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1971 J. Phys. A: Gen. Phys. 4 761

(http://iopscience.iop.org/0022-3689/4/6/003)

J. Phys. A: Gen. Phys., 1971, Vol. 4. Printed in Great Britain

Lagrange multipliers and bounds to quantum mechanical properties

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MS. received 15*th March* 1971

Abstract. Variational lower and upper bounds to energy levels of a quantum mechanical system with Hamiltonian H, as well as to overlap integrals between approximate and exact wavefunctions, have been obtained by a unified treatment. This is based on Lagrange's method of undetermined multipliers, in which a number of calculated moments of H play the role of constraints. New lower and upper bounds to the energy of the first excited state of the system are derived.

1. Introduction

In this paper, we describe a general procedure for calculating lower and upper bounds to various physical properties of a quantum mechanical system, based on Lagrange's method of 'undetermined multipliers'. This method provides a convenient general framework within which we obtain many of the known bounds to energies and overlaps (see for example Eckart 1930, Gordon 1968, Wang 1969, Weinhold 1970) as well as some new bounds. The basic idea of the procedure is as follows. In our search for a bound to the quantum mechanical property Q, we define a function which is formally identical with Q subjected to certain *constraints*, and investigate the extrema of this function. A maximum point then provides an upper bound, a minimum point a lower bound to Q.

In our treatment, the *variables* are taken to be the overlaps between the exact (unknown) wavefunctions and *all* approximate wavefunctions which yield *fixed values* of a number of moments of the Hamiltonian of the system under consideration. These fixed values of the moments represent the *constraints* on the variation. Our method is thus based on the same input data as Gordon's (1968) method, and so may be expected to yield his bounds fairly directly.

2. Formulation of the procedure

Consider a quantum mechanical system with Hamiltonian H. We assume the existence of a complete orthonormal set of real eigenfunctions $\{\psi_n\}$ with corresponding energy eigenvalues $\{E_n\}$ ordered so as to form a nondecreasing sequence, so that

$$H\psi_n = E_n\psi_n \tag{1}$$

and

$$E_n < E_{n+1}(n \geqslant 0). \tag{2}$$

We assume further that any real approximate solution ϕ of equation (1) which satisfies the physical boundary conditions may be expressed in terms of the $\{\psi_n\}$ by means of an eigenfunction expansion

$$\phi = \sum_n a_n\psi_n \tag{3}$$

in which the summation may include continuum contributions. The orthonormality of the set $\{\psi_n\}$ implies that

$$a_n = \langle\phi|\psi_n\rangle. \tag{4}$$

We now introduce the moments of the Hamiltonian H

$$I_k = \langle\phi|H^k\phi\rangle = \sum_n a_n^2 E_n^{\,k} \qquad (k = 0, 1, \dots m) \tag{5}$$

and suppose that these values of the moments are given *fixed* quantities. We thus consider the class of trial functions ϕ which satisfy the *conditions of constraint*

$$g_k(a_0, a_1, \dots a_n, \dots) = \Big(\sum_n a_n^2 E_n^{\,k} - I_k\Big) = 0 \qquad (k = 0, 1, \dots m) \tag{6}$$

and we now seek the extrema of the function

$$f(a_0, a_1, \dots a_n, \dots; \lambda_0, \lambda_1, \dots \lambda_m) = Q(a_0, a_1, \dots a_n \dots) + \sum_{k=0}^{m} \lambda_k g_k(a_0, a_1, \dots a_n, \dots). \tag{7}$$

The equations

$$\frac{\partial f}{\partial a_n} = 0 \qquad (n = 0, 1, \dots) \tag{8}$$

together with the conditions of constraint, equation (6), suffice to determine extremal values of the variables $(\bar{a}_0, \bar{a}_1, \dots \bar{a}_n, \dots)$ together with the corresponding values of the Lagrange multipliers $(\lambda_0, \lambda_1, \dots \lambda_m)$ and finally the extremal values of

