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Lagrange multipliers and bounds to quantum mechanical properties II

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Abstract. Bounds to overlap integrals between approximate and exact wavefunctions have been derived for arbitrary excited states of a quantum mechanical system, using the Lagrange multipliers technique. A new lower bound to the ground state energy which is an improvement over the classical result of Temple has also been derived.

1. Introduction

In an earlier paper (Cohen and Feldmann 1971, to be referred to as I) we have described a general procedure, based on Lagrange's method of undetermined multipliers, for calculating bounds to physical properties of a quantum mechanical system. In I, we dealt exclusively with lower and upper bounds which may be derived using a *single* trial function ϕ and a given number of moments $\langle H\rangle, \langle H^2\rangle, \ldots$ of the system Hamiltonian H calculated with this ϕ. The use of a single ϕ restricts the applicability of some of our earlier results to ground states, or to those excited states which are the lowest of some given symmetry species.

In order to obtain results valid for general excited states, we must use a set of N trial functions $\{\phi_n; n = 0, 1 \ldots N-1\}$, one for each of the N lowest states of given symmetry. The overlap integral $\langle\phi_n|\psi_\alpha\rangle$ between one such trial function ϕ_n and an exact eigenfunction ψ_α cannot be calculated directly, since ψ_α is unknown, but rigorous bounds to these integrals give useful estimates of the accuracy of a particular trial function ϕ_n as an approximation to a particular ψ_n. Clearly, one would wish to have $\langle\phi_n|\psi_n\rangle \sim 1$ and $\langle\phi_n|\psi_m\rangle \sim 0$ $(m \neq n)$ for accurate ϕ_n. A *lower bound* to the 'diagonal' overlap integral $\langle\phi_n|\psi_n\rangle$ was derived some time ago by Weinberger (1960). The present work extends Weinberger's treatment so as to yield *upper bounds* to a number of 'off-diagonal' integrals $\langle\phi_n|\psi_m\rangle$ $(m \neq n)$ as well as lower and upper bounds to certain sums of such overlaps. In addition, we have extended our earlier treatment of bounds to higher moments, and have obtained a new lower bound to the energy of the ground state, which improves Temple's (1928) classic result.

2. Formulation

We give here only a resumé of our procedures; full details may be found in I. We consider a quantal system with Hamiltonian H, possessing a complete orthonormal set of eigenfunctions $\{\psi_\alpha\}$ with corresponding eigenenergies $\{E_\alpha\}$. These satisfy

$$H\psi_\alpha = E_\alpha\psi_\alpha; \qquad \langle\psi_\alpha|\psi_\beta\rangle = \delta_{\alpha\beta}; \qquad E_\alpha < E_{\alpha+1}(\alpha \geqslant 0) \tag{1}$$

and, for simplicity of presentation, we assume that the $\{\psi_\alpha\}$ are *real* functions, and that the energy levels of specified symmetry are *non-degenerate*.

We now assume that we have obtained a set of orthogonal approximate solutions $\{\phi_n\}$ which may be expressed in terms of the eigenfunctions $\{\psi_\alpha\}$ by means of the expansions

$$\phi_n = \sum_\alpha a_{n\alpha}\psi_\alpha \qquad (n = 0, 1, \ldots N-1). \tag{2}$$

For simplicity of presentation, we take the expansion coefficients $\{a_{n\alpha}\}$ to be *real* and suppress all reference to the continuum. These trial functions $\{\phi_n\}$ are used to calculate a set of *moments* (non-diagonal as well as diagonal) of the system Hamiltonian H:

$$\begin{aligned} S_{mn} &= \langle\phi_m|\phi_n\rangle = \sum_\alpha a_{m\alpha}a_{n\alpha} \\ I_{mn} &= \langle\phi_m|H|\phi_n\rangle = \sum_\alpha a_{m\alpha}a_{n\alpha}E_\alpha \\ J_{mn} &= \langle\phi_m|H^2|\phi_n\rangle = \sum_\alpha a_{m\alpha}a_{n\alpha}E_\alpha^2, \quad \text{etc.} \end{aligned} \tag{3}$$

Some of these moments constitute the *constraints* on the variation of any quantity Q of interest which may be expressed as a function of the *variables* $\{a_{n\alpha}\}$. Variation of Q with respect to the coefficients $\{a_{n\alpha}\}$ subject to the constraints leads to extremal values $\bar{Q}$ which are sometimes (but not always) maxima or minima. A maximum provides an upper bound to Q, a minimum a lower bound.

Specifically, we consider functions of the general form

$$f(\{a_{n\alpha}\}; \{\lambda_m\}) = Q(\{a_{n\alpha}\}) + \sum_{m=1}^{M} \lambda_m g_m(\{a_{n\alpha}\}), \tag{4}$$

in which the $\{\lambda_m\}$ are Lagrange multipliers to be determined, and seek solutions of the equations

$$\frac{\partial f}{\partial a_{n\alpha}} = 0 \qquad (n = 0, 1, \ldots N-1; \text{all } \alpha) \tag{5}$$

together with the constraint equations

$$g_m = 0 \qquad (m = 1, 2, \ldots M). \tag{6}$$

Any solution of these equations determines an extremal point $\bar{A} = (\{\bar{\lambda}_m\}, \{\bar{a}_{n\alpha}\})$, while the *nature* of any particular extremum depends on the signs of the roots of the determinantal equation (Hancock 1960)

$$D(\rho) = \begin{vmatrix} \mathbf{F} - \rho\mathbf{I} & \mathbf{G} \\ \mathbf{G}^{\mathrm{T}} & \mathbf{0} \end{vmatrix} = 0. \tag{7}$$

Here, $\mathbf{F}$ and $\mathbf{G}$ are matrices with elements given by

$$F_{ij} = \left(\frac{\partial^2 f}{\partial a_i\, \partial a_j}\right)_{\bar{A}}, \qquad G_{mj} = \left(\frac{\partial g_m}{\partial a_j}\right)_{\bar{A}} \tag{8}$$

where i and j represent the index pairs $n\alpha$ and $n'\alpha'$ respectively, $\mathbf{G}^{\mathrm{T}}$ is the transpose of $\mathbf{G}$

and $\mathbf{I}$ and $\mathbf{0}$ represent unit and null matrices of appropriate dimensions. A strict minimum of Q occurs at $\bar{A}$ if every root ρ of equation (7) is positive, and a maximum if every root is negative. However, in order to obtain a bound, we do not require a *strict* maximum or minimum at $\bar{A}$. It is sufficient for our purposes (cf Chaundy 1935) that the *non-vanishing* roots of equation (7) are of constant sign.

