

Lower Bounds for Eigenvalues of Schrödinger's Equation*

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This paper gives new results that are useful in estimation of eigenvalues of Schrödinger's equation. Numerical applications are made for the helium atom, an anharmonic oscillator, and a radial Schrödinger equation.

I. INTRODUCTION

ALTHOUGH a given quantum mechanical eigenvalue problem may not have known solutions, it is often possible to find similar problems which can be solved exactly. In this paper we show how such information can be used to estimate numerically the eigenvalues in the initial part of the spectrum of the given problem.

Our procedures determine lower bounds to eigenvalues. Upper bounds can be obtained satisfactorily by the well-known Rayleigh-Ritz procedures; however, without lower bounds no rigorous estimate of the accuracy of the calculation can be made.

The procedures that we give are based on the method of intermediate problems originated by Weinstein¹ and extended and developed by Aronszajn.² Some of our results have features in common with recent work of Weinberger.³

The theoretical foundations of our work are given in Sec. II. In Secs. III-VI various procedures are developed for obtaining lower bounds through solvable algebraic problems. In Sec. VII numerical applications are carried out for the helium atom, an anharmonic oscillator, and a radial Schrödinger equation.

II. INTERMEDIATE HAMILTONIANS

In this section we introduce the procedure of Aronszajn² for the construction of intermediate Hamiltonians. This construction forms the basis of our procedures for determining lower bounds given in Secs. III-VI.

* Part of this research was started while the authors were in the Institute for Fluid Dynamics and Applied Mathematics, University of Maryland, and was summarized in American Mathematical Society Notices 6 (1959) and in the expository lecture of A. Weinstein, Proceedings of an International Conference on Partial Differential Equations and Continuum Mechanics, Madison, Wisconsin (1960). Also, parts were reported by the authors to the International Summer Symposium on Quantum Chemistry, Uppsala, Sweden (1960). This work was supported in part by the Department of the Navy under contract with the Bureau of Naval Weapons.

¹ A. Weinstein, *Mém. sci. math.* No. 88 (1937).

² N. Aronszajn, Proceedings of the Oklahoma Symposium on Spectral Theory and Differential Problems, 1959 (unpublished).

³ H. F. Weinberger, Institute for Fluid Dynamics and Applied Mathematics, University of Maryland, Technical Note BN-183 1959 (unpublished).

We consider Schrödinger's equation

$$H\psi = E\psi; \quad (2.1)$$

here H is a Hermitian operator⁴ with respect to the inner product (φ, ψ) given by $(\varphi, \psi) = \int \varphi^* \psi d\tau$. We assume that all continuous energy levels of H are higher than the discrete energy levels which we wish to estimate. We regard these lowest eigenvalues of H as ordered in a nondecreasing sequence,

$$E_1 \leq E_2 \leq \dots, \quad (2.2)$$

in which each degenerate energy level appears the number of times of its multiplicity. An eigenfunction ψ_i corresponding to E_i satisfies

$$H\psi_i = E_i \psi_i, \quad (\psi_i, \psi_j) = \delta_{ij}, \quad (2.3)$$

where δ_{ij} is Kronecker's delta.

We assume that the Hamiltonian H can be written as the sum of two parts H^0 and H' such that H^0 has known eigenvalues and eigenfunctions and H' is positive definite⁵ (but not necessarily small). That is

$$H = H^0 + H', \quad (2.4)$$

and

$$(\psi, H'\psi) = \int \psi^* H'\psi d\tau > 0, \quad (\psi \neq 0). \quad (2.5)$$

Further we assume that H^0 has ordered discrete energy levels

$$E_1^0 \leq E_2^0 \leq \dots, \quad (2.6)$$

below its continuous spectrum. We denote the corresponding orthonormalized eigenfunctions by ψ_i^0 , and thus we have

$$H^0 \psi_i^0 = E_i^0 \psi_i^0, \quad (\psi_i^0, \psi_j^0) = \delta_{ij}. \quad (2.7)$$

Since $H^0 \leq H$,⁶ it follows⁷ that

$$E_i^0 \leq E_i, \quad (i=1, 2, \dots), \quad (2.8)$$

⁴ We actually require that H have a unique self-adjoint (hypermaximal) extension in our Hilbert space. See T. Kato, *Trans. Am. Math. Soc.* 70, 195 (1951).

⁵ The case that H' is positive but not definite requires only a slight extension of the theory.

⁶ $H^0 \leq H$ means $(\psi, H^0 \psi) \leq (\psi, H \psi)$ for every ψ in the domain of H .

⁷ These inequalities can be traced back to H. Weyl, *J. reine angew. Math.* 141, 1 (1912). See also T. Kato, *Trans. Am. Math. Soc.* 70, 212 (1951).

and consequently the eigenvalues of H^0 give rough lower bounds to those of H .

The procedure of intermediate Hamiltonians links the *base* Hamiltonian H^0 to the *given* Hamiltonian H by a sequence H^k of *intermediate* Hamiltonians. These satisfy the inequalities

$$H^0 \leq H^k \leq H^{k+1} \leq H, \tag{2.9}$$

and hence their eigenvalues give intermediate lower bounds to those of H .

To define the Hamiltonians H^k we temporarily introduce the scalar product $[\psi, \varphi]$ given by

$$[\psi, \varphi] = (\psi, H' \varphi) = \int \psi^* H' \varphi \, d\tau \tag{2.10}$$

for every pair φ, ψ for which $H' \varphi$ and $H' \psi$ are defined. Let p_1, p_2, \dots , be a sequence of linearly independent functions in the vector space with inner product $[\psi, \varphi]$. The projection P^k of an element φ in this space on the span of p_1, p_2, \dots, p_k is given by

$$P^k \varphi = \sum_{i=1}^k \alpha_i p_i, \tag{2.11}$$

where the constants α_i must satisfy the equations

$$[\psi_j, P^k \varphi] = [\psi_j, \varphi] = \sum_{i=1}^k \alpha_i [\psi_j, p_i], \tag{2.12}$$

($j=1, 2, \dots, k$).

Since the projections P^k become larger as k is increased we have

$$0 \leq [\varphi, P^k \varphi] \leq [\varphi, P^{k+1} \varphi] \leq [\varphi, \varphi], \tag{2.13}$$

($k=1, 2, \dots$),

or equivalently, in our original space,

$$0 \leq (\varphi, H' P^k \varphi) \leq (\varphi, H' P^{k+1} \varphi) \leq (\varphi, H' \varphi), \tag{2.14}$$

($k=1, 2, \dots$).

By combining (2.11) and (2.12) we may write

$$H' P^k \varphi = \sum_{i,j=1}^k (H' p_i, \varphi) b_{ij} H' p_j, \tag{2.15}$$

where the numbers b_{ij} are the elements of the matrix inverse to that with terms $[\psi_j, p_i]$. From (2.14) we have

$$H' P^k \leq H' P^{k+1} \leq H', \tag{2.16}$$

($k=1, 2, \dots$).

We now define the intermediate Hamiltonians H^k by

$$H^k = H^0 + H' P^k, \tag{2.17}$$

($k=1, 2, \dots$).