$$\bar{Q} = Q(\bar{a}_0, \bar{a}_1, \dots \bar{a}_n, \dots).$$

However, not every extremal point $\bar{A} = A(\bar{a}_0, \bar{a}_1, \dots \bar{a}_n, \dots)$ defines a maximum or a minimum of f. The necessary and sufficient condition for a relative maximum or minimum at $\bar{A}$ is obtained by considering the determinantal equation (Hancock 1960 pp. 115–6)

$$\Delta(\mu) = \begin{vmatrix} \boldsymbol{F} - \mu\boldsymbol{I} & \boldsymbol{G} \\ \boldsymbol{G}^{\mathrm{T}} & \boldsymbol{0} \end{vmatrix} = 0. \tag{9}$$

in which the matrix $\boldsymbol{F}$ has elements

$$F_{ij} = \left(\frac{\partial^2 f}{\partial a_i \partial a_j}\right)_{\bar{A}} \qquad (i, j = 0, 1, \dots n \dots) \tag{10}$$

the matrix $\boldsymbol{G}$ has elements

$$G_{ij} = \left(\frac{\partial g_i}{\partial a_j}\right)_{\bar{A}} \qquad (i = 0, 1, \dots m; j = 0, 1, \dots n, \dots) \tag{11}$$

and $\boldsymbol{G}^{\mathrm{T}}$ is the transpose of $\boldsymbol{G}$.

In the usual case, $\boldsymbol{F}$ is a square matrix of order N and $\boldsymbol{G}$ is a rectangular matrix of order $N \times M$, corresponding to a function Q of N variables subjected to M conditions of constraint. The expansion of $\Delta(\mu)$ yields a polynomial of order $N - M$, whose roots are all *positive* if $\bar{Q}$ is a minimum at $\bar{A}$, and are all *negative* if $\bar{Q}$ is a maximum at $\bar{A}$.

In our case, $\boldsymbol{F}$ is actually of infinite order, but we assume that the basic theorem holds for this case also, since many of our results may be verified directly by other methods.

3. Lower bound to $\langle H \rangle$

We illustrate the general procedure by rederiving the well known Rayleigh–Ritz variation theorem, in the form of a *lower* bound to $\langle H \rangle$. Given only the single constraint of normalization, we have explicitly

$$f = \sum_n a_n{}^2 E_n + \lambda_0 \left(\sum_n a_n{}^2 - 1\right) \tag{12}$$

and at an extremum $\bar{A}$, we require *for all n*

$$\left(\frac{\partial f}{\partial a_n}\right)_{\bar{A}} = 2\bar{a}_n(E_n + \lambda_0) = 0. \tag{13}$$

The corresponding extremal value $\bar{f}$ is obtained by multiplying equation (13) by $\bar{a}_n$, summing, and using the condition of constraint, with the result that

$$\bar{f} = -\lambda_0. \tag{14}$$

In general, we satisfy equation (13) by choosing

$$\lambda_0 = -E_m \qquad \bar{a}_n = 0 \qquad (\text{all } n \neq m). \tag{15}$$

To determine the nature of the resulting extremum, we compute the matrix elements of $\boldsymbol{F}$ and $\boldsymbol{G}$

$$F_{ij} = 2(E_i + \lambda_0)\delta_{ij} = 2(E_i - E_m)\delta_{ij} \tag{16a}$$

and

$$G_{0j} = 2\bar{a}_j \tag{16b}$$

and derive the explicit form of equation (9):

$$\Delta(\mu) = \left|\begin{array}{ccccccc|c} 2(E_0-E_m)-\mu & & & & & & & \\ & \ddots & & & & & & \\ & & 2(E_{m-1}-E_m)-\mu & & & & & \\ & & & -\mu & \cdots & \cdots & \cdots & 2\bar{a}_m \\ & & & \vdots & 2(E_{m+1}-E_m)-\mu & & & \\ & & & \vdots & & \ddots & & \\ & & & \vdots & & & \cdot & \\ \hline & & & 2\bar{a}_m & & & & 0 \end{array}\right|. \tag{17a}$$

$$= 4\bar{a}_m{}^2 \prod_{i \neq m} \{2(E_i - E_m) - \mu\} = 0. \tag{17b}$$

For the sake of clarity, only the nonvanishing elements of the determinant $\Delta(\mu)$ are displayed in equation (17*a*).