The following two sections contain applications of the procedure to overlap integrals (§ 3) and to second moments (§ 4). The resulting bounds require knowledge of the energy levels E_α (perhaps from experiment) but they remain rigorous if these energies can themselves be bounded from below. This use of empirical data in otherwise purely theoretical calculations is almost universally accepted in the quantum mechanical bounds literature.

3. Bounds to overlap

Here, we seek bounds to overlap integrals $a_{i\beta}^2$, given by

$$a_{i\beta} = \langle \phi_i | \psi_\beta \rangle \tag{9}$$

and for generality, we consider the function

$$f = \sum_{i=0}^{N-1} c_i a_{i\beta}^2 + \sum_{i=0}^{N-1} \sum_{j=0}^{N-1} (\lambda_{ij} g_{ij} + \mu_{ij} h_{ij}). \tag{10}$$

Here, the c_i are constants to be chosen later, the λ_{ij} and μ_{ij} are Lagrange multipliers, and are elements of *symmetric* matrices, while the constraints are given by

$$g_{ij} = 0 = \langle \phi_i | \phi_j \rangle - \delta_{ij} = \sum_\alpha a_{i\alpha} a_{j\alpha} - \delta_{ij}$$

and (11)

$$h_{ij} = 0 = \langle \phi_i | H\phi_j \rangle - I_i \delta_{ij} = \sum_\alpha a_{i\alpha} a_{j\alpha} E_\alpha - I_i \delta_{ij} \qquad (i, j = 0, 1, \ldots N-1).$$

In the remaining sections of this paper, we denote *diagonal* first moments by I_i rather than I_{ii} for simplicity of presentation. The constraints (11) are sufficient to guarantee that for each i,

$$E_i \leqslant I_i \tag{12}$$

(Hylleraas and Undheim 1930, MacDonald 1933) but they do *not* automatically ensure that $I_i \leqslant E_{i+1}$. We shall assume later that these further conditions are also fulfilled, in order to obtain non-trivial bounds.

At an extremum $\bar{A}$, we must satisfy the conditions of constraint (11) together with

$$\left(\frac{\partial f}{\partial a_{i\alpha}}\right)_{\bar{A}} = 0 = 2c_i \bar{a}_{i\beta} \delta_{\beta\alpha} + 2\sum_{j=0}^{N-1} (\bar{\lambda}_{ij} + \bar{\mu}_{ij} E_\alpha) \bar{a}_{j\alpha} \qquad (i = 0, 1, \ldots N-1; \text{all } \alpha). \tag{13}$$

Thus, for $\alpha \neq \beta$, non-trivial solutions $\{\bar{a}_{i\alpha}\}$ exist if and only if

$$\det|\bar{\lambda}_{ij} + \bar{\mu}_{ij} E_\alpha| = 0 \qquad (i, j = 0, 1, \ldots N-1) \tag{14}$$

and since the $\bar{\lambda}_{ij}$, $\bar{\mu}_{ij}$ are fixed numbers, there will be a maximum of N distinct values of E_α which satisfy (14).

In addition, when $\alpha = \beta$, we have

$$\sum_{j=0}^{N-1} (\bar{\lambda}_{ij} + \bar{\mu}_{ij} E_\beta)\bar{a}_{j\beta} = -c_i \bar{a}_{i\beta} \qquad (i = 0, 1, \dots N-1). \tag{15}$$

Thus, (13) is satisfied by N values of α and the given β, or $(N+1)$ parameter values in all. We shall refer to these parameters collectively as the extremal set, which we denote as $\{\alpha\}$ or as $\{E_\alpha\}$. Since there are N functions $\{\phi_i\}$, it follows that at most $N(N+1)$ expansion coefficients $\bar{a}_{i\alpha}$ are non-vanishing, corresponding to the $N(N+1)$ constraints (11).

The extremal values of the multipliers $\bar{\lambda}_{ij}$ and $\bar{\mu}_{ij}$ are obtained by multiplying (13) by $\bar{a}_{s\alpha}$ for some s and summing over $\{\alpha\}$. On taking due account of the constraints (11), we obtain

$$\bar{\lambda}_{is} + \bar{\mu}_{is} I_s = -c_i \bar{a}_{i\beta}\bar{a}_{s\beta} \qquad (i, s = 0, 1, \dots N-1), \tag{16}$$

and since we may interchange i and s in (16), we obtain similarly

$$\bar{\lambda}_{si} + \bar{\mu}_{si} I_i = -c_s \bar{a}_{s\beta}\bar{a}_{i\beta} \qquad (i, s = 0, 1, \dots N-1). \tag{17}$$

Hence, since $\bar{\lambda}_{is} = \bar{\lambda}_{si}$, $\bar{\mu}_{is} = \bar{\mu}_{si}$ we have

$$\begin{aligned} \bar{\lambda}_{is} &= -(c_i I_i - c_s I_s)\bar{a}_{i\beta}\bar{a}_{s\beta}/(I_i - I_s) \qquad (i \neq s) \\ \bar{\mu}_{is} &= (c_i - c_s)\bar{a}_{i\beta}\bar{a}_{s\beta}/(I_i - I_s) \end{aligned} \tag{18}$$

while, when $i = s$, both (16) and (17) reduce to a single equation:

$$\bar{\lambda}_{ii} + \bar{\mu}_{ii} I_i = -c_i \bar{a}_{i\beta}^2 \qquad (i = 0, 1, \dots N-1). \tag{19}$$