It is clear from (2.16) that these satisfy the desired inequalities (2.9). If we could solve the eigenvalue problem for H^k , i.e.,

$$H^k \psi = E \psi, \tag{2.18}$$

to obtain the ordered eigenvalues E_i^k and the corresponding eigenfunctions ψ_i^k in the lowest part of the spectrum, we would have from (2.9)

$$E_i^0 \leq E_i^k \leq E_i^{k+1} \leq E_i \tag{2.19}$$

($i, k=1, 2, \dots$).

Although the solution of this problem can be accomplished quite generally,² the form of the result is not suitable for most applications. The remainder of this paper is devoted to procedures which overcome the difficulties in the applications.

III. METHOD OF TRUNCATION FOR INTERMEDIATE HAMILTONIANS

In this section we introduce new Hamiltonians $H^{l,k}$ which for each l are smaller than the corresponding intermediate Hamiltonians H^k . These Hamiltonians increase whenever the index l or k is increased and thus give *improvable* lower bounds for the initial eigenvalues of the given Hamiltonian H . Furthermore, these new Hamiltonians have the important property that their eigenvalues and eigenfunctions are determined from the solutions of algebraic problems that involve only the known eigenvalues and eigenfunctions of H^0 and the arbitrarily chosen functions p_i .

First define the Hamiltonians $H^{l,0}$ by

$$H^{l,0} \psi = \sum_{i=1}^l (\psi_i^0, \psi) E_i^0 \psi_i^0 + E_{l+1}^0 \left[\psi - \sum_{i=1}^l (\psi_i^0, \psi) \psi_i^0 \right], \tag{3.1}$$

($l=1, 2, \dots$).

These Hamiltonians, called the *truncations* of H^0 of order l , satisfy the inequalities

$$H^{l,0} \leq H^{l+1,0} \leq H^0, \tag{3.2}$$

($l=1, 2, \dots$).

These inequalities are easy to verify if the spectrum of H^0 consists of bound levels only that diverge to infinity with no finite limit points, for then we have

$$\begin{aligned} (\psi, H^{l,0} \psi) &= \sum_{i=1}^l E_i^0 |(\psi_i^0, \psi)|^2 + E_{l+1}^0 \sum_{i=l+1}^{\infty} |(\psi_i^0, \psi)|^2 \\ &\leq \sum_{i=1}^{l+1} E_i^0 |(\psi_i^0, \psi)|^2 + E_{l+2}^0 \sum_{i=l+2}^{\infty} |(\psi_i^0, \psi)|^2 \\ &= (\psi, H^{l+1,0} \psi), \end{aligned} \tag{3.3}$$

($l=1, 2, \dots$),

and

$$(\psi, H^{l+1,0} \psi) \leq \sum_{i=1}^{\infty} E_i^0 |(\psi_i^0, \psi)|^2 = (\psi, H^0 \psi), \tag{3.4}$$

($l=1, 2, \dots$).

In more general cases the proof follows⁸ from the spectral theorem.

The Hamiltonians $H^{l,k}$ are now obtained in terms of

⁸ For this and other mathematical details relating to Secs. II, III, and V see the paper of the authors in J. Research Natl. Bur. Standards **65B**, No. 2 (1961).

$H^{l,0}$ and $H'P^k$. The defining equations are

$$H^{l,k} = H^{l,0} + H'P^k, \quad (k, l = 1, 2, \dots). \quad (3.5)$$

According to (3.2) and (2.16) we have the inequalities

$$H^{l,k} \leq H^{l+1,k} \leq H^k \leq H, \quad (k, l = 1, 2, \dots), \quad (3.7)$$

and

$$H^{l,k} \leq H^{l,k+1} \leq H^{l,0} + H' \leq H, \quad (k, l = 1, 2, \dots). \quad (3.8)$$

These imply that the lowest ordered eigenvalues of $H^{l,k}$, denoted by $E_i^{l,k}$, satisfy the parallel inequalities

$$E_i^{l,k} \leq E_i^{l+1,k} \leq E_i^k \leq E_i, \quad (i, k, l = 1, 2, \dots), \quad (3.9)$$

and

$$E_i^{l,k} \leq E_i^{l,k+1} \leq E_i, \quad (i, k, l = 1, 2, \dots). \quad (3.10)$$

We now show how the eigenvalues and eigenfunctions of $H^{l,k}$ may be determined. Let us make the preliminary observation that according to (2.11), (2.12), and (3.5), $H^{l,k}$ is given by

$$H^{l,k}\psi = H^{l,0}\psi + \sum_{i=1}^k \alpha_i H' p_i, \quad (3.11)$$

where the constants α_i satisfy the conditions

$$\sum_{i=1}^k \alpha_i (H' p_j, p_i) = (H' p_j, \psi) \quad (j = 1, 2, \dots, k). \quad (3.12)$$

The eigenvalue equation for $H^{l,k}$ has the form

$$H^{l,0}\psi - E\psi = f_k, \quad (3.13)$$

with f_k given by

$$f_k = - \sum_{i=1}^k \alpha_i H' p_i. \quad (3.14)$$

The complete solution of $H^{l,k}\psi = E\psi$ is obtained in the following steps.

First, if E is not an eigenvalue of $H^{l,0}$ then the solution to (3.13) is given by

$$\psi = \sum_{\nu=1}^l \frac{(\psi_{\nu}^0, f_k) \psi_{\nu}^0}{E_{\nu}^0 - E} + \frac{f_k - \sum_{\nu=1}^l (\psi_{\nu}^0, f_k) \psi_{\nu}^0}{E_{l+1}^0 - E}. \quad (3.15)$$

When the expression (3.14) for f_k is inserted, we have

$$\psi = - \sum_{i=1}^k \alpha_i \left\{ \sum_{\nu=1}^l \frac{(\psi_{\nu}^0, H' p_i) \psi_{\nu}^0}{E_{\nu}^0 - E} + \frac{H' p_i - \sum_{\nu=1}^l (\psi_{\nu}^0, H' p_i) \psi_{\nu}^0}{E_{l+1}^0 - E} \right\}. \quad (3.16)$$

The constants α_i are now determined by substituting this expression for ψ in the relation (3.12). This gives the set of k homogeneous equations for the α 's,

$$\sum_{i=1}^k \alpha_i \left\{ (p_j, H' p_i) + \sum_{\nu=1}^l \frac{(\psi_{\nu}^0, H' p_i) (H' p_j, \psi_{\nu}^0)}{E_{\nu}^0 - E} + \frac{(H' p_j, H' p_i) - \sum_{\nu=1}^l (\psi_{\nu}^0, H' p_i) (H' p_j, \psi_{\nu}^0)}{E_{l+1}^0 - E} \right\} = 0 \quad (j = 1, 2, \dots, k). \quad (3.17)$$

In order that (3.17) have a nonzero solution it is necessary and sufficient that E be a solution of the equation

$$\det \left\{ (p_j, H' p_i) + \sum_{\nu=1}^l \frac{(\psi_{\nu}^0, H' p_i) (H' p_j, \psi_{\nu}^0)}{E_{\nu}^0 - E} + \frac{(H' p_j, H' p_i) - \sum_{\nu=1}^l (\psi_{\nu}^0, H' p_i) (H' p_j, \psi_{\nu}^0)}{E_{l+1}^0 - E} \right\} = 0. \quad (3.18)$$

For each such solution E of (3.18) that is not equal to $E_1^0, E_2^0, \dots, E_{l+1}^0$, there are n linearly independent sets of α 's which satisfy (3.17), where n is the nullity of the coefficient matrix displayed in (3.17) at the root E . From Eq. (3.16) these yield n linearly independent eigenfunctions of $H^{l,k}$.

