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Upper and Lower Bounds to the Eigenvalues of Double-Minimum Potentials*

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Several methods of obtaining upper and lower bounds to the eigenvalues of self-adjoint operators bounded from below have recently been developed by Löwdin. All these procedures are based on a bracketing theorem. We mention them and discuss one of the variants that makes use of intermediate Hamiltonians. To illustrate the power of the method, an application is made to various forms of double-minimum (D.M.) potentials, both symmetric and asymmetric, which have already been studied by Somorjai and Hornig. The new results show the importance of obtaining these lower bounds in connection with the resonance interaction between accidentally coincident "left" and "right" levels of weakly asymmetric D.M. potentials. An agreement between upper and lower bounds of 12-15 significant figures is obtained.

I. INTRODUCTION

SINCE the Schrödinger equation cannot be solved exactly in most cases, it is of fundamental importance to be able to estimate the margin of error in the eigenvalues obtained by approximate methods. Many criteria have been found by several investigators. 1-3 Although the partitioning technique for the solution of eigenvalue problems has been known to mathematicians for a long time, it is only recently that the same approach has been shown to contain a powerful tool for the obtention of upper and lower bounds to the eigenvalues of self-adjoint operators, namely, the bracketing theorem. 4, 5 In 1964, Löwdin connected some of A. Weinstein's and N. Aronszajn's ideas on intermediate problems with the bracketing theorem; he obtained a practical solution of an inhomogeneous differential equation, and from there he derived formulas for the upper and lower bounds to the eigenvalues of self-adjoint operators bounded from below. 6 The formulas give, in addition, exact solutions for the intermediate Hamiltonians. Later developments of the theory lead to the elimination of the intermediate Hamiltonians, and upper and lower bounds to the bracketing function are found directly. 7 In this way, the difficulties arising from the ordering theorem disappear. However, for this particular application all ordering problems are easily eliminated. Fortunately, although this work was carried out with intermediate Hamiltonians in mind, it can be translated into the language of the later developments due to the operational similarity of both procedures which, however, differ substantially in meaning.

In this work, Löwdin's procedure is applied to a particle in a double-minimum (D.M.) potential $V$ of the type $V = ax^2 + bx^4 + cx^6$. In order to be able to compare our results with those obtained by other authors, the potentials and the energy units are chosen identical with those of Somorjai and Hornig; 8 upper and lower bounds to the vibrational energy levels are calculated for most of the cases considered in their paper.

II. METHOD

Let us introduce a bracketing function $Y(H, \phi; \delta)$:

$$Y(H, \phi; \delta) = \delta - f(H, \phi; \delta),$$

where $f(H, \phi; \delta) = \langle \phi | H + HTH | \phi \rangle$ is given in Eq. (11) of Ref. 3, and the nodes of $Y(H, \phi; \delta)$ are eigenvalues to $H$. Equation (30) of Ref. 3 now reads

$$d^2Y(H, \phi; \delta)/d\delta^2 = \delta_{11} - (-1)^{n+1}\delta_{1} f(H, \phi; \delta).$$

Using the turnover rule for $H$ and $T$ it follows that $dY(H, \phi; \delta)/d\delta > 1$. Also $d^2Y(H, \phi; \delta)/d\delta^2 > 0$, and consequently the second derivative is a monotonically increasing function of $\delta$. In particular, this means that between two consecutive singularities of $Y(H, \phi; \delta)$ there must be one and only one inflexion point. The typical form of the curves is illustrated in Ref. 4. The function $Y(H, \phi; \delta)$ has not yet been evaluated exactly for an $H$ which cannot be solved by more conventional methods. The difficulty lies in the operator $T$. Two main alternatives are known:

1. At present, upper and lower bounds to $Y(H, \phi; \delta)$ have been found. 4, 5 One can use this information in two complementary ways:

(a) The intersection of the upper and lower bounds to $Y(H, \phi; \delta)$ with the abscissa give lower and upper bounds, respectively, for some eigenvalue; these always lie between two consecutive singularities.