Equation (19), together with equation (13) for any $\alpha \neq \beta$ now yields

$$\bar{\mu}_{ii} = -c_i\left(\frac{\bar{a}_{i\beta}^2}{I_i - E_\alpha} + \sum_{s\neq i} \frac{\bar{a}_{i\beta}\bar{a}_{s\beta}}{I_i - I_s}\frac{\bar{a}_{s\alpha}}{\bar{a}_{i\alpha}}\right) + \sum_{s\neq i} c_s \frac{\bar{a}_{i\beta}\bar{a}_{s\beta}}{I_i - I_s}\frac{I_s - E_\alpha}{I_i - E_\alpha}\frac{\bar{a}_{s\alpha}}{\bar{a}_{i\alpha}} \tag{20}$$

while (19) taken together with the same equation (13) for β yields

$$\bar{\mu}_{ii} = c_i\left(\frac{1 - \bar{a}_{i\beta}^2}{I_i - E_\beta} - \sum_{s\neq i} \frac{\bar{a}_{s\beta}^2}{I_i - I_s}\right) + \sum_{s\neq i} c_s \frac{\bar{a}_{s\beta}^2}{I_i - I_s}\frac{I_s - E_\beta}{I_i - E_\beta}. \tag{21}$$

These two expressions for $\bar{\mu}_{ii}$ must be identical for all $\{\alpha\}$ and, for convenience, for all choices of the constants c_i, c_s. Thus we have *for each* α, both

$$\frac{I_s - E_\alpha}{I_i - E_\alpha}\frac{\bar{a}_{s\alpha}}{\bar{a}_{i\alpha}} = \frac{I_s - E_\beta}{I_i - E_\beta}\frac{\bar{a}_{s\beta}}{\bar{a}_{i\beta}} \qquad \text{(all pairs } s, i\text{)} \tag{22}$$

and

$$\frac{1 - \bar{a}_{i\beta}^2}{I_i - E_\beta} - \sum_{s\neq i} \frac{\bar{a}_{s\beta}^2}{I_i - I_s} + \frac{\bar{a}_{i\beta}^2}{I_i - E_\alpha} + \sum_{s\neq i} \frac{\bar{a}_{i\beta}\bar{a}_{s\beta}}{I_i - I_s}\frac{\bar{a}_{s\alpha}}{\bar{a}_{i\alpha}} = 0. \tag{23}$$

Multiplying (22) by $\bar{a}_{i\alpha}\bar{a}_{s\alpha}$, summing over $\{\alpha\}$ and using the constraints (11) we obtain *when* $i \neq s$:

$$\sum_{\{\alpha\}} \frac{\bar{a}_{s\alpha}^2}{I_i - E_\alpha} = \frac{1}{I_i - I_s} \qquad (i \neq s). \tag{24}$$

Equations (24) together with the constraints $\Sigma_\alpha \bar{a}_{s\alpha}^2 = 1$, $\Sigma_\alpha \bar{a}_{s\alpha}^2 E_\alpha = I_s$ are sufficient to determine all the *extremal values*. We obtain quite generally

$$\bar{a}_{i\gamma}^2 = \prod_{\substack{m \neq i \\ m=0}}^{N-1} \frac{I_m - E_\gamma}{I_m - I_i} \prod_{n \neq \gamma} \frac{I_i - E_n}{E_\gamma - E_n} \qquad (i = 0, 1, \ldots N-1). \tag{25}$$

The second product is here over the extremal set $\{\alpha\}$, excluding the particular γ.

If we eliminate $\bar{a}_{s\alpha}/\bar{a}_{i\alpha}$ between equations (22) and (23) we obtain the equations

$$\sum_{\text{all } s} \frac{\bar{a}_{s\beta}^2}{I_s - E_\alpha} = \frac{1}{E_\beta - E_\alpha} \qquad (\alpha \neq \beta). \tag{26}$$

The solutions of equations (24) and (26) are identical.

Thus, with the $\bar{a}_{i\gamma}^2$ given by (25), the coefficients c_i, c_s occurring in (20), (21) may be chosen quite freely. Various possible choices are discussed below.

3.1. *Nature of the extrema*

We must now investigate the nature of the extrema given by (25). Using arguments similar to those employed in I (see especially the discussion following equation (17*b*)) it may be shown that the determinantal equation (7) reduces to a squared numerical factor multiplying a product of determinants:

$$D_N(E; \rho) = \det|\bar{\lambda}_{ij} + \bar{\mu}_{ij}E - \delta_{ij}\rho| \qquad (i, j = 0, 1, \ldots N-1) \tag{27}$$

one for each energy E *different* from the extremal set $\{E_\alpha\}$. Thus we must determine the *signs* of the latent roots of the matrix $(\bar{\boldsymbol{\lambda}} + \bar{\boldsymbol{\mu}}E)$ for all E different from the set $\{E_\alpha\}$.

Now each principal minor $M_n(E)$ of the determinant of $(\bar{\boldsymbol{\lambda}} + \bar{\boldsymbol{\mu}}E)$ may be written in the form

$$M_n(E) = \det(\bar{\boldsymbol{\lambda}} + \bar{\boldsymbol{\mu}}E)_{n \times n} = B_n \prod_{i=0}^{n-1} (E - \epsilon_i^{(n)}) \qquad (n = 1, 2, \ldots N) \tag{28}$$

where, using arguments similar to those of MacDonald (1933), it may be shown that the latent roots $\epsilon_i^{(n)}$ of $M_n(E)$ separate pairs of latent roots of $M_{n+1}(E)$. Thus, if the *highest* latent root of $M_N(E)$ is E_δ, the sign of $M_n(E)$ *for every n and for each* $E > E_\delta$ is determined entirely by the sign of B_n.

Now the latent roots of $M_N(E)$ are precisely the set E_α satisfying equation (14), i.e. the extremal set $\{E_\alpha\}$ *excluding* E_β. We now *assume* that the $\{I_i; i = 0, \ldots N-1\}$ are bracketed between successive energy levels, so that in general

$$E_i < I_i < E_{i+1} \qquad (i = 0, 1, \ldots N-1). \tag{29}$$

This implies that the extremal set includes the lowest N energy levels $\{E_\alpha; \alpha = 0 \ldots N-1\}$, if $E_\beta \geqslant E_N$. On the other hand, if $E_\beta \leqslant E_{N-1}$, the extremal set contains the lowest $N+1$ energy levels $\{E_\alpha; \alpha = 0, \ldots N\}$.