Second, we investigate whether $H^{l,k}$ has any of the eigenvalues $E_1^0, E_2^0, \dots, E_l^0$ of H^0 . For any one, suppose E_{σ}^0 of multiplicity r , to be an eigenvalue of $H^{l,k}$, we must have, in addition to (3.12) and (3.13), that f_k be orthogonal to each eigenfunction of $H^{l,0}$ corresponding to E_{σ}^0 . If for the moment we designate these eigenfunctions of $H^{l,0}$ at E_{σ}^0 by $\varphi_1, \varphi_2, \dots, \varphi_r$, then the orthogonality condition is expressed by

$$\sum_{i=1}^k \alpha_i (\varphi_j, H' p_i) = 0, \quad (j = 1, 2, \dots, r). \quad (3.19)$$

If this condition is satisfied, then each eigenfunction of $H^{l,k}$ corresponding to E_{σ}^0 is of the form

$$\psi = - \sum_{i=1}^k \alpha_i \left\{ \sum_{\nu=1}^l \frac{(\psi_{\nu}^0, H' p_i) \psi_{\nu}^0}{E_{\nu}^0 - E_{\sigma}^0} + \frac{H' p_i - \sum_{\nu=1}^l (\psi_{\nu}^0, H' p_i) \psi_{\nu}^0}{E_{l+1}^0 - E_{\sigma}^0} \right\} - \sum_{i=k+1}^{k+r} \alpha_i \varphi_{i-k}, \quad (3.20)$$

where the sum \sum' is taken over all indices ν for which $E_\nu^0 \neq E_\sigma^0$. For each such eigenfunction ψ , the constants α_i must satisfy the relations (3.12) and (3.19). In full, these are

$$\sum_{i=1}^k \alpha_i \left\{ (p_j, H' p_i) + \sum_{\nu=1}^l \frac{(\psi_\nu^0, H' p_i)(H' p_j, \psi_\nu^0)}{E_\nu^0 - E_\sigma^0} + \frac{(H' p_j, H' p_i) - \sum_{\nu=1}^l (\psi_\nu^0, H' p_i)(H' p_j, \psi_\nu^0)}{E_{l+1}^0 - E_\sigma^0} \right\} + \sum_{i=k+1}^{k+r} \alpha_i (H' p_j, \varphi_{i-k}) = 0, \quad (j=1, 2, \dots, k), \quad (3.21)$$

and

$$\sum_{i=1}^k \alpha_i (\varphi_{j-k}, H' p_i) = 0, \quad (j=k+1, k+2, \dots, k+r). \quad (3.22)$$

Thus the necessary and sufficient condition for E_σ^0 to be an eigenvalue of $H^{l,k}$ is that

$$\det \begin{pmatrix} (p_j, H' p_i) + \sum_{\nu=1}^l \frac{(\psi_\nu^0, H' p_i)(H' p_j, \psi_\nu^0)}{E_\nu^0 - E_\sigma^0} + \frac{(H' p_j, H' p_i) - \sum_{\nu=1}^l (\psi_\nu^0, H' p_i)(H' p_j, \psi_\nu^0)}{E_{l+1}^0 - E_\sigma^0} & \vdots & (H' p_j, \varphi_{i-k}) \\ \vdots & \ddots & \vdots \\ (\varphi_{j-k}, H' p_i) & \vdots & 0 \end{pmatrix} = 0. \quad (3.23)$$

The number of linearly independent solutions of Eqs. (3.21) and (3.22) is just the nullity of the matrix displayed in (3.23). It has been shown⁸ that linearly independent solutions of these equations yield linearly independent eigenfunctions (3.20) of $H^{l,k}$. Thus by examination of each distinct eigenvalue in the sequence $E_1^0, E_2^0, \dots, E_l^0$ we determine those which are also eigenvalues of $H^{l,k}$ and the corresponding eigenfunctions.

So far we have determined all of the eigenvalues of $H^{l,k}$ that are not equal to E_{l+1}^0 . These are, of course, finite in number and multiplicity.

We observe that all of the eigenfunctions of $H^{l,k}$ corresponding to eigenvalues different from E_{l+1}^0 are given by (3.16) and (3.20), and these are linear combinations of the functions ψ_ν^0 ($\nu=1, 2, \dots, l$) and $H' p_i$ ($i=1, 2, \dots, k$). As a consequence there can be at most $l+k$ such eigenfunctions.

Finally, we note that by the application⁸ of a theorem of H. Weyl, $H^{l,k}$ can have no continuous spectrum, and further it must have E_{l+1}^0 as an eigenvalue of infinite multiplicity. The eigenfunctions corresponding to E_{l+1}^0 are all functions orthogonal to the eigenfunctions of the form (3.16) and (3.20).

SUMMARY

The eigenvalues and eigenfunctions of $H^{l,k}$ are found in terms of the quantities $(\psi_\nu^0, H' p_i)$, $(p_j, H' p_i)$, $(H' p_j, H' p_i)$ and the functions $H' p_i$ and ψ_ν^0 ($i, j=1, 2, \dots, k; \nu=1, 2, \dots, l$). The procedure is as follows:

(1) Calculate the roots of the determinantal equation (3.18). For those which are not eigenvalues of $H^{l,0}$ calculate the linearly independent solutions of (3.17). By means of (3.16) calculate the corresponding eigenfunctions of $H^{l,k}$.

(2) If there are less than $k+l$ eigenfunctions determined by (1) then for each distinct eigenvalue of $H^{l,0}$

that is not equal to E_{l+1}^0 check to determine whether (3.21) and (3.22) have nontrivial solutions. For those for which nontrivial solutions exist, compute the corresponding eigenfunctions of $H^{l,k}$ by (3.20).

(3) Note that E_{l+1}^0 is an eigenvalue of $H^{l,k}$ of infinite multiplicity and has every function orthogonal to those eigenfunctions found in (1) and (2) as an eigenfunction.

To obtain the lower bounds, order the eigenvalues of $H^{l,k}$ that lie below E_{l+1}^0 in a nondecreasing sequence:

$$E_1^{l,k} \leq E_2^{l,k} \leq \dots \leq E_t^{l,k}, \quad t \leq l, \quad (3.24)$$

in which each eigenvalue is repeated according to its multiplicity. These then give lower bounds by the fundamental inequalities

$$E_i^{l,k} \leq E_i, \quad (i=1, 2, \dots, t) \quad (3.25)$$

and

$$E_{t+1}^0 \leq E_i, \quad (i=t+1, t+2, \dots). \quad (3.26)$$

The procedure just given is not the only one available for determining the eigenvalues and eigenfunctions of $H^{l,k}$. Another equivalent procedure is based on the observation of W. Börsch-Supan that the finite-dimensional space \mathfrak{N} generated by the eigenfunctions ψ_ν^0 ($\nu=1, 2, \dots, l$) and the functions $H' p_i$ ($i=1, 2, \dots, k$) reduces the Hamiltonian $H^{l,k}$. This allows determination of the eigenfunctions of $H^{l,k}$ lying in \mathfrak{N} from a linear algebraic eigenvalue problem of order $k+l$ for one symmetric indefinite matrix relative to another.