The form of the determinant appearing in equation (17) is typical of all the examples treated in the present paper, having nonvanishing elements appearing in the submatrices $\boldsymbol{G}$ and $\boldsymbol{G}^{\mathrm{T}}$ only in those rows and columns in which the diagonal elements of $\boldsymbol{F}$ vanish identically. Thus, in general, the roots of the equation $\Delta(\mu) = 0$ coincide with the nonvanishing diagonal elements of F and, since this is a general feature, it is sufficient in the following to consider only the signs of these diagonal matrix elements.

Now in equation (16a) the diagonal elements F_{ii} will all be positive if

$$E_i - E_m > 0 \qquad \text{for all } i \neq m. \tag{18}$$

Taking account of the ordering of the energy levels (equation (2)), we obtain a minimum for $\bar{f}$ if and only if $E_m = E_0$, which yields the familiar Rayleigh–Ritz result:

$$\langle H \rangle = I_1 \geqslant E_0. \tag{19}$$

Analogously, if ϕ is chosen orthogonal to the exact eigenfunctions $\psi_0, \ldots \psi_{k-1}$ so that $a_0 = \ldots = a_{k-1} = 0$, then starting from

$$f = \sum_{n \geqslant k} a_n{}^2 E_n + \lambda_0 \Big(\sum_{n \geqslant k} a_n{}^2 - 1 \Big) \tag{20}$$

we obtain the 'variation theorem for excited states':

$$\langle H \rangle = I_1 \geqslant E_k. \tag{21}$$

4. Simple bounds to the overlap

As a second example, we rederive Eckart's (1930) bound to an individual overlap, $a_k{}^2$, and give some generalizations. Here, we include *two* constraints, so that

$$f = a_k{}^2 + \lambda_0 \Big(\sum_n a_n{}^2 - 1 \Big) + \lambda_1 \Big(\sum_n a_n{}^2 E_n - I_1 \Big). \tag{22}$$

At an extremum $\bar{A}$, we require

$$\left(\frac{\partial f}{\partial a_k} \right)_{\bar{A}} = 2\bar{a}_k (1 + \bar{\lambda}_0 + \bar{\lambda}_1 E_k) = 0 \tag{23a}$$

and

$$\left(\frac{\partial f}{\partial a_s} \right)_{\bar{A}} = 2\bar{a}_s (\bar{\lambda}_0 + \bar{\lambda}_1 E_s) = 0 \qquad (\text{all } s \neq k) \tag{23b}$$

and by multiplying each of equations (23) by the appropriate $\bar{a}_s$, summing, and using the two conditions of constraint, we obtain the extremal value

$$\bar{f} = -(\bar{\lambda}_0 + \bar{\lambda}_1 I_1). \tag{24}$$

Equations (23) are satisfied by choosing

$$\bar{\lambda}_0 = \frac{E_m}{E_k - E_m} \qquad \bar{\lambda}_1 = -\frac{1}{E_k - E_m} \tag{25a}$$

and

$$\bar{a}_s = 0 \qquad (\text{all } s \neq k, m). \tag{25b}$$

Then the corresponding extremal value of $\bar{f}$ is

$$\bar{f} = \bar{a}_k^2 = \frac{I_1 - E_m}{E_k - E_m} \tag{26}$$

and it follows from the normalization constraint that

$$\bar{a}_m^2 = \frac{E_k - I_1}{E_k - E_m}. \tag{27}$$

Since these expressions for $\bar{a}_k^2$ and $\bar{a}_m^2$ must clearly be non-negative, it follows that I_1 must lie in the interval (E_k, E_m).