The coefficient B_n is given explicitly by

$$B_n = \det(\bar{\boldsymbol{\mu}})_{n \times n} = \begin{vmatrix} \bar{\mu}_{00} & \bar{\mu}_{01} & \cdots & \bar{\mu}_{0,n-1} \\ \bar{\mu}_{10} & \bar{\mu}_{11} & \cdots & \bar{\mu}_{1,n-1} \\ \vdots & \vdots & & \vdots \\ \bar{\mu}_{n-1,0} & \bar{\mu}_{n-1,1} & \cdots & \bar{\mu}_{n-1,n-1} \end{vmatrix} \tag{30}$$

and the detailed forms of the $\tilde{\mu}_{is}$, given by equations (18) and (21) depend on our choice of c_i, c_s.

3.2. Individual overlaps

The simplest choice in (10) is $c_i = 1$, $c_s = 0$ $(s \neq i)$; we are thus seeking bounds to a single overlap integral, $\langle\phi_i|\psi_\beta\rangle$. We obtain the following non-vanishing elements:

$$\begin{aligned}
\bar{\mu}_{ii} &= \frac{1-\bar{a}_{i\beta}^2}{I_i - E_\beta} + \sum_{s\neq i} \frac{\bar{a}_{s\beta}^2}{I_s - I_i} \\
\bar{\mu}_{is} &= \bar{a}_{i\beta}\bar{a}_{s\beta}/(I_i - I_s) \qquad (s \neq i) \\
\bar{\mu}_{ss} &= \frac{\bar{a}_{i\beta}^2(I_i - E_\beta)}{(I_s - I_i)(I_s - E_\beta)} \qquad (s \neq i).
\end{aligned} \tag{31}$$

Here, the determinants B_n have non-vanishing off-diagonal elements *only* in the ith row and column and, by suitable ordering, these elements may be brought to the last row and column of B_N. Then we need to consider only the signs of

$$B_n = \prod_{\substack{s=0\\ s\neq i}}^{n-1} \bar{\mu}_{ss} \qquad (n = 1, 2, \ldots N-1) \tag{32}$$

and

$$B_N = B_{N-1}\tilde{\mu}_{ii}$$

and using (31), we find the value of the discriminant

$$\tilde{\mu}_{ii} = \bar{\mu}_{ii} - \sum_{s\neq i} \frac{\bar{\mu}_{is}^2}{\bar{\mu}_{ss}} = \frac{1-S_N}{I_i - E_\beta} = \frac{1-\Sigma_{i=0}^{N-1}\bar{a}_{i\beta}^2}{I_i - E_\beta}. \tag{33}$$

In the appendix equation (A.6) we obtain an expression for S_N and show that $S_N < 1$, so that the sign of $\tilde{\mu}_{ii}$ depends only on the sign of $(I_i - E_\beta)$.

From (31), we see that all the $\bar{\mu}_{ss}$ will have the fixed sign of $(I_i - E_\beta)$ if and only if *none* of the remaining I_s $(s \neq i)$ lies in the interval containing the pair (I_i, E_β). We thus obtain fixed sign for *all* $\bar{\mu}_{ss}$ *and* $\tilde{\mu}_{ii}$ and bounds to the corresponding $a_{i\beta}^2$, in the following cases only:

$$E_\beta = E_i: \qquad a_{ii}^2 \geq \bar{a}_{ii}^2 = \prod_{\substack{m=0\\ m\neq i}}^{N-1} \frac{I_m - E_i}{I_m - I_i} \prod_{\substack{n=0\\ n\neq i}}^{N} \frac{I_i - E_n}{E_i - E_n} \qquad (i = 0, 1, \ldots N-1) \tag{34}$$

$$E_\beta = E_{i+1}: \qquad a_{i,i+1}^2 \leq \bar{a}_{i,i+1}^2 = \prod_{\substack{m=0\\ m\neq i}}^{N-1} \frac{I_m - E_{i+1}}{I_m - I_i} \prod_{\substack{n=0\\ n\neq i+1}}^{N} \frac{I_i - E_n}{E_{i+1} - E_n} \qquad (i = 0, 1, \ldots N-1) \tag{35}$$

$$E_\beta \geq E_N: \qquad a_{N-1,\beta}^2 \leq \bar{a}_{N-1,\beta}^2 = \prod_{m=0}^{N-2} \frac{I_m - E_\beta}{I_m - I_{N-1}} \prod_{n=0}^{N-1} \frac{I_{N-1} - E_n}{E_\beta - E_n} \qquad (\beta = N, N+1, \ldots). \tag{36}$$

The bounds (34) to (36) are all contained in (25). They remain rigorous if the energies E_i, E_n are replaced by *lower bounds*, provided only that the bracketing conditions (29) remain valid. We note from equations (34) and (35) that, as I_i

approaches E_i, $\bar{a}_{ii}^2 \to 1$ and $\bar{a}_{i,i+1}^2 \to 0$ as required. Similarly, equation (36) shows that $\bar{a}_{N-1,\beta}^2 \to 0$ for all $\beta \geq N$ as $I_{N-1} \to E_{N-1}$. These are *limiting situations* in which ϕ_i and ϕ_{N-1} approach *exact* eigenfunctions ψ_i and ψ_{N-1}. The lower bound (34) is Weinberger's (1960) result; the upper bounds (35) and (36) are new.

