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## A generalization of Weinstein's procedure for calculating bounds to quantum-mechanical quantities

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**Abstract.** A simple unified procedure, based on a generalization of a method first used by Weinstein in 1934, yields effective lower and upper bounds to energy levels and overlap integrals of quantum-mechanical systems. A further generalization yields bounds to expectation values.

### 1. Introduction

The search for effective error bounds to energy levels and other physical 'observables' of atomic and molecular systems remains one of the most challenging problems of non-relativistic quantum mechanics. Many procedures have been employed by different investigators over the past forty years, but the resulting formulae have usually been rather similar. It is therefore instructive to derive these formulae by means of a single unified procedure, one which not only demonstrates the relationships between them, but also indicates possible avenues of progress.

In this paper, we present a generalization of the classical work of Weinstein (1934), which was originally used to provide lower bounds to energy levels. Our procedure leads not only to bounds to energy levels but also to overlap integrals and expectation values, which are required in many applications. We first give a fairly detailed resumé of the Weinstein procedure so as to emphasize both its generality and its limitations.

We consider a general quantum system described by a non-relativistic hamiltonian  $H$ . The exact eigenfunctions  $\{\psi_n\}$  (of particular symmetry) and eigenvalues  $\{E_n\}$  satisfy the Schrödinger equation

$$H\psi_n = E_n\psi_n; \quad (1)$$

the eigenfunctions form a complete orthonormal set|| which satisfy

$$\langle \psi_n | \psi_m \rangle = \delta_{nm} \quad (2)$$

and the eigenvalues are arranged in order so that

$$E_n < E_{n+1} \quad (n = 0, 1, \dots). \quad (3)$$

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|| The eigenvalue spectrum of  $H$  is, in general, partly continuous with eigenfunctions  $\{\psi_E\}$  for all  $E > 0$ . Thus, the complete orthonormal set of eigenfunctions actually contains both  $\{\psi_n\}$  and  $\{\psi_E\}$ . It is only for simplicity of presentation that we use the notations  $\psi_n$ ,  $E_n$  and  $\Sigma_n$  for the entire spectrum.

A normalized approximate trial function  $\phi_i$  which satisfies the appropriate physical boundary conditions may be expanded in terms of the exact eigenfunctions according to

$$\phi_i = \sum_{n=0}^{\infty} a_{in} \psi_n. \quad (4)$$

Without loss of generality, we assume throughout this paper that the expansion coefficients  $a_{in}$  are real and suppress all explicit reference to the continuum. We choose  $\phi_i$  normalized so that

$$\langle \phi_i | \phi_i \rangle = \sum_{n=0}^{\infty} a_{in}^2 = 1 \quad (5)$$

and, provided that the integrals exist, we may calculate successive moments of the hamiltonian  $I_i, J_i, K_i, L_i$ , etc, where

$$I_i = \langle \phi_i | H | \phi_i \rangle = \sum_{n=0}^{\infty} a_{in}^2 E_n \quad (6a)$$

$$J_i = \langle \phi_i | H^2 | \phi_i \rangle = \sum_{n=0}^{\infty} a_{in}^2 E_n^2 \quad (6b)$$

$$K_i = \langle \phi_i | H^3 | \phi_i \rangle = \sum_{n=0}^{\infty} a_{in}^2 E_n^3 \quad (6c)$$

$$L_i = \langle \phi_i | H^4 | \phi_i \rangle = \sum_{n=0}^{\infty} a_{in}^2 E_n^4, \quad (6d)$$

etc.