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1 For references see the article by A. Weinstein, "Bounds for Eigenvalues and the Method of Intermediate Problems," in Partial Differential Equations and Continuum Mechanics, edited by R. E. Langer (University of Wisconsin Press, Madison, Wisconsin, 1961), and also Refs. 2 and 3.

2 P.-O. Löwdin, Phys. Rev. (to be published), referred to as Paper X in Ref. 3.


(b) By the same technique, we can get a lower bound to $E_\infty = E_\emptyset - V(H', \phi; E_\emptyset)$ which will be a lower bound to $E$ if $E_\emptyset$ is an upper bound to $E$. Conversely, an upper bound to $E_\infty$ will also be an upper bound to $E$ if $E_\emptyset$ is a lower bound to $E$.

In (a) one works with the parameter $\xi$. In (b) one has to distinguish between upper and lower bounds from the beginning. In both instances, the ordering theorem is out of the picture.

(2) An intermediate Hamiltonian $H'$ is constructed such that its spectrum lies, in order, below the spectrum of $H$. Clearly, an intermediate Hamiltonian $H''$ is built up so that its spectrum lies, in order, above the spectrum of $H$.

The function $V(H'', \phi; \xi)$ can be evaluated exactly. For $V(H', \phi; \xi)$ this is not true except in some cases like a one-dimensional motion in a potential $V_\infty = \mu + \lambda x^2 + V(x)$;  \[ V(x) = \sum_{j=0}^{n} a_j x^j \]  \[ \xi = a \lambda \]  where $\lambda$, $\alpha$, $a_j$ are real constants. The D.M. potentials considered here are a particular case of Eq. (2).

The ordering of the spectrum of $H$ would be broken if some eigenvalues between the lowest one and, say, the $p$th one, were lost. How this is avoided here, is discussed in Sec. IV.

III. Calculation

We consider the motion of a particle constrained to one dimension in space in a potential of the type
\[ U = q(x^2 + x^3 + x^4) \], where $\xi = a x$ is a nondimensional coordinate; $\alpha = (\mu / \beta) 1 / \beta$ is an arbitrary frequency, $\mu$ is the reduced mass of the moving particle in the given system; and $v_x, v_z, v_0$ are nondimensional parameters. When the potential is symmetric, $v_x = 0$. In units of $\hbar \beta / 4$, the Hamiltonian can be written as
\[ H = 2(\Delta + U / \hbar \beta) = 2(\Delta + v_x^2 + v_z^2 + v_0^2) \].

$H$ may be split up into $H_0 + V$ with $V > 0$ in the following way:
\[ H_0 = 2[-\Delta + (-v_0) \xi^2 - \alpha] \]
\[ V = 2[\alpha - 2(-v_0) \xi^2 + v_z^2 + v_0 \xi^4], \]
where the constant $\alpha$ is chosen so that $V$ be positive definite. $H_0$ is a harmonic-oscillator Hamiltonian; its Schrödinger equation is
\[ [\Delta - (-v_0) \xi^2 + a] \phi_\alpha = 0, \]
whose solutions are
\[ E_\alpha = 2[2(n+1) - (-v_0) \xi^2 - \alpha] \]
in units of $\hbar \beta / 4$,
and $\phi_\alpha(x) = N_n \exp(-x^2 / 2) H_n(x) \xi$, where $z = (-v_0) \xi$ and $H_n(x)$ is the Hermite polynomial of order $n$. $H_0$ could have been chosen to be
\[ H_0 = 2[-\Delta + K(-v_0) \xi^2 - \alpha], \]
where $K$ is any positive number. The choice of $K$ determines the scaling of the eigenfunctions to $H_0$. Since the Aronszajn space $\mathfrak{g}$ was chosen to be made out of a finite number of them, the importance of $K$ lies in its relationship to the rate of convergence of $H'$ towards $H$, when the size of $\mathfrak{g}$ is increased. However, for a large $\mathfrak{g}$, the scaling has practically no influence. Convergence is expected in this example because $H_0$ does not have a continuum spectrum.