3.3. *Sums of overlaps*

In addition to the few individual overlaps $a_{i\beta}^2$ which are bounded by the corresponding extremal $\bar{a}_{i\beta}^2$ certain sums can be treated analogously. The simplest example corresponds to the choice $c_i = c_j = 1$, $c_s = 0$ $(s \neq i, j)$, and we obtain straightforwardly:

$$\begin{aligned}
\bar{\mu}_{kk} &= \frac{1 - \bar{a}_{i\beta}^2 - \bar{a}_{j\beta}^2}{I_k - E_\beta} + \sum_{s \neq i,j} \frac{\bar{a}_{s\beta}^2}{I_s - I_k} && (k = i, j) \\
\bar{\mu}_{ks} &= \bar{a}_{k\beta}\bar{a}_{s\beta}/(I_k - I_s) && (s \neq i, j) \\
\bar{\mu}_{ss} &= \sum_{k=i,j} \frac{\bar{a}_{k\beta}^2 (I_k - E_\beta)}{(I_s - I_k)(I_s - E_\beta)} && (s \neq i, j)
\end{aligned} \tag{37}$$

which are obvious generalizations of (31). In this case, we have non-diagonal elements in the ith and jth rows and columns, and, as before, we bring these to the last two rows and columns of B_N. This procedure allows us to consider the signs of

$$\begin{aligned}
B_n &= \sum_{\substack{s=0 \\ s \neq i,j}}^{n-1} \bar{\mu}_{ss} \qquad (n = 1, \ldots N-2) \\
B_{N-1} &= \tilde{\mu}_{ii} B_{N-2}
\end{aligned} \tag{38}$$

and

$$B_N = (\tilde{\mu}_{ii}\tilde{\mu}_{jj} - \tilde{\mu}_{ij}^2) B_{N-2}$$

where

$$\tilde{\mu}_{kk} = \bar{\mu}_{kk} - \sum_{s \neq i,j} \frac{\bar{\mu}_{ks}^2}{\bar{\mu}_{ss}} \qquad (k = i, j); \qquad \tilde{\mu}_{ij} = -\sum_{s \neq i,j} \frac{\bar{\mu}_{is}\bar{\mu}_{js}}{\bar{\mu}_{ss}}. \tag{39}$$

It may now be shown that

$$\begin{aligned}
\tilde{\mu}_{ii} &= \frac{1 - S_N}{I_i - E_\beta} + \frac{\bar{a}_{j\beta}^2 (I_j - E_\beta)}{I_i - E_\beta} \Sigma \\
\tilde{\mu}_{jj} &= \frac{1 - S_N}{I_j - E_\beta} + \frac{\bar{a}_{i\beta}^2 (I_i - E_\beta)}{I_j - E_\beta} \Sigma
\end{aligned} \tag{40}$$

and

$$\tilde{\mu}_{ii}\tilde{\mu}_{jj} - \tilde{\mu}_{ij}^2 = \frac{(1 - S_N)^2}{(I_i - E_\beta)(I_j - E_\beta)} + \frac{1 - S_N}{(I_i - E_\beta)(I_j - E_\beta)} [\bar{a}_{i\beta}^2 (I_i - E_\beta) + \bar{a}_{j\beta}^2 (I_j - E_\beta)] \Sigma$$

where we have written

$$\Sigma = \sum_{s \neq i,j} \frac{\bar{a}_{s\beta}^2}{(I_i - I_s)(I_j - I_s)\bar{\mu}_{ss}}. \tag{41}$$

From (37), we see that whenever $(I_i - E_\beta)$ and $(I_j - E_\beta)$ have the *same* sign, all the $\bar{\mu}_{ss}$ have the fixed sign of $(I_i - E_\beta)$ provided that none of the remaining I_s $(s \neq i, j)$ lies in the interval containing I_i, I_j and E_β. Under these circumstances, Σ, $\tilde{\mu}_{ii}$ and $\tilde{\mu}_{jj}$ are of the same sign as $\bar{\mu}_{ss}$, while the discriminant $\tilde{\mu}_{ii}\tilde{\mu}_{jj} - \tilde{\mu}_{ij}^2$ is clearly positive. We thus obtain bounds to the following sums:

$$a_{ii}^2 + a_{i+1,i}^2 \geqslant \bar{a}_{ii}^2 + \bar{a}_{i+1,i}^2 \qquad (i = 0, 1, \ldots N-1) \tag{42}$$

$$a_{i,i+2}^2 + a_{i+1,i+2}^2 \leqslant \bar{a}_{i,i+2}^2 + \bar{a}_{i+1,i+2}^2 \qquad (i = 0, 1, \ldots N-1) \tag{43}$$

$$a_{N-2,\beta}^2 + a_{N-1,\beta}^2 \leqslant \bar{a}_{N-2,\beta}^2 + \bar{a}_{N-1,\beta}^2 \qquad (\beta = N, N+1, \ldots). \tag{44}$$

Sums of more than two overlaps may be treated similarly, but the algebra becomes cumbersome, and we present only the results:

$$\sum_{i \geqslant \beta} a_{i\beta}^2 \geqslant \sum_{i \geqslant \beta} \bar{a}_{i\beta}^2 \qquad \text{and} \qquad \sum_{i \leqslant \beta-1} a_{i\beta}^2 \leqslant \sum_{i \leqslant \beta-1} \bar{a}_{i\beta}^2. \tag{45}$$

Clearly, equations (34)–(36) and (42)–(44) are all special cases of (45). Unfortunately, no new bounds to *individual* overlaps result from these sums.

3.4. Other linear combinations

We now consider two slightly different choices of the $\{c_i\}$, which lead to new results. First, taking

$$c_i = \frac{1}{I_i - E_\beta} \qquad (i = 0, 1, \ldots N-1) \tag{46}$$

we obtain

$$\bar{\mu}_{ii} = (1 - \bar{a}_{i\beta}^2)/(I_i - E_\beta)^2, \qquad (i = 0, 1, \ldots N-1)$$

and

$$\bar{\mu}_{ij} = -\bar{a}_{i\beta}\bar{a}_{j\beta}/(I_i - E_\beta)(I_j - E_\beta) \qquad (i \neq j). \tag{47}$$

In this case, direct expansion of the determinant B_n yields

$$B_n = (1 - S_n) \prod_{i=0}^{n-1} \frac{1}{(I_i - E_\beta)^2} \qquad (n = 1, \ldots N) \tag{48}$$

where

$$S_n = \sum_{i=0}^{n-1} \bar{a}_{i\beta}^2. \tag{49}$$

Here, the B_n are clearly all positive and we thus obtain a lower bound for every β:

$$\sum_{i=0}^{N-1} \frac{a_{i\beta}^2}{I_i - E_\beta} \geqslant \sum_{i=0}^{N-1} \frac{\bar{a}_{i\beta}^2}{I_i - E_\beta}. \tag{50}$$