Clearly, as  $\phi_i$  approaches an exact eigenfunction  $\psi_i$ ,

$$a_{in} \rightarrow 0 \quad (\text{all } n \neq i); \quad a_{ii} \rightarrow 1 \quad (7)$$

so that

$$I_i \rightarrow E_i, \quad J_i \rightarrow E_i^2, \quad K_i \rightarrow E_i^3, \quad L_i \rightarrow E_i^4, \quad \text{etc.} \quad (8)$$

## 2. Resumé of the Weinstein procedure

Weinstein (1934) considered the positive semi-definite quadratic function

$$A_i(\lambda, \lambda) = \langle (H - \lambda)\phi_i | (H - \lambda)\phi_i \rangle \quad (9a)$$

$$= J_i - 2I_i\lambda + \lambda^2 \quad (9b)$$

$$= \sum_{n=0}^{\infty} a_{in}^2 (E_n - \lambda)^2 \quad (9c)$$

where  $\lambda$  is any real parameter for which the integrals exist. By introducing the normalization condition for  $\phi_i$ , he obtained the following *identity* valid for any particular energy level  $E_j$  of interest:

$$A_i(\lambda, \lambda) \equiv (E_j - \lambda)^2 + \sum_{n \neq j} a_{in}^2 [(E_n - \lambda)^2 - (E_j - \lambda)^2]. \quad (10)$$

Now, provided only that the sum in equation (10) is non-negative, one obtains both lower and upper bounds to  $E_j$ :

$$E_j \leq \lambda \pm A_i^{1/2}(\lambda, \lambda). \quad (11)$$

It is clear that the residual sum in equation (10) will be non-negative if we can choose  $\lambda$  so that each term in the sum is separately non-negative, so that

$$|E_j - \lambda| \leq |E_n - \lambda| \quad (12)$$

for every  $n \neq j$ ; this condition is sufficient, but not necessary. Various choices of  $\lambda$  now lead to a number of different energy bounds.

### 2.1. Weinstein's bounds

In his original work, Weinstein (1934) chose the parameter  $\lambda$  by minimizing the function  $A_i(\lambda, \lambda)$ , a procedure which brackets  $E_j$  between symmetrically situated lower and upper bounds. His results are:

$$\lambda = I_i \quad (13)$$

and

$$E_j \leq I_i \pm \Delta_i, \quad (14)$$

where we have introduced the variance of  $\phi_i$ :

$$\Delta_i^2 = J_i - I_i^2 \geq 0. \quad (15)$$

The bounds of inequality (14), though very simple in form, suffer from a serious drawback which was actually emphasized in Weinstein's (1934) paper. The problem is that more than one of the exact energy levels  $E_j$  may satisfy the conditions for (14) to guarantee bounds; and even if there is only a single level in the range, it is not clear which level  $E_j$  is bounded, unless one knows *a priori* that the calculated  $I_i$  lies closer to one particular  $E_j$  than to all the others.

### 2.2. Bounds of Stevenson and Crawford

Condition (12) is clearly satisfied if we choose  $\lambda$  in the range

$$\mu = \frac{1}{2}(E_{j-1} + E_j) \leq \lambda \leq \frac{1}{2}(E_j + E_{j+1}) = \nu \quad (16)$$

where  $E_{j-1}$ ,  $E_j$  and  $E_{j+1}$  are the exact energy levels. This choice yields the Stevenson and Crawford (1938) bounds to  $E_j$ :

$$\nu - A_i^{1/2}(\nu, \nu) \leq E_j \leq \mu + A_i^{1/2}(\mu, \mu), \quad (17)$$

but since the parameters  $\mu$  and  $\nu$  require knowledge of exact energy levels, these bounds are not completely satisfactory.

### 2.3. Temple's bounds

If an approximate upper bound to  $E_{j-1}$  and an approximate lower bound to  $E_{j+1}$  are available, we satisfy condition (12) by choosing  $\lambda$  in the restricted range

$$\mu^U = \frac{1}{2}(E_{j-1}^U + E_j) \leq \lambda \leq \frac{1}{2}(E_j + E_{j+1}^L) = \nu^L. \quad (18)$$

Substitution of these parameters in (17) leads (after some reduction) to the Temple (1928) bounds to  $E_j$ :

$$I_i - \frac{\Delta_i^2}{E_{j+1}^L - I_i} \leq E_j \leq I_i + \frac{\Delta_i^2}{I_i - E_{j-1}^U}. \quad (19)$$

Kato (1949) has shown that these are the best energy bounds obtainable, using the calculated moments  $I_i$  and  $J_i$  and given the rough estimates  $E_{j-1}^U$  and  $E_{j+1}^L$ .