The nature of the extremum is now obtained from the diagonal elements

$$F_{ii} = 2(\delta_{ik} + \lambda_0 + \lambda_1 E_i) \tag{28a}$$

$$= 2\{\delta_{ik} - (E_i - E_m)/(E_k - E_m)\}. \tag{28b}$$

Here, there are two distinct possibilities. If $E_k = E_0$ and $E_m = E_1$, the F_{ii} are all *positive*, and we obtain from equation (26) the *lower* bound

$$a_0^2 \geqslant \bar{a}_0^2 = \frac{E_1 - I_1}{E_1 - E_0} \tag{29}$$

which is just Eckart's (1930) result. However, if $E_m = E_0$ then the F_{ii} are all *negative* in which case we have the *upper* bounds

$$a_k^2 \leqslant \bar{a}_k^2 = \frac{I_1 - E_0}{E_k - E_0} \qquad (\text{all } k \geqslant 1). \tag{30}$$

For the case in which ϕ can be chosen orthogonal to the exact eigenfunctions $\psi_0, \ldots \psi_{j-1}$ so that $a_0 = \ldots = a_{j-1} = 0$, the function

$$f = a_k^2 + \lambda_0(\sum_{n \geqslant j} a_n^2 - 1) + \lambda_1(\sum_{n \geqslant j} a_n^2 E_n - I_1) \tag{31}$$

leads similarly to the analogous results

$$a_j^2 \geqslant \bar{a}_j^2 = \frac{E_{j+1} - I_1}{E_{j+1} - E_j} \tag{32a}$$

and

$$a_k^2 \leqslant \bar{a}_k^2 = \frac{I_1 - E_j}{E_k - E_j} \qquad (\text{all } k \geqslant j+1). \tag{32b}$$

Somewhat weaker bounds, which remain valid when the restrictive orthogonality constraints are relaxed, will be derived in the following section.

5. Overlap bounds for excited states

Rigorous bounds to an individual overlap, a_k^2, cannot be obtained for excited states unless the appropriate trial function fulfills highly restrictive orthogonality conditions. However, it is possible to obtain rigorous bounds to certain *sums* of a finite number of such overlaps, which may be useful. Thus, defining

$$S_N = \sum_{n=0}^{N} a_n^2 \tag{33}$$

and again including *two* constraints so that

$$f = S_N + \lambda_0(\sum_n a_n^2 - 1) + \lambda_1(\sum_n a_n^2 E_n - I_1) \tag{34}$$

we obtain at an extremum $\bar{A}$

$$\left(\frac{\partial f}{\partial a_k}\right)_{\bar{A}} = 2\bar{a}_k(1 + \bar{\lambda}_0 + \bar{\lambda}_1 E_k) = 0 \qquad (\text{all } k \leqslant N) \tag{35a}$$

and

$$\left(\frac{\partial f}{\partial a_s}\right)_{\bar{A}} = 2\bar{a}_s(\bar{\lambda}_0 + \bar{\lambda}_1 E_s) = 0 \qquad (\text{all } s \geqslant N+1) \tag{35b}$$

with the corresponding extremal value

$$\bar{f} = \bar{S}_N = -(\bar{\lambda}_0 + \bar{\lambda}_1 I_1). \tag{36}$$

We satisfy equation (35) by choosing

$$\bar{\lambda}_0 = \frac{E_n}{E_m - E_n} \qquad \bar{\lambda}_1 = -\frac{1}{E_m - E_n} \tag{37a}$$

and

$$\bar{a}_k = \bar{a}_s = 0 \qquad (\text{all } k \neq m, s \neq n) \tag{37b}$$

leading to

$$\bar{f} = \bar{S}_N = \frac{E_n - I_1}{E_n - E_m} \tag{38}$$

and clearly, I_1 lies in the interval (E_m, E_n) with $E_m \leqslant E_N \leqslant E_n$.

In this case, we find that

$$F_{ii} = 2\frac{E_m - E_i}{E_m - E_n} \qquad (i \leqslant N) \tag{39a}$$

$$= 2\frac{E_n - E_i}{E_m - E_n} \qquad (i \geqslant N+1) \tag{39b}$$

so that here the F_{ii} are all *positive* if and only if $E_m = E_0$ and $E_n = E_{N+1}$, giving the *lower* bound

$$S_N \geqslant \bar{S}_N = \frac{E_{N+1} - I_1}{E_{N+1} - E_0}. \tag{40}$$

For the ground state, this result reduces naturally to Eckart's bound, equation (29) above.