Using the results of the appendix equation (A.7) we have explicitly

$$\sum_{i=0}^{N-1} \frac{a_{i\beta}^2}{I_i - E_\beta} \geqslant \sum_{i=0}^{N-1} \frac{1}{I_i - E_\beta} - \sum_{\alpha \neq \beta} \frac{1}{E_\alpha - E_\beta}. \tag{51}$$

Finally, if we choose

$$c_i = \frac{1}{I_i - E_\alpha} \qquad (i = 0, 1, \ldots N-1) \tag{52}$$

where E_α is any one of the extremal set $\{E_\alpha\}$ *except* E_β, we find

$$\bar{\mu}_{ii} = -\bar{a}^2_{i\beta}/(I_i - E_\alpha)^2 \qquad (i = 0, 1, \ldots N-1)$$

and (53)

$$\bar{\mu}_{ij} = -\bar{a}_{i\beta}\bar{a}_{j\beta}/(I_i - E_\alpha)(I_j - E_\alpha) \qquad (i \neq j).$$

In this case, the diagonal elements of B_n are all negative, but every $B_n\,(n \geqslant 2)$ vanishes. We thus have the upper bounds

$$\sum_{i=0}^{N-1} \frac{a^2_{i\beta}}{E_i - E_\alpha} \leqslant \sum_{i=0}^{N-1} \frac{\bar{a}^2_{i\beta}}{I_i - E_\alpha} = \frac{1}{E_\beta - E_\alpha} \qquad (\alpha \neq \beta), \tag{54}$$

the final expression being simply (26).

The inequalities (54) thus complement (51). They have been derived recently by other means (Cohen and Leopold 1976) and used to obtain certain additional bounds to overlaps.

4. Bounds to the second moment

Here, we consider the function

$$f_k = \sum_\alpha a^2_{k\alpha}E^2_\alpha + \sum_{i=0}^{N-1}\sum_{j=0}^{N-1} (\lambda_{ij}g_{ij} + \mu_{ij}h_{ij}) \tag{55}$$

where the constraints are given by (11), as before. At an extremum $\bar{A}$, we have

$$\left(\frac{\partial f_k}{\partial a_{i\alpha}}\right)_{\bar{A}} = 0 = 2\bar{a}_{k\alpha}E^2_\alpha\delta_{ki} + 2\sum_{j=0}^{N-1} (\bar{\lambda}_{ij} + \bar{\mu}_{ij}E_\alpha)\bar{a}_{j\alpha} \qquad (i = 0, 1, \ldots N-1;\ \text{all}\ \alpha) \tag{56}$$

and in this case, non-trivial solutions $\{\bar{a}_{i\alpha}\}$ exist if and only if

$$\det|\bar{\lambda}_{ij} + \bar{\mu}_{ij}E_\alpha + \delta_{ik}\delta_{jk}E^2_\alpha| = 0 \qquad (i, j = 0, 1, \ldots N-1). \tag{57}$$

This secular equation is of degree $(N+1)$ in E_α, so that, as in the previous case, there are a maximum of $(N+1)$ distinct roots. In this case, the extremal set $\{E_\alpha\}$ contains $(N+1)$ roots; there is no significance to be attached to any particular E_β. The extremal values of the multipliers $\bar{\lambda}_{ij}$ and $\bar{\mu}_{ij}$ are derived exactly as before, and we simply give the results:

$$\begin{aligned}
&\bar{\lambda}_{is} = \bar{\mu}_{is} = 0 && (i \neq k, s \neq k, i \neq s)\\
&\bar{\lambda}_{ii} + \bar{\mu}_{ii}I_i = 0 && (i \neq k)\\
&\bar{\lambda}_{ks} = -I_k\bar{\mu}_{ks}, \qquad \bar{\mu}_{ks} = \bar{J}_{ks}/(I_k - I_s) && (s \neq k)\\
&\bar{\lambda}_{kk} + \bar{\mu}_{kk}I_k = -\bar{J}_{kk}
\end{aligned} \tag{58}$$

where we use the notations

$$\bar{J}_{ks} = \sum_\alpha \bar{a}_{k\alpha}\bar{a}_{s\alpha}E^2_\alpha, \qquad \bar{J}_{kk} = \sum_\alpha \bar{a}^2_{k\alpha}E^2_\alpha \tag{59}$$

to denote extremal values of the second moments. From (56) when $i \neq k$, we have here

$$(\bar{\lambda}_{ii} + \bar{\mu}_{ii} E_\alpha)\bar{a}_{i\alpha} = -(\bar{\lambda}_{ik} + \bar{\mu}_{ik} E_\alpha)\bar{a}_{k\alpha}. \tag{60}$$

Combined with (58), this implies that

$$\bar{\mu}_{ii} = \frac{-\bar{J}_{ik}}{I_k - I_i} \frac{\bar{a}_{k\alpha}(I_k - E_\alpha)}{\bar{a}_{i\alpha}(I_i - E_\alpha)} \tag{61}$$

and the invariance of $\bar{\mu}_{ii}$ to the choice of any particular α now allows us to repeat the arguments which yield equation (22). Furthermore, it is clear from the symmetry of the extremal values (25) that we would obtain exactly the same result if, instead of the function f_k in (55), we had chosen the function:

$$f_l = \sum_\alpha a_{l\alpha}^2 E_\alpha^2 + \sum_{i=0}^{N-1} \sum_{j=0}^{N-1} (\lambda_{ij} g_{ij} + \mu_{ij} h_{ij}). \tag{62}$$

Now, once again using the invariance of $(I_k - E_\alpha)\bar{a}_{k\alpha}/(I_i - E_\alpha)\bar{a}_{i\alpha}$ together with (24) and (11) we obtain

$$\bar{J}_{ik} \frac{\bar{a}_{k\alpha}(I_k - E_\alpha)}{\bar{a}_{i\alpha}(I_i - E_\alpha)} = \sum_\alpha \bar{a}_{k\alpha}^2 E_\alpha^2 \frac{I_k - E_\alpha}{I_i - E_\alpha} = \bar{J}_{kk} - I_k^2 = \bar{\Delta}_k^2, \quad \text{say} \tag{63}$$

and, interchanging i and k,

$$\bar{J}_{ki} \frac{\bar{a}_{i\alpha}(I_i - E_\alpha)}{\bar{a}_{k\alpha}(I_k - E_\alpha)} = \bar{J}_{ii} - I_i^2 = \bar{\Delta}_i^2. \tag{64}$$