#### 2.4. Bounds of Cohen and Feldmann

Returning to (9c), we see that for all  $\lambda$ ,

$$A_i(\lambda, \lambda) \geq \sum_{n \in g} a_{in}^2 (E_n - \lambda)^2 \quad (20)$$

for any subset  $g$  of the complete set of exact eigenfunctions. In particular, if  $g$  contains only a single element  $\phi_j$  then

$$A_i(\lambda, \lambda) \geq a_{ij}^2 (E_j - \lambda)^2 \quad (21)$$

which leads (following optimization with respect to  $\lambda$ ) to the Cohen and Feldmann (1969) bounds to  $E_j$ :

$$E_j \leq I_i \pm k_{ij} \Delta_i \quad (22)$$

with

$$k_{ij}^2 = (1 - a_{ij}^2)/a_{ij}^2. \quad (23)$$

The Cohen–Feldmann energy bounds, though free of the ambiguities associated with Weinstein's bounds, require an independent means of estimating the overlap integral  $a_{ij}^2$  in order to be quantitatively useful. On the other hand, the result may be written alternatively as an upper bound to the overlap

$$a_{ij}^2 \leq \Delta_i^2 / A_i(E_j, E_j) \quad (24)$$

whenever the energy  $E_j$  is known independently (perhaps from experiment). More complicated bounds to individual overlaps, and bounds to particular sums of overlaps are easily obtained by including additional members of the subset  $g$  in the partial sum of inequality (20) (Cohen and Feldmann 1970a,b).

### 3. Generalization of the Weinstein procedure

We now consider the positive semi-definite quadratic function

$$W(\lambda, \lambda; F) = \langle (H - \lambda)\phi | F | (H - \lambda)\phi \rangle \geq 0 \quad (25)$$

in which  $F$  is any positive semi-definite operator (which may or may not commute with the hamiltonian  $H$ ). We note first that the particular choice

$$\phi = \phi_i, \quad F = 1 - \sum_{n \in g} |\psi_n\rangle \langle \psi_n| \quad (26)$$

leads directly to inequality (20), but our definition of  $W(\lambda, \lambda; F)$  allows the possibility of making a more general choice of  $F$ , thus leading to new results.

In the following sections, we shall find it convenient to use the notations

$$A_i(\lambda, \mu) = J_i - (\lambda + \mu)I_i + \lambda\mu, \quad (27a)$$

$$B_i(\lambda, \mu) = K_i - (\lambda + \mu)J_i + \lambda\mu I_i, \quad (27b)$$

$$C_i(\lambda, \mu) = L_i - (\lambda + \mu)K_i + \lambda\mu J_i; \quad (27c)$$

$$2\alpha_i = (K_i - I_i J_i) / \Delta_i^2, \quad (28a)$$

$$\beta_i^2 = (L_i - J_i^2) / \Delta_i^2 \geq 0 \quad (28b)$$

and

$$\delta_i^2 = \beta_i^2 - 4\alpha_i^2 \geq 0. \quad (28c)$$

### 3.1. Gordon's bounds

In (25), if we choose

$$\phi = \phi_0, \quad F = (H - E_0), \quad (29)$$

where  $\phi_0$  is an approximation to the ground state eigenfunction  $\psi_0$ , we obtain the inequality, valid for all  $\lambda$ :

$$B_0(\lambda, \lambda) - E_0 A_0(\lambda, \lambda) \geq 0. \quad (30)$$

Optimization with respect to  $\lambda$  now leads to Gordon's (1968) upper bound to  $E_0$ :

$$E_0 \leq \alpha_0 - A_0^{1/2}(\alpha_0, \alpha_0). \quad (31)$$

The alternative choice

$$\phi = \phi_0, \quad F = (H - E_1)(1 - |\psi_0\rangle\langle\psi_0|) \quad (32)$$

leads to the inequality:

$$B_0(\lambda, \lambda) - E_1 A_0(\lambda, \lambda) + a_{00}^2 (E_1 - E_0)(E_0 - \lambda)^2 \geq 0. \quad (33)$$