6. Bounds to energy levels involving higher moments

The procedure of § 3 may be extended straightforwardly to yield lower bounds to higher moments $\langle H^n \rangle$ of the Hamiltonian. It is instructive to rewrite the resulting inequalities in the form of bounds to individual energy levels, many of which have been obtained by other authors.

6.1. *Energy bounds of Temple, Kato and Weinstein*

We seek a bound to $\langle H^2 \rangle$ subject to *two* constraints, and take in this case

$$f = \sum_n a_n^2 E_n^2 + \lambda_0(\sum_n a_n^2 - 1) + \lambda_1(\sum_n a_n^2 E_n - I_1). \tag{41}$$

Two distinct lower bounds may be obtained here. First, we find for *all n* (ie without restriction on I_1)

$$\langle H^2 \rangle = I_2 \geqslant \bar{I}_2 = 2I_1E_n - E_n{}^2. \tag{42}$$

Second, provided that I_1 lies in the interval (E_n, E_{n+1}), we obtain

$$\langle H^2 \rangle = I_2 \geqslant \bar{I}_2 = I_1(E_n + E_{n+1}) - E_nE_{n+1}. \tag{43}$$

Equation (43) naturally provides a more precise bound to I_2 than does the more generally valid equation (42).

From equation (42), we have quite generally

$$\Delta^2 + (E_n - I_1)^2 \geqslant 0 \tag{44}$$

where we have written

$$\Delta^2 = I_2 - I_1{}^2 \geqslant 0. \tag{45}$$

The inequality of equation (44) clearly cannot be used to obtain a bound to E_n.

On the other hand, we see from the inequality of equation (43) that

$$\Delta^2 - (E_{n+1} - I_1)(I_1 - E_n) \geqslant 0 \tag{46}$$

which leads immediately to the bounds of Temple (1928) and Kato (1949):

$$I_1 - \frac{\Delta^2}{E_{n+1} - I_1} \leqslant E_n \leqslant I_1 \leqslant E_{n+1} \leqslant I_1 + \frac{\Delta^2}{I_1 - E_n}. \tag{47}$$

Note that the inequality of equation (46) holds trivially if I_1 lies *outside* the interval (E_n, E_{n+1}).

If we now assume that I_1 lies in the interval

$$E_n \leqslant I_1 \leqslant \tfrac{1}{2}(E_n + E_{n+1}) \tag{48}$$

then from equation (46)

$$\Delta^2 \geqslant (E_{n+1} - I_1)(I_1 - E_n) \geqslant (I_1 - E_n)^2 \tag{49}$$

and similarly, if I_1 lies in the interval

$$\tfrac{1}{2}(E_{n-1} + E_n) \leqslant I_1 \leqslant E_n \tag{50}$$

then

$$\Delta^2 \geqslant (E_n - I_1)(I_1 - E_{n-1}) \geqslant (E_n - I_1)^2. \tag{51}$$

Thus, for I_1 closer to E_n than to any other level, we have Weinstein's (1934) bounds

$$I_1 - \Delta \leqslant E_n \leqslant I_1 + \Delta. \tag{52}$$

6.2. *Gordon's bound to E_0, and bounds to E_1*

Now consider bounds to $\langle H^3 \rangle$ subject to *three* constraints, so that here

$$f = \sum_n a_n{}^2E_n{}^3 + \lambda_0\Big(\sum_n a_n{}^2 - 1\Big) + \lambda_1\Big(\sum_n a_n{}^2E_n - I_1\Big) + \lambda_2\Big(\sum_n a_n{}^2E_n{}^2 - I_2\Big). \tag{53}$$

In this case, we obtain three lower bounds of increasing precision, namely

$$\langle H^3 \rangle = I_3 \geqslant \bar{I}_3 = 3I_2E_0 - 3I_1E_0{}^2 + E_0{}^3 \tag{54a}$$

$$\langle H^3 \rangle = I_3 \geqslant \bar{I}_3 = I_2(E_0 + 2E_n) - I_1E_n(2E_0 + E_n) + E_0E_n{}^2 \tag{54b}$$

valid for *any* E_n; and

$$\langle H^3 \rangle = I_3 \geqslant \bar{I}_3 = I_2(E_0+E_n+E_{n+1})-I_1(E_0E_n+E_0E_{n+1}+E_nE_{n+1}) + E_0E_nE_{n+1} \tag{54c}$$

valid for *any pair* E_n and E_{n+1}.