Returning to (56) when $i = k$ and using (58) and (64), we have for each of the $(N+1)$ extremal values of α,

$$\bar{\mu}_{kk} = -(I_k + E_\alpha) - \left(\sum_{i \neq k} \frac{\bar{\Delta}_i^2}{I_k - I_i} + \sum_i \frac{\bar{\Delta}_i^2}{I_i - E_\alpha} \right). \tag{65}$$

Using this result for any two *distinct* values α and β say, we obtain

$$\sum_{i=0}^{N-1} \frac{\bar{\Delta}_i^2}{(I_i - E_\alpha)(I_i - E_\beta)} = -1 \qquad (\alpha \neq \beta). \tag{66}$$

Finally, rewriting (66) for each of the N possible pairs (α, β) with *fixed* α, and solving, we obtain the extremal value, valid for each i:

$$\bar{\Delta}_i^2 = -\prod_\alpha (I_i - E_\alpha) \prod_{n \neq i} \frac{1}{(I_i - I_n)}. \tag{67}$$

4.1. *Nature of the extremum*

The determinantal equation (7) reduces in this case to a squared numerical factor multiplying a product of determinants

$$D_N(E; \rho) = \det|\bar{\lambda}_{ij} + \bar{\mu}_{ij} E + \delta_{ik}\delta_{jk} E^2 - \delta_{ij}\rho| \qquad (i, j = 0, 1, \ldots N-1). \tag{68}$$

The matrix $D_N(E) = (\bar{\lambda} + \bar{\mu} E + \delta_{ik}\delta_{jk} E^2)$ has $(N+1)$ latent roots $\{E_\alpha\}$, which we take to be the lowest eigenvalues $\{E_i; i = 0, 1, \ldots N\}$. It has non-diagonal elements in the kth row and column only, which we bring to the last row and column as usual. The presence of a quadratic term in the kth diagonal position now allows us to write

$$D_N(E) = B_N \prod_{\alpha} (E - E_\alpha) \tag{69}$$

where

$$B_N = \prod_{i \neq k} \bar{\mu}_{ii} \tag{70}$$

while the diagonal elements of $D_N(E)$ are given explicitly by

$$\bar{\mu}_{ii}(E - I_i) = (E - I_i)\bar{\Delta}_k^2/(I_i - I_k) \qquad (i \neq k). \tag{71}$$

Thus, we obtain a lower bound if every $\bar{\mu}_{ii}$ is positive, which will be the case if and only if $I_i > I_k$ for all $i \neq k$. Thus we identify I_k with I_0, and obtain

$$\Delta_0^2 \geqslant \bar{\Delta}_0^2 = (E_1 - I_0)(I_0 - E_0) \prod_{n=1}^{N-1} \frac{E_{n+1} - I_0}{I_n - I_0}. \tag{72}$$

4.2. Generalizations of Temple's lower bound to the energy

Rewriting (72), we obtain a lower bound to the ground-state energy:

$$E_0 \geqslant I_0 - \frac{\Delta_0^2}{E_1 - I_0} \prod_{n=1}^{N-1} \frac{I_n - I_0}{E_{n+1} - I_0}. \tag{73}$$

This is a generalization of Temple's (1928) lower bound

$$E_0 \geqslant I_0 - \frac{\Delta_0^2}{E_1 - I_0} \tag{74}$$

and (73) clearly improves (74) since the bracketing conditions (29) ensure that *each* factor $(I_n - I_0)/(E_{n+1} - I_0)$ is less than unity. Furthermore, as each I_n approaches the corresponding exact E_n, (73) approaches a limiting value:

$$E_0 \geqslant I_0 - \frac{\Delta_0^2}{E_N - I_0}. \tag{75}$$

The optimal lower bound which might be obtained by this process is seen to be

$$E_0 \geqslant I_0 - \frac{\Delta_0^2}{E_{\text{ion}} - I_0} \tag{76}$$

where E_{ion} is the energy of the ionic ground state.

All these lower bound formulae, (73) to (76), remain valid if the exact excited-state energies are replaced by lower bounds, but the bounds are unlikely to be effective unless the excited-state energies are known with considerable precision. The numerical improvement which may be obtained from (73), (75) or (76) (by comparison with the Temple bound (74)) is ultimately limited by the accuracy of Δ_0^2.

The discussion of the preceding section indicates that in general, no comparable rigorous lower bound can be obtained for any excited state energy. But if we assume that the N trial functions $\{\phi_i; i=1, \ldots N\}$ are all orthogonal to the *exact* ψ_0, we may easily obtain the analogue of (73):

$$E_1 \geqslant I_1 - \frac{\Delta_1^2}{E_2 - I_1} \prod_{n=2}^{N} \frac{I_n - I_1}{E_{n+1} - I_1} \tag{77}$$

with corresponding extensions of (75) and (76).

5. An example

We now illustrate the results of the two preceding sections with a numerical example. We consider the finite symmetric matrix operator (which may be regarded as the representation of a physical Hamiltonian in a truncated basis)

$$H = \begin{bmatrix} 0 & -1 & 0 & 0 & 0 \\ -1 & -1 & 0 & 1 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 \end{bmatrix}. \tag{78}$$

The normalized eigenvectors are easily found to be

$$\psi_0 = \tfrac{1}{\sqrt{6}}(1, 2, 0, -1, 0), \qquad \psi_1 = (0, 0, 1, 0, 0), \qquad \psi_2 = \tfrac{1}{\sqrt{2}}(1, 0, 0, 1, 0)$$
$$\psi_3 = \tfrac{1}{\sqrt{3}}(1, -1, 0, -1, 0), \qquad \psi_4 = (0, 0, 0, 0, 1) \tag{79}$$

and the corresponding eigenvalues

$$E_0 = -2, \qquad E_1 = -1, \qquad E_2 = 0, \qquad E_3 = 1, \qquad E_4 = 2. \tag{80}$$

We used the trial vectors (these were normalized in the calculations)

$$\phi_0 = (7, 16, 0, -9, 4), \qquad \phi_1 = (1, -1, 24, -1, 0), \qquad \phi_2 = (49, 2, 0, 47, 12) \tag{81}$$

and obtained the results summarized in table 1. Extremal values are based on equations (25) and (67) with $N=3$; the corresponding exact values were calculated directly.