Optimization with respect to  $\lambda$  leads in this case to Gordon's (1968) lower bound to  $a_{00}^2$ :

$$a_{00}^2 \geq \frac{E_1 - I_0}{E_1 - E_0} + \frac{[A_0(E_0, E_1)]^2}{(E_1 - E_0)[B_0(E_0, E_0) - E_1 A_0(E_0, E_0)]}. \quad (34)$$

The first term on the right-hand side is simply Eckart's (1930) lower bound to  $a_{00}^2$ .

The complementary upper bound to  $a_{0n}^2$  is obtained by choosing

$$\phi = \phi_0, \quad F = (H - E_0)(1 - |\psi_n\rangle\langle\psi_n|) \quad (35)$$

which leads to (cf Cohen and Feldmann 1971):

$$a_{0n}^2 \leq \frac{I_0 - E_0}{E_n - E_0} - \frac{[A_0(E_0, E_n)]^2}{(E_n - E_0)[B_0(E_n, E_n) - E_0 A_0(E_n, E_n)]}. \quad (36)$$

### 3.2. Excited states

For the  $n$ th excited state, we choose

$$\phi = \phi_n, \quad F = (H - E_n) \left( 1 - \sum_{k=0}^{n-1} |\psi_k\rangle\langle\psi_k| \right) \quad (37)$$

and obtain

$$B_n(\lambda, \lambda) - E_n A_n(\lambda, \lambda) + \sum_{k=0}^{n-1} a_{nk}^2 (E_n - E_k)(E_k - \lambda)^2 \geq 0. \quad (38)$$

To proceed, we require rather precise knowledge of all the lower  $E_k$  ( $0 \leq k \leq n-1$ ) so as to determine suitable upper bounds to the overlaps  $a_{nk}^2$ . Denoting these upper bounds by  $\bar{a}_{nk}^2$ , optimization of (38) leads to the analogue of (31):

$$E_n \leq \bar{\alpha}_n - \bar{A}_n^{1/2}(\bar{\alpha}_n, \bar{\alpha}_n) \quad (39)$$

where

$$2\bar{\alpha}_n = \frac{(1 - \Sigma \bar{a}_{nk}^2)(K_n - \Sigma \bar{a}_{nk}^2 E_k^3) - (I_n - \Sigma \bar{a}_{nk}^2 E_k)(J_n - \Sigma \bar{a}_{nk}^2 E_k^2)}{(1 - \Sigma \bar{a}_{nk}^2)(J_n - \Sigma \bar{a}_{nk}^2 E_k^2) - (I_n - \Sigma \bar{a}_{nk}^2 E_k)^2} \quad (40)$$

and

$$\bar{A}_n(\lambda, \mu) = \frac{J_n - \Sigma \bar{a}_{nk}^2}{1 - \Sigma \bar{a}_{nk}^2} - (\lambda + \mu) \frac{I_n - \Sigma \bar{a}_{nk}^2 E_k}{1 - \Sigma \bar{a}_{nk}^2} + \lambda \mu. \quad (41)$$

We thus obtain a simple bound to  $E_n$  only if  $\phi_n$  is strictly orthogonal to all the lower  $\psi_k$ , so that all  $a_{nk}^2$  are zero. The excited state analogues of (34) and (36) suffer from the same drawback, and are probably not useful in practice.