To demonstrate this we start from an expression of the eigenvalue equation for $H^{l,k}$ in terms of the vectors ψ_ν^0 and $H' p_i$,

$$\sum_{\nu=1}^l (\psi_\nu^0, \psi) (E_\nu^0 - E_{l+1}^0) \psi_\nu^0 + \sum_{i,j=1}^k (H' p_i, \psi) b_{ij} H' p_j - (E - E_{l+1}^0) \psi = 0. \quad (3.27)$$

Take inner products with the functions ψ_μ^0 and $H'p_j$, let $(\psi_\nu^0, \psi)(E_\nu^0 - E_{l+1}^0) = \gamma_\nu$ ($\nu = 1, 2, \dots, l$), and let $\sum_{i=1}^k (H'p_i, \psi)b_{i, \nu-l} = \gamma_\nu$ ($\nu = l+1, l+2, \dots, l+k$). The resulting system of equations has the form

$$\sum_{\nu=1}^{k+l} \gamma_\nu \{C_{\mu\nu} - (E - E_{l+1}^0)D_{\mu\nu}\} = 0, \quad (\mu = 1, 2, \dots, k+l), \quad (3.28)$$

where

$$(C_{\mu\nu}) = \begin{pmatrix} \delta_{\mu\nu} & (\psi_\mu^0, H'p_{\nu-l}) \\ (H'p_{\mu-l}, \psi_\nu^0) & (H'p_{\mu-l}, H'p_{\nu-l}) \end{pmatrix}, \quad (3.29)$$

and

$$(D_{\mu\nu}) = \begin{pmatrix} \delta_{\mu\nu} / (E_\nu^0 - E_{l+1}^0) & 0 \\ 0 & (H'p_{\mu-l}, p_{\nu-l}) \end{pmatrix}. \quad (3.30)$$

For the eigenvalues E of the problem (3.28) which are not equal to E_{l+1}^0 , the corresponding eigenfunctions of $H^{l,k}$ are obtained from (3.27) by solving for ψ . The resulting expression is

$$\psi = \left(\sum_{\nu=1}^l \gamma_\nu \psi_\nu^0 + \sum_{\nu=l+1}^{l+k} \gamma_\nu H'p_{\nu-l} \right) / (E - E_{l+1}^0). \quad (3.31)$$

One can show that (3.31) gives a one-to-one correspondence. As before, E_{l+1}^0 is an eigenvalue of infinite multiplicity.

Still other procedures for the solution of the eigenvalue problem for $H^{l,k}$ can be found by considering the eigenvalue equation in the form

$$H'P^k\psi + (E_{l+1}^0 - E)\psi = (E_{l+1}^0 - H^{l,0})\psi, \quad (3.32)$$

and then inverting the Hamiltonian $H'P^k + E_{l+1}^0 - E$. The resulting matrix problems are similar to (3.17) but of order l . Details of these procedures will not be given here.

IV. ANOTHER METHOD OF TRUNCATION

The procedure of Secs. II and III may be modified in the following way. We observe that under the assumptions (2.4) and (2.5) the Hamiltonian H can be written as

$$H = H^{l,0} + \{H - H^{l,0}\}, \quad (l = 1, 2, \dots), \quad (4.1)$$

where the difference $H - H^{l,0}$ is positive. This difference provides a means to construct Hamiltonians intermediate between $H^{l,0}$ and H .

Following the development of Sec. II, we introduce the scalar products $[\psi, \varphi]_l$ ($l = 1, 2, \dots$) given by

$$[\psi, \varphi]_l = (\psi, \{H - H^{l,0}\}\varphi). \quad (4.2)$$

We let P_l^k denote the projection with respect to these scalar products on the span of the arbitrary functions p_1, p_2, \dots, p_k . New intermediate Hamiltonians $\tilde{H}^{l,k}$ are given by

$$\tilde{H}^{l,k} = H^{l,0} + \{H - H^{l,0}\}P_l^k. \quad (4.3)$$

Since

$$H^{l,0} \leq \tilde{H}^{l,k} \leq \tilde{H}^{l,k+1} \leq H, \quad (4.4)$$

we have the corresponding inequalities for the ordered eigenvalues $\tilde{E}_1^{l,k}, \tilde{E}_2^{l,k}, \dots$ of $\tilde{H}^{l,k}$, namely,

$$E_i^0 \leq \tilde{E}_i^{l,k} \leq \tilde{E}_i^{l,k+1} \leq E_i, \quad (i = 1, 2, \dots, l) \quad (4.5)$$

and

$$E_{l+1}^0 = \tilde{E}_i^{l,k} = \tilde{E}_i^{l,k+1} \leq E_i, \quad (i = l+1, l+2, \dots). \quad (4.6)$$

As in Sec. III, the eigenvalue E_{l+1}^0 appears as an eigenvalue of $\tilde{H}^{l,k}$ with infinite multiplicity.

The procedures for finding the eigenvalues and eigenfunctions of $\tilde{H}^{l,k}$ are identical with those of Sec. III. In fact, one may simply replace H' by $H - H^{l,0}$, wherever it appears in the final formulas of that section. We observe, however, that

$$\begin{aligned} (\psi_\nu^0, \{H - H^{l,0}\}p_i) &= (\psi_\nu^0, H'p_i) + (\{H^0 - H^{l,0}\}\psi_\nu^0, p_i) \\ &= (\psi_\nu^0, H'p_i), \end{aligned} \quad (4.7)$$

for $\nu \leq l$. Thus the only inner products that must be computed in order to determine the eigenvalues and eigenfunctions of $\tilde{H}^{l,k}$ are $(\{H - H^{l,0}\}p_j, \{H - H^{l,0}\}p_i)$, $(p_j, \{H - H^{l,0}\}p_i)$, and $(\psi_\nu^0, H'p_i)$ for $i, j = 1, 2, \dots, k$ and $\nu = 1, 2, \dots, l$.

The Hamiltonians $\tilde{H}^{l,k}$ (and also the H^k of Sec. II) have the property that they agree with H on the span of the functions p_1, p_2, \dots, p_k ; that is,

$$\tilde{H}^{l,k}p_i = Hp_i, \quad (i = 1, 2, \dots, k). \quad (4.8)$$

Thus if an eigenfunction ψ_ν of H is one of the p_i 's (or included in their span) then it will be an eigenfunction $\tilde{\psi}^{l,k}$ of $\tilde{H}^{l,k}$ with E_ν as the corresponding eigenvalue.

There is in general no guarantee that E_ν will be the ν th ordered eigenvalue of $\tilde{H}^{l,k}$. Nevertheless, one can show that if H is a Hamiltonian having bound states only and E_ν is less than the first limit point of the spectrum of H^0 , then there exist intermediate Hamiltonians $\tilde{H}^{l,k}$ (of sufficiently high order l and k) which have

$$\tilde{\psi}_i^{l,k} = \psi_i, \quad (i = 1, 2, \dots, \nu) \quad (4.9)$$

and

$$\tilde{E}_i^{l,k} = E_i, \quad (i = 1, 2, \dots, \nu). \quad (4.10)$$

The same results hold for the Hamiltonians H^k of Sec. II.

V. LOWER BOUNDS BY CHOICE OF ELEMENTS

We introduce another method for determining the spectra of the operators H^k previously defined. This method depends on special choices of the elements p_i that determine the Hamiltonians $H'P^k$ and generalizes an earlier method⁹ so that it applies to a far wider class of problems.