Table 1. Exact and extremal values.

	Extremal			Exact		
i	0	1	2	0	1	2
I_i	—	—	—	−1·831	−0·990	0·058
J_i	—	—	—	3·980	1·0	0·126
Δ_i^2	0·458†	0·023	0·060	0·628	0·021	0·123
a_{i0}^2	0·939†	0·001	0·001	0·955	0·0	0·001
a_{i1}^2	0·003‡	0·992†	0·000	0·0	0·995	0·0
a_{i2}^2	0·007	0·001‡	0·939†	0·005	0·0	0·968
a_{i3}^2	0·051	0·005	0·060‡	0·0	0·005	0·0
a_{i4}^2	0·039	0·004	0·030‡	0·040	0·0	0·030

† Rigorous lower bound. ‡ Rigorous upper bound.

Those individual extremal values which are rigorous lower or upper bounds are indicated in this table. In addition, the following sums contained in (45) are also rigorous bounds:

$$a_{10}^2 + a_{00}^2 = 0{\cdot}955 \geqslant 0{\cdot}940 = \bar{a}_{10}^2 + \bar{a}_{00}^2$$
$$a_{20}^2 + a_{10}^2 + a_{00}^2 = 0{\cdot}956 \geqslant 0{\cdot}941 = \bar{a}_{20}^2 + \bar{a}_{10}^2 + \bar{a}_{00}^2$$
$$a_{21}^2 + a_{11}^2 = 0{\cdot}995 \geqslant 0{\cdot}992 = \bar{a}_{21}^2 + \bar{a}_{11}^2$$
$$a_{02}^2 + a_{12}^2 = 0{\cdot}005 \leqslant 0{\cdot}008 = \bar{a}_{02}^2 + \bar{a}_{12}^2.$$

On the other hand, we emphasize that $\bar{\Delta}_1^2$ is *not* a lower bound to Δ_1^2, *neither* is $\bar{a}_{04}^2$ an upper bound to a_{04}^2.

In table 2, we display the convergence with increasing N of the rigorous lower bounds to the ground-state energy based on (73), and of the 'limiting' values based on (75). *Effective* bounds to the first excited state, based on (77) and the analogue of (75) are also displayed.

Table 2. Convergence of lower bounds to the energy.

	Ground state		First excited state	
N	(73)	(75)	(77)	(75)
1	−2·587	−2·587	—	—
2	−2·178	−2·174	−1·011	−1·011
3	−2·063	−2·053	−1·001	−1·001
$E_0 = -2{\cdot}0$			$E_1 = -1{\cdot}0$	
$I_0 = -1{\cdot}831$			$I_1 = -0{\cdot}990$	

6. Discussion and conclusions

All the bounds formulae derived in this work (equations (34) to (36), (45) and (72)) require as input data *calculated* first moments $\{I_i\}$ and *exact* energies $\{E_i\}$. These latter may be known empirically (from experiment) or they may be approximated by lower bounds. The results summarized in tables 1 and 2 show that some of our bounds may be quite precise. The Lagrange multipliers procedure is clearly capable of providing a wide variety of other results, but it is disappointing that our generalization of Temple's (1928) energy bound cannot be applied rigorously to excited states. Further work on excited states would be extremely valuable.

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Appendix

We derive here explicit expressions for the extremal sums

$$S_N = \sum_{i=0}^{N-1} \bar{a}_{i\beta}^2 \tag{A.1}$$

and

$$T_N = \sum_{i=0}^{N-1} \frac{\bar{a}_{i\beta}^2}{I_i - E_\beta}. \tag{A.2}$$

Consider the function $F(\eta)$ defined by

$$F(\eta) = 1 - (E_\beta - \eta) \sum_{i=0}^{N-1} \frac{\bar{a}_{i\beta}^2}{I_i - \eta}. \tag{A.3}$$

From equation (26) of the text, we see that

$$F(E_\alpha) = 0 \tag{A.4}$$

for *each* of the N extremal values $\{E_\alpha\}$. Thus we may write

$$F(\eta) = (1 - S_N) \prod_\alpha (E_\alpha - \eta) \Big/ \prod (I_i - \eta). \tag{A.5}$$

Then, assuming that the sum $\Sigma_{i=0}^{N-1} \bar{a}_{i\beta}^2/(I_i - \eta)$ is finite when $\eta = E_\beta$, we have from (A.3) and (A.5)

$$1 - S_N = \prod_{i=0}^{N-1} (I_i - E_\beta) \Big/ \prod_{\alpha \neq \beta} (E_\alpha - E_\beta). \tag{A.6}$$

Thus, S_N is less than unity *unless* one of the I_i is equal to E_β.

To obtain T_N, we differentiate $F(\eta)$ with respect to η and set $\eta = E_\beta$, assuming now that the sum $\Sigma_{i=0}^{N-1} \bar{a}_{i\beta}^2/(I_i - \eta)^2$ is finite when $\eta = E_\beta$. The result is

$$\begin{aligned}\left(\frac{\mathrm{d}F}{\mathrm{d}\eta}\right)_{\eta=E_\beta} = T_N &= \left[F(\eta)\left(\sum_i \frac{1}{(I_i - \eta)} - \sum_\alpha \frac{1}{(E_\alpha - \eta)}\right)\right]_{\eta=E_\beta} \\ &= \sum_{i=1}^{N-1} \frac{1}{I_i - E_\beta} - \sum_\alpha \frac{1}{E_\alpha - E_\beta}.\end{aligned} \tag{A.7}$$

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