An alternative choice avoids the difficulties associated with overlaps to lower-lying eigenfunctions  $\psi_k$ , by introducing a higher (fourth) moment. Thus, with

$$\phi = \phi_n, \quad F = (H - E_n)(H - I_n) \quad (42)$$

where it is assumed that

$$E_n < I_n < E_{n+1} \quad (43)$$

(so that  $F$  is positive as required), we obtain from (25)

$$C_n(\lambda, \lambda) - (E_n + I_n)B_n(\lambda, \lambda) + E_n I_n A_n(\lambda, \lambda) \geq 0. \quad (44)$$

Optimization now leads to the bounds to  $E_n$ :

$$E_n \leq \alpha_n \pm [A_n(\alpha_n, \alpha_n) + \delta_n^2]^{1/2}. \quad (45)$$

But since the alternative choice

$$\phi = \phi_n, \quad F = (H - I_n)(H - E_{n+1}) \quad (46)$$

leads to *identical* bounds to  $E_{n+1}$ :

$$E_{n+1} \leq \alpha_n \pm [A_n(\alpha_n, \alpha_n) + \delta_n^2]^{1/2} \quad (47)$$

we conclude that this procedure yields only a useful lower bound to  $E_n$  and an upper bound to  $E_{n+1}$ . Thus, for the special case  $n = 0$ , we have the combined result (from (45) and (31) together)

$$\alpha_0 - [A_0(\alpha_0, \alpha_0) + \delta_0^2]^{1/2} \leq E_0 \leq \alpha_0 - A_0^{1/2}(\alpha_0, \alpha_0) \quad (48)$$

giving tight bounds whenever  $\delta_0^2$  is sufficiently small, while for excited states, we have

$$\alpha_n - [A_n(\alpha_n, \alpha_n) + \delta_n^2]^{1/2} \leq E_n \leq I_n. \quad (49)$$

The lower bounds of (48) and (49) have not been given previously.

### 3.3. Bounds to the resolvent operator

The resolvent operator

$$R(E_0) = (H - E_0)^{-1}(1 - |\psi_0\rangle\langle\psi_0|) \quad (50)$$

is positive semi-definite so that

$$S_i = \langle\phi_i|R(E_0)|\phi_i\rangle \geq 0. \quad (51)$$

Similarly, the operator  $(H - E_1)R(E_0)$  is positive semi-definite so that

$$S_i \leq \frac{1 - a_{i0}^2}{E_1 - E_0} \quad (52)$$

A more precise lower bound to  $S_i$  is obtained either via the Cauchy-Schwarz inequality, or from (25) using

$$\phi = \phi_i, \quad F = R(E_0). \quad (53)$$

The result is

$$S_i \geq \frac{(1 - a_{i0}^2)^2}{I_i - E_0} \geq 0, \quad (54)$$

and in the case  $i = 0$ , (54) combined with (52) leads to Eckart's lower bound to  $a_{00}^2$ , given by the first term on the right-hand side of (34).

### 3.4. Bounds of Weinhold and Wang to expectation values

A very slight modification of our general procedures will yield bounds to expectation values, such as those of Weinhold (1968) and Wang (1969). For the positive definite operator  $L$ , we construct the functional

$$V(\lambda, \lambda; F) = \langle(L - \lambda)\phi|F|(L - \lambda)\phi\rangle \geq 0 \quad (55)$$

where  $F$  is a positive semi-definite operator, as in (25). Then, with the simple choice

$$\phi = \phi_0, \quad F = 1 - |\psi_0\rangle\langle\psi_0| \quad (56)$$

we obtain the inequality

$$(1 - a_{00}^2)\lambda^2 - 2(\langle L \rangle - a_{00}\bar{L})\lambda + (\langle L^2 \rangle - \bar{L}^2) \geq 0 \quad (57)$$

where we have used the notations

$$\langle L \rangle = \langle\phi_0|L|\phi_0\rangle, \quad \bar{L} = \langle\phi_0|L|\psi_0\rangle, \quad \langle L^2 \rangle = \langle\phi_0|L^2|\phi_0\rangle. \quad (58)$$