From equation (54*b*) we have that

$$(I_1-E_0)E_n{}^2-2(I_2-I_1E_0)E_n+(I_3-I_2E_0) \geqslant 0 \tag{55}$$

and since this holds *for all n*, we conclude that

$$(I_1-E_0)(I_3-I_2E_0) \geqslant (I_2-I_1E_0)^2 \tag{56a}$$

which may be written alternatively

$$\Delta^2(E_0{}^2-2\alpha E_0+2\alpha I_1-I_2) \geqslant 0 \tag{56b}$$

where

$$2\alpha = (I_3-I_1I_2)/\Delta^2. \tag{56c}$$

We now define

$$A(x,y) = I_2-I_1(x+y)+xy \tag{57a}$$

$$= \Delta^2+(I_1-x)(I_1-y) \tag{57b}$$

and obtain from equation (56*b*)

$$(\alpha-E_0)^2 \geqslant A(\alpha,\alpha). \tag{58}$$

Since, quite generally,

$$2\alpha = \frac{\Sigma_n\Sigma_m a_n{}^2a_m{}^2(E_n+E_m)(E_n-E_m)^2}{\Sigma_n\Sigma_m a_n{}^2a_m{}^2(E_n-E_m)^2} \geqslant E_0+E_1 \tag{59}$$

we obtain from equation (58) Gordon's (1968) *upper bound* to E_0

$$E_0 \leqslant \alpha - A^{1/2}(\alpha,\alpha). \tag{60}$$

It is of interest that the *lower bound* to E_0 of Stevenson and Crawford (1938) may be written similarly

$$E_0 \geqslant \beta - A^{1/2}(\beta,\beta) \tag{61}$$

where β is any real number satisfying the inequality

$$\beta \leqslant \tfrac{1}{2}(E_0+E_1). \tag{62}$$

Thus, we see from equations (59) and (62) that whenever 2α is close to E_0+E_1 it is to be expected that Gordon's upper bound will be rather precise.

Now, from equation (54*c*) with $n = 0$, we obtain the *upper bound* to E_0

$$E_0 \leqslant \frac{B(E_0,E_1)}{A(E_0,E_1)} \tag{63}$$

where we have written

$$B(x,y) = I_3-I_2(x+y)+I_1xy \tag{64a}$$

$$= I_1A(x,y)+\Delta^2\{2\alpha-(x+y)\}. \tag{64b}$$

Also, from equation (47) we have the *lower bound* to E_0, valid for $I_1 \leqslant E_1$

$$E_0 \geqslant I_1 - \Delta^2/(E_1 - I_1). \tag{65}$$

Thus, we deduce from equations (63) and (65) that

$$\{2\alpha - (E_0 + E_1)\}(E_1 - I_1) + A(E_0, E_1) \geqslant 0 \tag{66}$$

which reduces to

$$I_2 - 2\alpha I_1 + 2\alpha E_1 - E_1^2 \geqslant 0 \tag{67a}$$

or, alternatively

$$A(\alpha, \alpha) \geqslant (\alpha - E_1)^2. \tag{67b}$$

We thus obtain new *lower and upper bounds* to E_1

$$\alpha - A^{1/2}(\alpha, \alpha) \leqslant E_1 \leqslant \alpha + A^{1/2}(\alpha, \alpha). \tag{68}$$

Both Gordon's bound to E_0 and the present bounds to E_1 require no knowledge of exact energy levels. By contrast, equations (54) give upper bounds to E_0 in the form

$$E_0 \leqslant \frac{B(E_n, E_n)}{A(E_n, E_n)} \tag{69a}$$

valid for *any* E_n, and in the form

$$E_0 \leqslant \frac{B(E_n, E_{n+1})}{A(E_n, E_{n+1})} \tag{69b}$$

valid for *any pair* E_n, E_{n+1}. Certain of these bounds will be more precise than Gordon's but since they require knowledge of the exact energy levels, they must be regarded as less satisfactory.