We suppose that it is possible to choose elements p_i ($i = 1, 2, \dots, k$) such that the relations

$$H'p_i = \sum_{\nu=1}^N \beta_{i\nu} \psi_\nu^0, \quad (i = 1, 2, \dots, k) \quad (5.1)$$

⁹ N. Bazley, Phys. Rev. 120, 144 (1960).

are satisfied; that is, functions p_i can be found such that each of the quantities $H'p_i$ can be expressed in terms of a finite number N of eigenvectors of H^0 . The number N must, of course, depend on k .

Using the expressions (2.15) and (2.17) and the relation (5.1), a Hamiltonian H^k takes the form

$$H^k\psi = H^0\psi + \sum_{i,j=1}^k \sum_{\nu,\mu=1}^N (\psi_\nu^0, \psi) \beta_{i\nu}^* b_{ij} \beta_{j\mu} \psi_\mu^0. \quad (5.2)$$

Equation (5.2) permits the determination of the eigenvalues and eigenfunctions of H^k by inspection. In fact, if ψ is such that $(\psi_\nu^0, \psi) = 0$ ($\nu = 1, 2, \dots, N$) then from (5.2), $H^k\psi = H^0\psi$. This shows that each eigenfunction ψ_σ^0 of H^0 not used in the relations (5.1) is an eigenfunction of H^k with the same energy E_σ^0 . The remaining eigenfunctions of H^k must be of the form

$$\psi = \sum_{\nu=1}^N \gamma_\nu \psi_\nu^0. \quad (5.3)$$

When this expression for ψ is inserted in (5.2), the equation $H^k\psi = E\psi$ leads to the equivalent algebraic system,

$$\sum_{\nu=1}^N \gamma_\nu \left\{ \sum_{i,j=1}^k \beta_{i\nu}^* b_{ij} \beta_{j\mu} + (E_\nu^0 - E) \delta_{\nu\mu} \right\} = 0, \quad (\mu = 1, 2, \dots, N). \quad (5.4)$$

Thus the determination of the eigenvalues and eigenfunctions of the Hamiltonian H^k is reduced to a matrix eigenvalue problem.

When all of the eigenvalues of H^k determined above are ordered in the usual way according to magnitude and multiplicity, then the lower bounds are obtained from the inequalities

$$E_i^k \leq E_i, \quad (i = 1, 2, \dots). \quad (5.5)$$

Often relations (5.1) are obtained with $p_i = \psi_i^0$ from a recursion relation among the functions ψ_i^0 . In these cases the N th order Rayleigh-Ritz upper bound computation based on the trial functions $\psi_1^0, \psi_2^0, \dots, \psi_N^0$ leads to an eigenvalue problem closely related to that stated by (5.4). In fact, the coefficient matrix displayed in (5.4) differs from that of the Rayleigh-Ritz matrix only in the terms for which μ and ν are both greater than k .

The method of this section is applicable in the estimation of the eigenvalues of the spheroidal wave equation,¹⁰ anharmonic oscillators,¹¹ and many other similar examples.

VI. SUM OF TWO SOLVABLE HAMILTONIANS

In those cases in which H is decomposable into two Hamiltonians,

$$H = H^0 + H', \quad (6.1)$$

¹⁰ Numerical applications in this case have been made by W. Börsch-Supan.

¹¹ See Sec. VII.

each of which has bound states before the appearance of continuous spectrum, it is quite easy to use the methods of the previous sections singly or in combination to obtain lower bounds. Here we have

$$H^0\psi_i^0 = E_i^0\psi_i^0, \quad (i = 1, 2, \dots) \quad (6.2)$$

and

$$H'\psi_i' = E_i'\psi_i', \quad (i = 1, 2, \dots). \quad (6.3)$$

We suppose that $E_1' > 0$.¹²

A first procedure uses the method of truncation of Sec. III without modification. We take $p_i = \psi_i'$ ($i = 1, 2, \dots, k$). Then since $H'p_i = H'\psi_i' = E_i'\psi_i'$, the only terms to be computed in (3.18) and (3.23) or (3.29) and (3.30) are

$$(\psi_\nu^0, \psi_i'), \quad (i = 1, 2, \dots, k; \nu = 1, 2, \dots, l). \quad (6.4)$$

A second procedure depends on truncating both H^0 and H' . That is, we replace H by the sum of the truncations of H^0 of order l and of H' of order k . This will always give better bounds than those of the procedure just outlined. After truncation the eigenvalue equation becomes

$$(H^{l,0} + E_{k+1}')\psi - E\psi = - \sum_{i=1}^k \alpha_i (H' - E_{k+1}')\psi_i', \quad (6.5)$$

where the constants α_i satisfy the equations

$$\sum_{i=1}^k \alpha_i ((H' - E_{k+1}')\psi_j', \psi_i') = ((H' - E_{k+1}')\psi_j', \psi), \quad (j = 1, 2, \dots, k). \quad (6.6)$$

These equations are of the same form as (3.12), (3.13), and (3.14) and thus can be solved by the techniques of Sec. III. Again the only inner products to be calculated appear in (6.4). We note that $E_{l+1}^0 + E_{k+1}'$ appears as the eigenvalue of infinite multiplicity.

A third procedure uses truncation in order to obtain a special choice. We replace the Hamiltonian H by the sum of H^0 and the n th order truncation of H' , which for convenience we designate by H_n' . The eigenvalue problem

$$H_n^k\psi = (H^0 + H_n'P^k)\psi = E\psi, \quad (6.7)$$

in which P^k is the projection on the span of p_1, p_2, \dots, p_k with respect to the inner product $[\psi, \varphi]_n = (\psi, H_n'\varphi)$, gives lower bounds. It is now easy to use the special choice

$$H_n'p_i = \psi_i^0, \quad (i = 1, 2, \dots, k). \quad (6.8)$$

In fact, the elements p_i are given by

$$p_i = \sum_{\sigma=1}^n \frac{(\psi_\sigma', \psi_i^0)\psi_\sigma'}{E_\sigma'} + \frac{\psi_i^0 - \sum_{\sigma=1}^n (\psi_\sigma', \psi_i^0)\psi_\sigma'}{E_{n+1}'}. \quad (6.9)$$

¹² If $E_1' \leq 0$, we replace H^0 by $H^0 - c$ and H' by $H' + c$, where c is a real constant greater than $-E_1'$, and proceed as above.

The solution of the eigenvalue problem for H_n^k is then obtained from the results of Sec. V. Here $N=k$ and $\beta_{i\nu}=\delta_{i\nu}$ ($i, \nu=1, 2, \dots, k$). Those eigenvalues that correspond to eigenfunctions ψ of the form

$$\psi = \sum_{\nu=1}^k \gamma_{\nu} \psi_{\nu}^0 \tag{6.10}$$

are obtained from the solution of the algebraic problem

$$\sum_{\nu=1}^k \gamma_{\nu} \{ (E_{\nu}^0 - E) \delta_{\nu\mu} + b_{\nu\mu} \} = 0, \quad (\mu = 1, 2, \dots, k) \tag{6.11}$$

where $b_{\nu\mu}$ is an element of the matrix inverse to that with terms $(\psi_{\mu}^0, \psi_{\nu}^0)$. These inner products have the form

$$(\psi_{\mu}^0, \psi_{\nu}^0) = \frac{\delta_{\nu\mu}}{E_{n+1}'} + \sum_{\sigma=1}^n \left(\frac{1}{E_{\sigma}'} - \frac{1}{E_{n+1}'} \right) (\psi_{\sigma}', \psi_{\nu}^0) (\psi_{\mu}^0, \psi_{\sigma}'), \tag{6.12}$$

$(\nu, \mu = 1, 2, \dots, k).$

We note from this that the only inner products to enter the computations are $(\psi_{\nu}^0, \psi_{\sigma}')$ ($\sigma=1, 2, \dots, n; \nu=1, 2, \dots, k$). Further, each ψ_{ν} for $\nu > k$ remains as an eigenfunction of H_n^k with the corresponding eigenvalue E_{ν}^0 , and the continuous spectrum of H_n^k is the same as that of H^0 .

