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A coordinate-free treatment of Bazley lower bounds to the eigenvalues of atomic Hamiltonians

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Abstract. The coordinate-free analysis developed in our earlier paper is used to provide a simplified proof of the Bazley inequalities for establishing lower bounds to the eigenvalues of atomic Hamiltonians. It is then explained how Bazley lower bounds enable one to get other lower bounds to eigenvalues without using empirical values of higher eigenvalues.

1. Introduction

Continuing the work of Sharma and co-workers (Sharma and Rebelo 1973a, b, 1975, Sharma and SriRankanathan 1975) we now present simplified proofs of propositions leading to lower bounds of atomic Hamiltonians. We then show how Bazley (1961) bounds can be used to obtain better lower bounds on a purely theoretical basis by using the formulae of Stevenson and Crawford (1938), Weinstein (1932) and Temple (1928).

2. Formalities

We use notations and definitions established in our earlier work (Sharma and SriRankanathan 1975, to be referred to as I): these we now recapitulate for the convenience of the reader.

Let $\mathscr{H}$ be a Hilbert space over the real or complex field. Let A be a self-adjoint operator on $\mathscr{H}$; it is not assumed that A is bounded. We shall denote the domain of A by $\mathscr{D}_A$ and the spectrum of A by SpA. We shall say that the spectrum of A is of type **H** if SpA is bounded below, the lower part of the spectrum is purely discrete, and the first **N** points of the spectrum ordered to form an increasing enumeration have finite multiplicities (here **N** is either a positive integer or the cardinality $\aleph_0$ of the set of positive integers). We shall denote the eigenvalues in this enumeration by λ_i^A and the corresponding multiplicity by m_i^A. Let E_i^A be the orthogonal projection on the eigenspace $\mathscr{E}_i^A$ belonging to the eigenvalue λ_i^A, noting that the dimension of $\mathscr{E}_i^A$ is m_i^A. We denote the orthogonal complement of $\oplus_{i=1}^{\mathbf{N}} \mathscr{E}_i^A$ by $\mathscr{E}_c^A$ and the orthogonal projection on $\mathscr{E}_c^A$ by E_c^A. We have thus the following decompositions of $\mathscr{H}$ and the identity operator I on $\mathscr{H}$:

$$\mathscr{H} = \left(\bigoplus_{i=1}^{\mathbf{N}} \mathscr{E}_i^A \right) \oplus \mathscr{E}_c^A$$

$$I = \left(\sum_{i=1}^{\mathbf{N}} E_i^A \right) + E_c^A.$$

For $n \leqslant \mathbf{N}$ we define

$$F_n^A = \sum_{i=1}^{n} E_i^A$$

and the image of F_n^A is a subspace which we denote by $\mathscr{F}_n^A$. We denote the dimension of $\mathscr{F}_n^A$ by d_n^A; clearly

$$d_n^A = \sum_{i=1}^{n} m_i^A.$$

In our treatment eigenvalues are arranged to form an increasing enumeration and each eigenvalue is counted just once. However, people using coordinate-dependent treatments find it convenient to use an enumeration in which an eigenvalue λ_i of multiplicity m_i is counted m_i times. We shall call this alternative enumeration the *primed enumeration* and eigenvalues in this enumeration will carry a prime each. For a given $j \in \mathbb{Z}^+$ the two enumerations are related by

$$\lambda_j' = \lambda_i$$

where i is the smallest integer for which $j \leqslant d_i$. For a given i there are m_i different values of j for which the above relation holds and these values of j are $d_{i-1}+1$, $d_{i-1}+2, \ldots, d_i - 1, d_i$. The primed enumeration from the point of view of coordinate-free analysis is wasteful and clumsy; nevertheless we use this to establish contact with the classical formulation.

It is usual to define a partial ordering of symmetric operators on $\mathscr{H}$ in the following way: we define

$$A_1 \leqslant A_2$$

if and only if $\mathscr{D}_{A_1} \subset \mathscr{D}_{A_2}$ and

$$\langle u, A_1 u \rangle \leqslant \langle u, A_2 u \rangle \qquad \forall u \in \mathscr{D}_{A_1}$$

where $\langle \cdot , \cdot \rangle$ is the positive definite Hermitian form on $\mathscr{H}$.

We say that a self-adjoint operator A on $\mathscr{H}$ is *atomic* if (i) SpA is of type **H** and (ii) A can be written as a sum of two self-adjoint operators B and C, thus

$$A = B + C \tag{2.1}$$

where B is a self-adjoint operator whose spectrum is completely known and is of type **H** and C is a strictly positive self-adjoint operator. It follows from the definition of the sum of two operators that

$$\mathscr{D}_A = \mathscr{D}_B \cap \mathscr{D}_C \tag{2.2}$$

whence

$$\mathscr{D}_A \subset \mathscr{D}_B. \tag{2.3}$$

Thus A and B satisfy the conditions set out in proposition 6.2 of I. It follows immediately from that proposition that the eigenvalues of B are lower bounds to eigenvalues of A, but these bounds are usually not very good. The method of Bazley (1961) provides better bounds by generating a sequence of intermediate operators which lie between A and B and in the limit converge to A and it is possible to compute exactly the eigenvalues of the intermediate operators which provide lower bounds to

appropriate eigenvalues of A. The method is sometimes described as the intermediate problem of Aronszajn (1952).