a. Lower Bounds

The lower bounds are obtained from (1) by replacing $H$ by $H' = H_0 + V(\mathfrak{g} \mathfrak{g} \mathfrak{g})^2 + V [\text{see Eq. (41)}]$. The corresponding $V(H', \phi; \xi)$ can be derived by replacing Eq. (43) into (1):
\[ V(H', \phi; \xi) = \xi - \xi V_0 + V_0 \xi - \xi V_3 \]
\[ \xi = \xi V_3 + \xi V_4 \]
\[ \xi = \xi V_5 \]
\[ \xi = \xi V_6 \]
The manifold $\mathfrak{g}$ was chosen to be made out of 50 eigenfunctions (orthonormal) to $H_0$. For the symmetric cases:

\[ g = (| \phi_0 \rangle | \phi_0 \rangle | \phi_0 \rangle | \phi_0 \rangle | \phi_0 \rangle ) \]
\[ g = (| \phi_0 \rangle | \phi_0 \rangle | \phi_0 \rangle | \phi_0 \rangle | \phi_0 \rangle ) \]
For the asymmetric cases:

\[ g = (| \phi_0 \rangle | \phi_0 \rangle | \phi_0 \rangle | \phi_0 \rangle | \phi_0 \rangle ) \]

A necessary condition for an efficient hunting of the nodes of $Y(H', \phi; \xi)$ is that its slope be not too large in their vicinity. This condition is, in turn, linked to the reference function $\phi$ being as close as possible to the true wavefunction, since $dV / d\phi = 1 + || \Psi - \phi ||^2$. The function $\phi_\alpha$ is then approximated by $\chi_\alpha = \sum \phi_\alpha \phi_\alpha^* \alpha$ and the $\alpha$'s being determined by the variational principle, and the reference function is chosen to be $\phi = \phi_\alpha$ where $\phi_\alpha$ is the function in the above expansion which has the largest weight for the level considered.

The second term in (3) is simply
\[ \langle \phi | H_0 | \phi \rangle = \langle \phi_\alpha | H_0 | \phi_\alpha \rangle = E_\alpha \].

The third term, however, is more complicated:
\[ a = g \xi V | \phi \rangle = g \xi V | \phi \rangle \]
\[ \langle \alpha | a = \langle \phi_\alpha | V | \phi_\alpha \rangle = V_{\alpha, \xi} \]

and
\[ \Lambda = g \xi (V - V T_0 V) \xi \]
so that, if $n_\alpha$ is the dimension of $\mathfrak{g}$,
\[ (A)_{n, m} = V_{n, m} - \sum_{\alpha=1,\xi}^{m} \frac{V_{\alpha, \xi}^2}{E_\alpha} \]
\[ N = \begin{cases} n_\alpha + 4 & \text{for asymmetric cases} \\ n_\alpha + 2 & \text{for symmetric cases} \end{cases} \]

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and \( \alpha \Delta^{-1} \alpha = \alpha \Delta \); \( n \) is obtained from \( \Delta n = \alpha \) by means of an elimination procedure. The matrix elements of \( V \) are as follows:

<table>
<thead>
<tr>
<th>Symmetric case</th>
<th>Asymmetric case</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{M,M+2} )</td>
<td>( V_{M,M+4} )</td>
</tr>
<tr>
<td>( V_{M,M+4} )</td>
<td>( V_{M,M+6} )</td>
</tr>
<tr>
<td>( V_{M,M} )</td>
<td>( V_{M,M} )</td>
</tr>
</tbody>
</table>