VII. APPLICATIONS

In this section we present several examples that illustrate the methods of Secs. III and V. The calculations are of quite limited scope, for the most part having been carried out by the authors on a desk calculator; nevertheless, the numbers may have some interest of themselves.

A. Helium Atom

The procedures of Secs. III and IV can be used to obtain lower bounds to ground- and excited-state energies in many-electron atomic systems. However, here we limit ourselves to a simple hand computation for a lower bound to the ground-state energy of the helium atom. Our result gives the best lower bound so far obtained directly by intermediate problems.

We restrict ourselves to S states of parahelium. The Hamiltonians H^0 and H' in atomic units are given by

$$H^0 \psi = -\frac{1}{2} \Delta_1 \psi - \frac{1}{2} \Delta_2 \psi - (2/r_1) \psi - (2/r_2) \psi, \tag{7.1}$$

and

$$H' \psi = (1/r_{12}) \psi, \tag{7.2}$$

where \mathbf{r}_1 and \mathbf{r}_2 denote the position vectors of the electrons, $r_i = |\mathbf{r}_i|$ ($i=1, 2$), $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, and Δ_i is

the Laplacian operator in the coordinates \mathbf{r}_i ($i=1, 2$). The lowest part of the spectrum of H consists of ordered bound states,⁷ $E_1 \leq E_2 \leq \dots$.

As is well known, the lowest ordered eigenvalues of H^0 are given by

$$E_i^0 = -2(1+1/i^2), \quad (i=1, 2, \dots) \tag{7.3}$$

with the corresponding eigenfunctions,

$$\begin{aligned} \psi_1^0 &= (1/4\pi) R_{10}(r_1) R_{10}(r_2), \\ \psi_i^0 &= (1/4\pi\sqrt{2}) [R_{10}(r_1) R_{i0}(r_2) + R_{10}(r_2) R_{i0}(r_1)], \end{aligned} \tag{7.4}$$

$(i=2, 3, \dots),$

where R_{i0} is the normalized hydrogen radial wave function for zero angular momentum. Between -2 and zero, H^0 has infinitely many bound states in addition to continuous energy levels which extend from -2 to infinity.

We consider first the lower bounds given by the operator $H^{1,1}$ for two choices of p_1 . For p_1 given by

$$p_1 = (\alpha^3/\pi) e^{-\alpha(r_1+r_2)}, \tag{7.5}$$

Eq. (3.18) becomes

$$\begin{aligned} & \frac{5}{8} \frac{5^2 \times 2^{10} [\alpha^6 / (2+\alpha)^{10}]}{-4-E} \\ & + \frac{\frac{2}{3}\alpha^2 - 5^2 \times 2^{10} [\alpha^6 / (2+\alpha)^{10}]}{-\frac{5}{2}-E} = 0. \end{aligned} \tag{7.6}$$

The lower bound for E_1 , given as the smallest root of (7.6), is maximized for α near 1.5. For $\alpha=1.5$ we have

$$-3.29 \leq E_1, \quad -2.5 \leq E_i, \quad (i=2, 3, \dots). \tag{7.7}$$

For p_1 given by

$$p_1 = (\beta^3/\pi) r_{12} e^{-\beta(r_1+r_2)}, \tag{7.8}$$

Eq. (3.18) becomes

$$0 = \frac{35}{16\beta} + \frac{2^{18} [\beta^6 / (2+\beta)^{12}]}{-4-E} + \frac{1 - 2^{18} [\beta^6 / (2+\beta)^{12}]}{-\frac{5}{2}-E}. \tag{7.9}$$

Here the optimum lower bound is found near $\beta=\sqrt{5}$. For $\beta=\sqrt{5}$ we find

$$-3.03 \leq E_1, \quad -2.50 \leq E_i, \quad (i=2, 3, \dots). \tag{7.10}$$

We improve these bounds by solving the eigenvalue problem for the Hamiltonian $H^{2,2} = H^{2,0} + H'P^2$, where P^2 denotes the projection (2.11) on the span of the two vectors

$$p_1 = [(1.5)^3/\pi] e^{-1.5(r_1+r_2)}, \tag{7.11}$$

$$p_2 = [5\sqrt{5}/\pi] r_{12} \exp[-(5)^{\frac{1}{2}}(r_1+r_2)]. \tag{7.12}$$

Equation (3.18) becomes

$$\left| \begin{array}{cc|cc} 0.937500000 + \frac{1.057078102}{-4-E} + \frac{0.002938082}{-\frac{5}{2}-E} & & 0.888014669 + \frac{1.018593688}{-4-E} + \frac{0.004393440}{-\frac{5}{2}-E} & \\ & \frac{0.439983816}{-20/9-E} & & \frac{0.013788862}{-20/9-E} \\ \hline 0.888014669 + \frac{1.018593688}{-4-E} + \frac{0.004393440}{-\frac{5}{2}-E} & & 0.978279740 + \frac{0.981510355}{-4-E} + \frac{0.006569699}{-\frac{5}{2}-E} & \\ & \frac{0.013788862}{-20/9-E} & & \frac{0.011919946}{-20/9-E} \end{array} \right| = 0. \quad (7.13)$$

We determine the lower bound to E_1 as the first root of (7.13) and obtain

$$-3.0008 \leq E_1. \quad (7.14)$$

The combination of (7.14) with a well-known upper bound gives

$$-3.0008 \leq E_1 \leq -2.9037. \quad (7.15)$$

In order to obtain a useful lower bound for E_2 it would be necessary to consider at least the Hamiltonian $H^{3,3}$.

In an earlier paper⁹ the solution of a third-order intermediate problem by use of a special choice of the elements p_i gave the poorer estimate $-3.0637 \leq E_1$. One expects that calculations using the method of Sec. IV will yield further improvements.

B. Anharmonic Oscillator

We treat the well-known problem of estimating the eigenvalues of an anharmonic oscillator. Our procedure here is the generalized special choice of Sec. V. We consider the ordinary differential equation

$$-d^2\psi/dx^2 + x^2\psi + \epsilon x^4\psi = E\psi, \quad (7.16)$$

where $\epsilon > 0$ and ψ is square integrable on the infinite interval $-\infty < x < \infty$. For simplicity we restrict our attention to the symmetry class of even solutions.