7. Improved bounds to the overlap

Bounds to an individual overlap, a_k^2, more precise than Eckart's (1930) lower bound and the upper bounds derived in § 4, may be obtained by means of additional constraints. For example, if we choose

$$f = a_k^2 + \lambda_0(\sum_n a_n^2 - 1) + \lambda_1(\sum_n a_n^2 E_n - I_1) + \lambda_2(\sum_n a_n^2 E_n^2 - I_2) \tag{70}$$

the usual analysis leads to the extremal value

$$\bar{f} = \bar{a}_k^2 = A(E_l, E_m)/(E_k - E_l)(E_k - E_m) \geqslant 0 \tag{71}$$

while the conditions of constraint here yield

$$\bar{a}_l^2 = A(E_k, E_m)/(E_l - E_k)(E_l - E_m) \geqslant 0 \tag{72a}$$

and

$$\bar{a}_m^2 = A(E_k, E_l)/(E_m - E_k)(E_m - E_l) \geqslant 0. \tag{72b}$$

In general, equation (71) constitutes an *upper* bound if *either* $l = m = n$, giving

$$a_k^2 \leqslant A(E_n, E_n)/(E_k - E_n)^2 \qquad (k \neq n) \tag{73a}$$

or $l = n$, $m = n+1$, so that

$$a_k^2 \leqslant A(E_n, E_{n+1})/(E_k - E_n)(E_k - E_{n+1}) \qquad (k \neq n, n+1). \tag{73b}$$

In the former case, it follows from equations (72) that $A(E_k, E_n) = 0$. In the latter case, we require either

$$A(E_k, E_{n+1}) \leqslant 0 \leqslant A(E_k, E_n) \qquad \text{if } E_k \leqslant E_n \tag{74a}$$

or

$$A(E_k, E_n) \leqslant 0 \leqslant A(E_k, E_{n+1}) \qquad \text{if } E_k \geqslant E_{n+1}. \tag{74b}$$

If we now compare the upper bound of equation (73*b*) with $n = 0$

$$a_k^2 \leqslant A(E_0, E_1)/(E_k - E_0)(E_k - E_1) \qquad (k \neq 0, 1) \tag{75}$$

with the upper bound of equation (30), it follows easily using equation (74*b*) that the higher order bound is always more precise. Similarly, it may be shown quite generally that equation (73*b*) gives a more precise upper bound than our earlier result

$$a_k^2 \leqslant \Delta^2 / A(E_k, E_k) \tag{76}$$

(Cohen and Feldmann 1969), but equation (76) gives a better bound than equation (73*a*).

In the exceptional case $l = n-1$, $m = n+1$, equation (71) may be shown to yield a *lower* bound to a_n^2

$$a_n^2 \geqslant \frac{A(E_{n-1}, E_{n+1})}{(E_n - E_{n-1})(E_n - E_{n+1})} \tag{77}$$

which is useful only if

$$A(E_{n-1}, E_{n+1}) \leqslant 0. \tag{78}$$

Equation (77) clearly cannot be used to obtain a lower bound to a_0^2. In order to obtain such a lower bound, it is necessary to include an additional constraint, by taking

$$f = a_k^2 + \lambda_0\Big(\sum_n a_n^2 - 1\Big) + \lambda_1\Big(\sum_n a_n^2 E_n - I_1\Big) + \lambda_2\Big(\sum_n a_n^2 E_n^2 - I_2\Big) + \lambda_3\Big(\sum_n a_n^2 E_n^3 - I_3\Big). \tag{79}$$