Equations (4), (5), and (6) apply to both even and odd states of the symmetric potentials as well as to the asymmetric ones, the only difference being in the labeling of the matrix elements of \( V \). The \( M \)'s in (6) are ordering subscripts. The constant \( AM \) is equal to \( M-1 \) for asymmetric cases, \( 2M-2 \) for even, symmetric cases, and \( 2M-1 \) for odd, symmetric cases. A program has been written to calculate \( Y(H', \phi; \varepsilon) \) for different values of the parameter \( \varepsilon \) and has been carried out on an IBM 709. It is imperative to use double precision because of the large accumulation of rounding-off errors, especially for potential \( V_0 \) for which the curves are not reproducible at all when using single precision. The nodes are obtained by interpolation, assuming that the error depends on how constant the slope of \( Y(H', \phi; \varepsilon) \) is, near the nodes;

\[
E' = \varepsilon_i - Y(H', \phi; \varepsilon_i)/(\text{slope}),
\]

\[
\frac{\delta (\text{slope})}{E'} \approx \frac{e_i}{(\text{slope})^2},
\]

where \( \delta (\text{slope}) \) is maximum variation among the slopes in the different intervals. This assumption is correct whenever the inflexion point of \( Y(H', \phi; \varepsilon) \) is not in between; when the \( \delta \)'s are relatively large or when the above assumption fails, the lower bounds are given with less precision. This, however, could have been improved by using a machine subroutine to read data with 16 figures.

b. Upper Bounds

As for the lower bounds, the upper bounds are obtained by evaluating \( Y(H'', \phi; \varepsilon) \) for various values of \( \varepsilon \). The "standard space" \( \varepsilon \) is chosen to be identical with the \( \varepsilon \) used above. The \( H'' \) is constructed by an "external projection" of \( V \): \( H'' = H_0 + V''; \) \( V'' = Vf(ff)^{-1}fVf \); and \( Y(H'', \phi; \varepsilon) \) is given by

\[
Y(H'', \phi; \varepsilon) = \varepsilon - \langle \phi | H_0 | \phi \rangle - \langle \phi | fKf^{-1}f \phi \rangle,
\]

where \( K = (ff)^{-1}fVf, B = (ff)^{-1}fT_0f \) and \( f \) determines the "standard space" \( \varepsilon \).

IV. DISCUSSION

Tables I and II contain the characteristic data of the D.M. potentials considered, as well as the upper and lower bounds obtained by Löwdin's procedure.

The comparison with Somorjai and Hornig's results is left to the reader. A significant discrepancy arises in \( V_0 \), where the energy gap between Levels 1 and 2 must be reduced by a factor of 2.2.

In all cases, except for potential \( V_0 \), the curves \( Y(H', \phi; \varepsilon) \) and \( Y(H'', \phi; \varepsilon) \) are found to satisfy

\[
| Y(H', \phi; \varepsilon) - Y(H'', \phi; \varepsilon) | \leq 10^{-12}
\]

when \( | \text{eigenvalue} - \varepsilon | < 10^{-8} \) and, since the slopes are always greater than 1, we have, in a linear approximation

\[
E'' - E' < 10^{-12},
\]

where \( E'' \) and \( E' \) are a pair of corresponding eigenvalues to \( H'' \) and \( H' \), respectively. The significant figures given in the tables represent the accuracy with which the nodes are obtained rather than the degree of approach of \( E'' \) to \( E' \) when \( \varepsilon \) and \( \varepsilon \) are of dimension 50.

In some cases, the number of coincident significant figures may seem unreasonably large. However, they are obtained because the slopes remain constant over the intervals considered and hence the interpolation could be carried out with a high degree of accuracy. For example, for the Level 3 of Potential \( V_4 \)

\[
Y(H', \phi; \varepsilon) - Y(H'', \phi; \varepsilon) < 10^{-14}
\]

for

\[
\varepsilon = \begin{cases} 4.879840 \\ 4.879841 \\ 4.879842 \end{cases}
\]

The slope showed no variations in its first eight figures, and there was no inflexion point in these intervals.