We take

$$H^0\psi = -d^2\psi/dx^2 + x^2\psi \quad (7.17)$$

and

$$H^1\psi = \epsilon x^4\psi. \quad (7.18)$$

The even solutions of $H^0\psi = E\psi$ are the well-known linear oscillation eigenfunctions

$$\psi_i^0 = C_i \exp(-x^2/2) H_{2i-2}(x), \quad (i=1, 2, \dots), \quad (7.19)$$

where $C_i = 2^{1-i} [(2i-2)!]^{-1/2} \pi^{-1/4}$ and $H_n(x)$ is the n th Hermite polynomial. The corresponding eigenvalues are

$$E_i^0 = 4i - 3, \quad (i=1, 2, \dots); \quad (7.20)$$

so that we have the rough lower bounds

$$4i - 3 \leq E_i, \quad (i=1, 2, \dots). \quad (7.21)$$

The generalized special choice,

$$H^1 p_i = \sum_{\nu=1}^N \beta_{i\nu} \psi_\nu^0, \quad (i=1, 2, \dots, k) \quad (7.22)$$

can be satisfied by taking $p_i = \psi_i^0$ and using a recurrence relationship among the Hermite polynomials. In fact, we have

$$\begin{aligned} x^4 \psi_i^0 = & (2i-2)(2i-3)(2i-4)(2i-5)(C_i/C_{i-2})\psi_{i-2}^0 \\ & + (2i-2)(2i-3)(4i-5)(C_i/C_{i-1})\psi_{i-1}^0 \\ & + \frac{3}{4}(8i^2 - 12i + 5)\psi_i^0 + \frac{1}{4}(4i-1)(C_i/C_{i+1})\psi_{i+1}^0 \\ & + \frac{1}{16}(C_i/C_{i+2})\psi_{i+2}^0, \quad (7.23) \end{aligned}$$

so that $N = k + 2$. The $\beta_{i\nu}$ matrix of (5.1) is symmetric and is given for $i, \nu = 1, 2, \dots, 5$ by

$$\beta_{i\nu} = \frac{1}{4} \begin{pmatrix} 3 & 6\sqrt{2} & 2\sqrt{6} & 0 & 0 \\ 6\sqrt{2} & 39 & 28\sqrt{3} & 6\sqrt{10} & 0 \\ 2\sqrt{6} & 28\sqrt{3} & 123 & 22\sqrt{30} & 4\sqrt{105} \\ 0 & 6\sqrt{10} & 22\sqrt{30} & 255 & 60\sqrt{14} \\ 0 & 0 & 4\sqrt{105} & 60\sqrt{14} & 435 \end{pmatrix}. \quad (7.24)$$

For $k = 3$ the lower bounds are determined by (5.4) from the eigenvalues of the linear system

$$\sum_{\nu=1}^5 \gamma_\nu \{ (4\nu - 3 - E)\delta_{\nu\mu} + \epsilon t_{\nu\mu} \} = 0, \quad (\mu=1, 2, 3, 4, 5) \quad (7.25)$$

where

$$(t_{\nu\mu}) = \frac{1}{4} \begin{pmatrix} 3 & 6\sqrt{2} & 2\sqrt{6} & 0 & 0 \\ 6\sqrt{2} & 39 & 28\sqrt{3} & 6\sqrt{10} & 0 \\ 2\sqrt{6} & 28\sqrt{3} & 123 & 22\sqrt{30} & 4\sqrt{105} \\ 0 & 6\sqrt{10} & 22\sqrt{30} & 192 & 24\sqrt{14} \\ 0 & 0 & 4\sqrt{105} & 24\sqrt{14} & 48 \end{pmatrix}. \quad (7.26)$$

When the eigenvalues of (7.25) are ordered with the eigenvalues 21, 25, 29, \dots which persist from H^0 to form the ordered sequence $E_1^5 \leq E_2^5 \leq \dots$, we have the inequalities

$$E_i^5 \leq E_i, \quad (i=1, 2, \dots). \quad (7.27)$$

Upper bounds given by the Rayleigh-Ritz procedure based on the trial functions $\psi_1^0, \psi_2^0, \dots, \psi_5^0$ are the

ordered eigenvalues of

$$\sum_{\nu=1}^5 \alpha_{\nu} \{ [4\nu - 3 - E] \delta_{\nu\mu} + \epsilon \beta_{\nu\mu} \} = 0, \quad (\mu = 1, 2, 3, 4, 5). \tag{7.28}$$

We note again that the Rayleigh-Ritz matrix differs from the matrix displayed in (7.25) by the 2-by-2 lower right-hand corner only.

Our numerical estimates for the first five eigenvalues are listed in Table I.

Figure 1 shows our estimate for E_1 together with those of first and second order perturbation theory.¹³

TABLE I. Upper and lower bounds for eigenvalues of an anharmonic oscillator. For each value of ϵ from 0 to 1.0, the Rayleigh-Ritz upper bounds are listed above and our lower bounds below. The lower bounds marked with an asterisk are those which persist from the base problem.

ϵ	E_1	E_2	E_3	E_4	E_5
0.0	1.000000 1.000000	5.000000 5.000000	9.000000 9.000000	13.000000 13.000000	17.000000 17.000000
0.1	1.065286 1.065278	5.748178 5.746596	11.10038 10.95333	17.51524 16.17279	30.94592 21.00000*
0.2	1.118293 1.118255	6.278820 6.260404	12.48016 12.22585	21.87339 16.90845	45.99933 21.00000*
0.3	1.164055 1.163987	6.708557 6.655885	13.67853 13.25990	26.41021 17.64313	61.16365 21.00000*
0.4	1.204848 1.204738	7.075869 6.979830	14.82828 14.03037	31.03013 18.63119	76.36088 21.00000*
0.5	1.241957 1.241746	7.400376 7.258083	15.96821 14.55430	35.69220 19.88068	91.57225 21.00000*
0.6	1.276195 1.275773	7.694107 7.505763	17.11054 14.90630	40.37815 21.00000*	106.7910 21.31832
0.7	1.308110 1.307324	7.965074 7.732038	18.25889 15.15526	45.07885 21.00000*	122.0141 22.87292
0.8	1.338096 1.336760	8.218847 7.942661	19.41390 15.34432	49.78925 21.00000*	137.2399 24.49895
0.9	1.366442 1.364349	8.459408 8.141353	20.57519 15.49781	54.50637 21.00000*	152.4676 25.00000*
1.0	1.393371 1.390301	8.689663 8.330586	21.74203 15.62953	59.22833 21.00000*	167.6966 25.00000*

To the scale of this graph our upper and lower bounds are indistinguishable. Figure 2 shows our upper and lower bounds for E_2 .

C. Radial Schrödinger Equation

As our final example we give an application to a radial Schrödinger equation. Our example demonstrates a useful modification² of the method of truncation developed in Sec. III.

¹³ See, for example, E. C. Titchmarsh, *Eigenfunction Expansions Associated with Second-Order Differential Equations* Clarendon Press, Oxford, (1958), Part II.

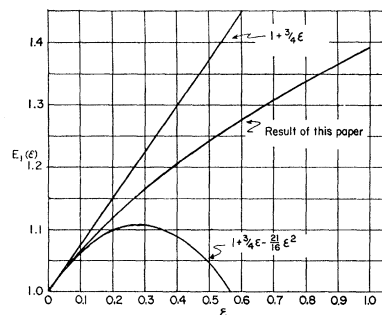


FIG. 1. Estimates for the first eigenvalue of an anharmonic oscillator.