Optimization with respect to  $\lambda$  immediately yields Weinhold's bounds to  $\bar{L}$ :

$$\bar{L} \leq a_{00}\langle L \rangle \pm (1 - a_{00}^2)^{1/2}(\Delta L) \quad (59)$$

where we have written

$$(\Delta L)^2 = \langle L^2 \rangle - \langle L \rangle^2. \quad (60)$$

Weinhold's (1968) lower bound for positive operators  $L$ :

$$\langle\psi_0|L|\psi_0\rangle \geq [a_{00}\langle L \rangle - (1 - a_{00}^2)^{1/2}\Delta L]^2 / \langle L \rangle \quad (61)$$

now follows from (59) on use of the Cauchy-Schwarz inequality. Weinhold has shown



that the bound (61) is uniformly superior to the rigorous lower bound of Bazley and Fox (1966) and usually improves the approximate bound of Jennings and Wilson (1967).

Finally, the choice

$$\phi = \phi_0, \quad F = (H - E_1)(1 - |\psi_0\rangle\langle\psi_0|) \quad (62)$$

leads to Wang's (1969) more complicated lower bounds.

#### 4. Conclusions

It is clear from all these examples that the Weinstein procedure, suitably generalized, is capable of producing many of the known bounds formulae for energies, overlap integrals and expectation values, as well as new results. It is not claimed that this procedure yields all the known results naturally, and we have given one example (cf § 3.3 above) of the Eckart lower bound to  $a_{00}^2$  which is obtained more easily by other means. However, we have shown how the Eckart lower bound may be deduced using the Weinstein procedure, and it seems likely that the overlap bounds of Weinberger (1960), Rayner (1962) and Delves (1964) can be deduced similarly.

We have not investigated the error associated with individual bounds formulae. Ideally, both lower and upper bounds should be computed and the difference between them minimized in order to obtain reliable estimates of physical observables. For expectation values, the most hopeful results appear to be those of Mazziotti (1971), whose lower bound formula yields results only slightly poorer than Weinhold's lower bound. Mazziotti's procedure yields an upper bound as well as a lower bound, and has the additional advantage of involving only first moments of  $H$  and  $L$ .

The principal disadvantage of the Weinstein procedure is the need to compute higher moments of  $H$  and  $L$ , and it is well known that the necessary integrals frequently diverge. Similar difficulties apply to most of the bounds procedures in the literature and are not confined to the Weinstein procedure. Any future progress will depend on developing efficient means of calculating these higher moments with variational wavefunctions.

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#### References

- Bazley N W and Fox D W 1966 *J. math. Phys.* **7** 413-6  
 Cohen M and Feldmann T 1969 *Can. J. Phys.* **47** 1877-9  
 — 1970a *Can. J. Phys.* **48** 1681-6  
 — 1970b *Chem. Phys. Lett.* **6** 43-5  
 — 1971 *J. Phys. A: Gen. Phys.* **4** 761-72  
 Delves L M 1964 *J. math. Phys.* **5** 1055-60  
 Eckart C 1930 *Phys. Rev.* **36** 878-92  
 Gordon R G 1968 *J. chem. Phys.* **48** 4984-8  
 Jennings P and Wilson E B Jr 1967 *J. chem. Phys.* **47** 2130-6  
 Mazziotti A 1971 *J. chem. Phys.* **55** 2657-60

- Kato T 1949 *J. Phys. Soc. Japan* **4** 334-9  
Rayner M E 1962 *Q. J. Math.* **13** 61-74  
Stevenson A F and Crawford M F 1938 *Phys. Rev.* **54** 375-9  
Temple G 1928 *Proc. R. Soc. A* **119** 276-93  
Wang P S C 1969 *J. chem. Phys.* **51** 4767-9  
Weinberger H F 1960 *J. Res. Natn. Bur. Stand. B* **64** 217-25  
Weinhold F 1968 *J. Phys. A: Gen. Phys.* **1** 305-13  
Weinstein D H 1934 *Proc. Natn. Acad. Sci. USA* **20** 529-32