To observe the influence of the size of the manifold \( \varepsilon \) let us consider the most slowly convergent case, found in level 4 of \( V_1 \). The upper bound with a manifold of 50 functions is \( E_{\text{upper}} = 11.5077397 \). The lower bounds are:

\[
E_{\text{lower}} = \begin{cases} 11.25666 & n_0 = 20 \\ 11.499407 & = 30 \\ 11.50775695 & = 50 \end{cases}
\]

7 The graphs of the D.M. potential functions may be found in Ref. 6.
### Table I. Upper and lower bounds to the vibrational energy levels of the symmetric potentials.

<table>
<thead>
<tr>
<th>Level</th>
<th>( \psi_1 )</th>
<th>( \psi_3 )</th>
<th>( \psi_5 )</th>
<th>( \psi_7 )</th>
<th>( \psi_9 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \phi_1^a )</td>
<td>( \phi_3^a )</td>
<td>( \phi_5^a )</td>
<td>( \phi_7^a )</td>
<td>( \phi_9^a )</td>
</tr>
<tr>
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<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
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</tr>
<tr>
<td>4</td>
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<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
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<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
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<td>9</td>
</tr>
</tbody>
</table>

*We also indicate the subscript \( \kappa \) of the reference function \( \psi_\kappa \) which was used in each case, as well as the corresponding characteristic data of the potential functions. Only one value is given because the upper bounds are found to be equal to the lower bounds.*
The eigenfunctions $\Psi''$ and $\Psi$ may be obtained from an equation analogous to Eq. (27) of Ref. 3 in the form:

$$\Psi'' = \phi_k^2 + \sum_{l=6}^{\infty} c_l' \phi_l^2;$$

$$c_l'' = \left[ 1/(E'' - E_l') \right] \langle \phi_l^2 | fK_{B-1}^2 | \phi_k^2 \rangle;$$  \hspace{1cm} (7)

$$\Psi' = \phi_k^2 + \sum_{l=6}^{\infty} c_l' \phi_l^2;$$

$$c_l' = \left[ 1/(E' - E_l') \right] \langle \phi_l^2 | VgA^{-1}gV | \phi_k^2 \rangle.$$  \hspace{1cm} (8)

It is seen that the vector $f_l' | \phi_k^2 \rangle$ in (7) is zero unless $\phi_k^2$ is contained in $f$. Hence, the operator $H''$ has $n_p$ eigenfunctions $\Psi'' = \phi^2$ in $\mathcal{F}$, and the others are identical with those solutions to $H_0$ not in $\mathcal{F}$; these are called persistent solutions. The wavefunctions $\Psi^2$ coincide with the variational approximations to $\Psi$ in $\mathcal{F}$.

Analogously, the vector $g_l'V | \phi_k^2 \rangle$ in (8) is zero unless $\phi_k^2$ is contained in $Vg$. There are persistent solutions if there exists a proper subspace of $| \phi_l^2 \rangle$ which is orthogonal to $Vg$. Accidental persistence occurs when either $f$ or $Vg$ is made out of a single element $\phi_k^2$.

From the above discussion it is seen that persistent eigenvalues do not occur through the range of $\delta$ for which the calculations were made. Also, since the manifold $\mathcal{G}$ contains the minimum Aronszajn space $\mathcal{E}$ in all examples considered, $t'' < t'$ is satisfied. The lower bounds could have been obtained from the upper bounds by means of a 45° construction from the curve $Y(t', \phi; \varepsilon)$, which is an upper bound to $Y(t', \phi; \varepsilon)$. Also, since $Y(t', \phi; \varepsilon) = Y(H', \phi; \varepsilon)$ in this case, the interpolation can be readily done. The above paragraphs express the translation of the intermediate Hamiltonian's approach into the language of Paper X and Paper XI, for this particular application.

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