We consider the equation

$$-d^2\psi/dx^2 - z[(1 - e^{-\alpha x})/x]\psi = E\psi \tag{7.29}$$

on the interval $0 < x < \infty$ for α and z real and positive. The potential $-z(1 - e^{-\alpha x})/x$ behaves like the Coulomb potential $-z/x$ for large values of x , while near the origin it approaches $-\alpha z$. Furthermore, the potential differs from that of the hydrogenic wave equation by the positive term $ze^{-\alpha x}/x$.

In our treatment of (7.29) we are interested in the bound states only. We fix the energy E and take the charge z as the eigenvalue. The numerical results of such calculations (done in sufficient detail) may be inverted to give energy eigenvalues as a function of charge. The advantage of taking z as the eigenvalue is that it eliminates the continuous spectrum.

We put $E = -\kappa^2$ and introduce the transformations

$$t = 2\kappa x, \quad \varphi(t) = t^{-1/2}\psi(t), \tag{7.30}$$

so that (7.29) becomes

$$-\frac{d}{dt} \left(t \frac{d\varphi}{dt} \right) + \frac{t^2 + 1}{4t} \varphi = \mu(1 - e^{-\alpha t/2\kappa}) \varphi, \tag{7.31}$$

where $\mu = z/2\kappa$. Equation (7.31) is an eigenvalue problem of the form

$$H^0 \varphi = \mu(I - K) \varphi, \tag{7.32}$$

where

$$H^0 \varphi = -\frac{d}{dt} \left(t \frac{d\varphi}{dt} \right) + \frac{t^2 + 1}{4t} \varphi, \tag{7.33}$$

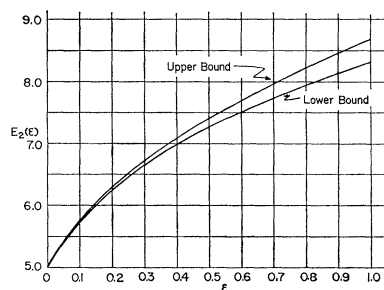


FIG. 2. Upper and lower bounds for the second eigenvalue of an anharmonic oscillator.

TABLE II. Lower bounds for eigenvalues of a radial Schrödinger equation.

l	k	$\mu_1^{l,k}$	$\mu_2^{l,k}$	$\mu_3^{l,k}$	$\mu_i^{l,k} (i \geq 4)$
1	0	1.000	2.000	2.000	2.000
1	1	1.234985	2.000	2.000	2.000
1	2	1.251726	2.000	2.000	2.000
2	0	1.000	2.000	3.000	3.000
2	1	1.248252	2.358910	3.000	3.000
2	2	1.258266	2.363134	3.000	3.000
3	0	1.000	2.000	3.000	4.000
3	1	1.249540	2.380424	3.349294	4.000
3	2	1.258725	2.394445	3.420742	4.000

and

$$K\varphi = e^{-\alpha t/2\kappa} \varphi. \tag{7.34}$$

A suitable family of functions on which to define (7.31) are those functions which vanish at the origin, are square integrable, and for which $H^0\varphi$ is square integrable.

We note that $0 \leq (\varphi, K\varphi) \leq 1$ for normalized φ ; also, H^0 has known eigenvalues and normalized eigenfunctions,

$$\mu_i^0 = i, \quad (i=1, 2, \dots) \tag{7.35}$$

and

$$\varphi_i^0 = (t^{1/2}/i!i^{1/2})L_i'(t)e^{-t/2}, \quad (i=1, 2, \dots), \tag{7.36}$$

where L_i' is the first derivative of the i th Laguerre polynomial. Equation (7.31) has a pure point spectrum $\mu_1 \leq \mu_2 \leq \dots$, diverging to infinity, and it satisfies

$$\mu_i^0 \leq \mu_i \quad (i=1, 2, \dots). \tag{7.37}$$

We may proceed in direct analogy with our previous theory and introduce the eigenvalue problems

$$H^{l,0}\varphi = \mu(I - KQ^k)\varphi, \tag{7.38}$$

where $H^{l,0}$ has been previously defined by (3.1) and Q^k denotes a projection on arbitrary vectors p_1, p_2, \dots, p_k with respect to the inner product $[\psi, \varphi] = (\psi, K\varphi)$. If we denote the ordered eigenvalues and eigenfunctions of (7.38) by $\mu_i^{l,k}$ and $\varphi_i^{l,k}$, respectively, we have

$$\mu_i^{l,k} \leq \mu_i \quad (i=1, 2, \dots), \tag{7.39}$$

and $\mu_i^{l,k}$ are monotonic in both l and k .

In the solution of (7.38) we choose

$$p_j = \varphi_j^0 \quad (j=1, 2, \dots, k)$$

TABLE III. Upper bounds for eigenvalues of a radial Schrödinger equation.

$\mu_1^{R_4}$	$\mu_2^{R_4}$	$\mu_3^{R_4}$	$\mu_4^{R_4}$
1.259005	2.416443	3.557628	6.091083

and find, by analogy with (3.5), (3.11), and (3.16), that

$$\varphi^{l,k} = \mu \sum_{i=1}^k \alpha_i \left\{ \sum_{\nu=1}^l \frac{(\varphi_\nu^0, K\varphi_i^0)\varphi_\nu^0}{\nu - \mu} + \frac{K\varphi_i^0 - \sum_{\nu=1}^l (\varphi_\nu^0, K\varphi_i^0)\varphi_\nu^0}{l+1-\mu} \right\}. \tag{7.40}$$

Here the values of α_i and μ are found as solutions of the algebraic system

$$0 = \sum_{i=1}^k \alpha_i \left\{ (\varphi_j, K\varphi_i) + \mu \sum_{\nu=1}^l \frac{(\varphi_\nu^0, K\varphi_i^0)(K\varphi_j^0, \varphi_\nu^0)}{\nu - \mu} + \mu \frac{(K\varphi_j, K\varphi_i) - \sum_{\nu=1}^l (\varphi_\nu^0, K\varphi_i)(K\varphi_j, \varphi_\nu^0)}{l+1-\mu} \right\}. \tag{7.41}$$

As before, the multiplicity of each root is just the number of linearly independent solutions to the algebraic problem (7.41), and μ_{l+1}^0 appears as an eigenvalue of infinite multiplicity.

For our example we have fixed the value of α and chosen $\kappa = \alpha/2$ so that $E = -\alpha^2/4$. We have computed our lower bounds from (7.41) for several values of l and k . Since, in each case considered (7.41) has $l+k$ distinct solutions, there is no need to consider the equations analogous to (3.20) and (3.23), which would tell when a value μ_i^0 persists as an eigenvalue of (7.38). The computations, carried out on a desk calculator, yielded the results given in Table II.

Upper bounds obtained by solving a fourth-order Rayleigh-Ritz problem based on the trial functions $\varphi_1^0, \varphi_2^0, \varphi_3^0$, and φ_4^0 give the values listed in Table III.

The lower bounds $\mu_i^{\beta,2}$ and the Rayleigh-Ritz upper bounds provide the following estimate:

$$\begin{aligned} 1.2587 \alpha &\leq z_1 \leq 1.2590 \alpha, \\ 2.3944 \alpha &\leq z_2 \leq 2.4164 \alpha, \\ 3.4207 \alpha &\leq z_3 \leq 3.5576 \alpha. \end{aligned} \tag{7.42}$$