A large number of different extrema can now be deduced in the usual way, and in particular we obtain the *lower* bound

$$a_0^2 \geqslant \bar{a}_0^2 = \frac{E_1 - I_1}{E_1 - E_0} + \frac{(E_n - E_0)A(E_0, E_1) + E_{n+1}A(E_0, E_1) - B(E_0, E_1)}{(E_1 - E_0)(E_n - E_0)(E_{n+1} - E_0)} \tag{80}$$

together with the extremal values

$$\bar{a}_1^2 = \frac{I_1 - E_0}{E_1 - E_0} - \frac{(E_n - E_1)A(E_0, E_1) + E_{n+1}A(E_0, E_1) - B(E_0, E_1)}{(E_1 - E_0)(E_n - E_1)(E_{n+1} - E_0)} \tag{81a}$$

$$\bar{a}_n^2 = \frac{E_{n+1}A(E_0, E_1) - B(E_0, E_1)}{(E_n - E_0)(E_n - E_1)(E_{n+1} - E_n)} \tag{81b}$$

and

$$\bar{a}_{n+1}^2 = \frac{B(E_0, E_1) - E_n A(E_0, E_1)}{(E_{n+1} - E_0)(E_{n+1} - E_1)(E_{n+1} - E_n)}. \tag{81c}$$

Since these latter two expressions cannot be negative, we deduce that

$$E_n \leqslant \frac{B(E_0, E_1)}{A(E_0, E_1)} \leqslant E_{n+1} \tag{82}$$

showing at once that the bound (equation (80)) is always an improvement over Eckart's bound (equation (29)). In fact, it may be shown similarly using equation (82) that equation (80) also provides a more precise lower bound than Gordon's (1968) lower bound to a_0^2

$$a_0^2 \geqslant \frac{E_1 - I_1}{E_1 - E_0} + \frac{\{A(E_0, E_1)\}^2}{(E_1 - E_0)\{B(E_0, E_1) - E_0 A(E_0, E_1)\}}. \tag{83}$$

However, our new bound requires knowledge of the energy levels E_n, E_{n+1} which are not required by Gordon.

8. Improved bounds to S_N

The extension of the method of § 5 to obtain improved bounds to S_N by including additional constraints is straightforward, and we give here only some results.

With *three* constraints, we obtain two upper bounds to S_N

$$S_N \leqslant \frac{A(E_n, E_n)}{(E_N - E_n)^2} \qquad (n \geqslant N+1) \tag{84a}$$

and

$$S_N \leqslant \frac{A(E_n, E_{n+1})}{(E_N - E_n)(E_N - E_{n+1})} \qquad (n \geqslant N+1). \tag{84b}$$

Using considerations similar to those of § 7, it may be shown that a previously determined upper bound (Cohen and Feldmann 1970)

$$S_N \leqslant \Delta^2/A(E_N, E_N) \qquad (I \geqslant E_N) \tag{85}$$

lies between the bounds of equations (84). Thus, the upper bounds to S_N are seen to coincide with earlier bounds to a_N^2 (cf equations (73) and (76) above), and we again emphasize that what appears to be an upper bound to an *individual* overlap a_N^2 may in practice turn out to be a bound to the *sum* S_N of all overlaps up to and including a_N^2.

We also obtain two lower bounds to S_N

$$S_N \geqslant 1 - \frac{A(E_n, E_n)}{(E_{N+1} - E_n)^2} \qquad (n \leqslant N) \tag{86a}$$

and

$$S_N \geqslant 1 - A(E_n, E_{n+1})/(E_{N+1} - E_n)(E_{N+1} - E_{n+1}) \qquad (n \leqslant N-1) \tag{86b}$$

and note that it may be shown that the analogue of equation (85)

$$S_N \geqslant 1 - \Delta^2/A(E_{N+1}, E_{N+1}) \qquad (E_{N+1} \geqslant I) \tag{87}$$

lies between the bounds of equations (86).

9. Conclusions

The procedures described in the earlier sections of this paper may be extended without difficulty to obtain more precise bounds, provided that higher moments of the Hamiltonian can be computed. Unfortunately, for most systems of physical interest, moments higher than $\langle H^2 \rangle$ are extremely difficult to calculate, and for many of the usual choices of trial function ϕ the necessary integrals fail to converge. This difficulty applies also to other *methods* of computing bounds. The formalism developed here nevertheless yields most of the known bounds to energy levels and to overlap integrals between approximate and exact wave functions, as well as some new bounds to moments and to sums of overlap integrals.

Acknowledgments

We are greatly indebted to Professor Shmuel Agmon who provided both the initial stimulus for this work and for his encouragement throughout its course. We are grateful to Professors S. Baer and R. P. McEachran for a number of helpful discussions.

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