are ignorant) produces the required lower bound. Let the substitute value be E_s. If E_s satisfies

$$\bar{E} > E_s > E \tag{7}$$

then we have

$$(E - H_{11})(E - E_s) < \sigma^2 . \tag{8}$$

After some algebra on inequality (8), remembering that $E_s > E$, one obtains finally

$$E > \frac{H_{11} + E_s}{2} - \sqrt{\sigma^2 + \frac{(E_s - H_{11})^2}{4}} . \tag{9}$$

Inequality (9) is the general form of our lower bound. If we take H_{11} as E_s, i.e. if we assume that H_{11} is lower than a weighted average of the eigenvalues of the b space, we obtain inequality (2), D. Weinstein's lower bound. Any value substituted for E_s in inequality (9) will increase the value of the right side of the inequality as long as the value substituted for E_s is greater than H_{11}. A reasonable choice appears to be H_{22}, the second best energy derived from the original n basis functions. Calculations using large values of n should have no difficulty in satisfying the requirement that $H_{22} < \bar{E}$, which plays the same role in the present formula that the requirement $H_{11} < \frac{1}{2}(E_1 + E_2)$ played for the recipe of inequality (2). Substitution of H_{22} for E_s in (9) gives a higher upper bound than that of (2), as can be easily shown by some simple algebra. To give an example of the extent of improvement, which is only moderate, we cite the case of the hydrogen atom ground state problem using as basis functions the energy eigenfunctions of a spherical harmonic oscillator. If we take $n = 8$, then $\bar{E} = -0.48695166$ is the upper bound; $\sigma = 0.55381853$ is the standard deviation. The lower bound of (2) is then -1.04077019; the lower bound of (9), using H_{22} as E_s, is -0.82966672.

It is evident that the present lower bound is more satisfactory than that derived from the D. Weinstein theorem. However, it is still far less accurate than the upper bound. Future work may provide a value of E_s which is higher, hence better, than H_{22}.

The authors wish to acknowledge support for this work from the National Research Council of Ottawa. They are also deeply indebted for inspiration to Professor P. O. Löwdin of Uppsala.

References

1. Bazley, N. W.: Proc. nat. Acad. Sci. USA **45**, 850 (1959); – Physic. Rev. **120**, 144 (1960); — Bazley, N. W., and D. W. Fox: Rev. mod. Physics **35**, 712 (1963); — J. Math. Physics **3**, 469 (1962); — Physic. Rev. **124**, 483 (1961); — J. Math. Physics **4**, 1147 (1963).
2. Löwdin, P.-O.: J. Math. Physics **3**, 969 (1962); — Physic. Rev. **139**, A 357 (1965); — J. chem. Physics **43**, S 175 (1965).
3. Choi, J. H., and D. W. Smith: J. chem. Physics **45**, 4425 (1966).
4. Weinstein, D. H.: Proc. nat. Acad. Sci. USA **20**, 529 (1934).
5. Löwdin, P.-O.: J. molecular Spectroscopy **10**, 12 (1963).
6. — The calculation of upper and lower bounds of energy eigenvalues in perturbation theory by means of partitioning techniques; in: H. Wilcox (Ed.), Perturbation theory and its applications in quantum mechanics. New York: Wiley 1966.

Professor M. Bersohn
University of Toronto
Department of Chemistry
Lash Miller Chemical Laboratories
80 St. George St.
Toronto 5, Canada