Since C is strictly positive, both $C^{1/2}$ and C^{-1} are well defined (Kato 1966) and

$$\mathscr{D}_C \subset \mathscr{D}_{C^{1/2}}, \qquad C(\mathscr{D}_C) = \mathscr{D}_{C^{-1}} \qquad \text{and} \qquad C^{-1}(\mathscr{D}_{C^{-1}}) = \mathscr{D}_C.$$

In what follows it is assumed that

$$\mathscr{F}_N^B \subset \mathscr{D}_C \cap \mathscr{D}_{C^{-1}} \tag{2.4}$$

3. The main results of this work

Proposition 3.1. (Aronszajn 1952) Let $\mathscr{P}_n (\subset \mathscr{D}_A)$ be an n dimensional subspace of a Hilbert space $\mathscr{H}$. Let P_n be the orthogonal projection on $\mathscr{P}_n$. Let A be an atomic self-adjoint operator on $\mathscr{H}$ having the decomposition described in § 2. Let

$$A_n = B + C^{1/2} P_n C^{1/2}. \tag{3.1}$$

Then

$$B \leqslant A_n \leqslant A \qquad \text{in } \mathscr{D}_A. \tag{3.2}$$

Proof. For any $u \in \mathscr{D}_A$

$$\langle u, A_n u\rangle = \langle u, Bu\rangle + \langle u, C^{1/2} P_n C^{1/2} u\rangle = \langle u, Bu\rangle + \langle P_n C^{1/2} u, P_n C^{1/2} u\rangle$$
$$= \langle u, Bu\rangle + \|P_n C^{1/2} u\|^2. \tag{3.3}$$

But it is evident that

$$0 \leqslant \|P_n C^{1/2} u\|^2 \leqslant \|C^{1/2} u\|^2 = \langle C^{1/2} u, C^{1/2} u\rangle = \langle u, Cu\rangle. \tag{3.4}$$

Hence

$$\langle u, Bu\rangle \leqslant \langle u, A_n u\rangle \leqslant \langle u, Au\rangle \tag{3.5}$$

which is equivalent to the desired result.

Corollary 3.1.1. In the primed enumeration of eigenvalues the ith eigenvalue of A_n lies between the ith eigenvalues of B and A.

Proof. Follows immediately from the proposition above and corollary 6.2.1 of I. (Note that it is not difficult to prove that A_n is essentially self-adjoint.)

Observation 3.1.1. If a sequence of subspaces $\mathscr{P}_n$ is constructed in such a way that $\mathscr{P}_n \subset \mathscr{P}_{n+1}$ for all n and $\bigvee_n \mathscr{P}_n = \mathscr{H}$, then the ith eigenvalue of A_n in the primed enumeration will form a numerical sequence converging to the ith eigenvalue of A in a similar enumeration.

Observation 3.1.2. Proposition 3.1 gives a formal procedure for finding better lower bounds to eigenvalues of A than those given by eigenvalues of B. But unless we can devise a procedure for determining the eigenvalues of A_n, this procedure is quite useless. The next proposition tells us how for a particular choice of the subspaces $\mathscr{P}_n$ the eigenvalues of A_n can be readily determined.

Proposition 3.2. (Bazley 1961) Let $d_i^B = n$. Let $\mathscr{P}_n = C^{-1/2}(\mathscr{F}_i^B)$. Let P_n be the orthogonal projection on $\mathscr{P}_n$. Then $\mathscr{F}_i^B$ is invariant under $B + C^{1/2}P_nC^{1/2}$.

Proof. Let $u \in \mathscr{F}_i^B$. Clearly $Bu \in \mathscr{F}_i^B$. From the definition of P_n it follows that there exists a $v \in \mathscr{F}_i^B$ such that

$$C^{-1/2}v = P_nC^{1/2}u \tag{3.6}$$

whence

$$v = C^{1/2}P_nC^{1/2}u \in \mathscr{F}_i^B.$$

This completes the proof.

Observation 3.2.1. With this particular definition A_n restricted to $\mathscr{F}_i^B$ is a self-adjoint operator on a finite dimensional space and because of the invariance established in the preceding proposition, the eigenvalues of the restriction are also the eigenvalues of the unrestricted operator. Eigenvalues of a self-adjoint operator on a finite dimensional space can be readily determined. Thus we have an intermediate operator whose eigenvalues are easily determinable and which provide better lower bounds on the eigenvalues of A.

4. Lower bounds of Stevenson and Crawford, Weinstein and Temple

Proposition 4.1. (Stevenson and Crawford 1938). Let A be an atomic Hamiltonian. Let μ be an upper bound to the ith eigenvalue λ_i of A satisfying

$$\mu - \lambda_i \leqslant \lambda_{i+1} - \mu. \tag{4.1}$$

Let unit vector $u \in \mathscr{D}_A$ and let

$$\sigma^2 = \langle u, (A-\mu)^2 u\rangle. \tag{4.2}$$

Then $\mu - \sigma$ is a lower bound to λ_i.

Proof.

$$0 \leqslant \sigma^2 = \|(A-\mu)u\|^2 = \left\| \int_{\Lambda(A)} (\lambda - \mu)u \right\|^2 \geqslant (\lambda_i - \mu)^2 \tag{4.3}$$

where the integral is over the spectrum $\Lambda(A)$ of A and is with respect to the spectral measure induced by A. It immediately follows that

$$\sigma \geqslant \mu - \lambda_i \tag{4.4}$$

which is the desired result.

Corollary 4.1.1. (Weinstein 1932) Let the upper bound μ and the vector u in proposition 4.1 satisfy

$$\mu = \langle u, Au\rangle. \tag{4.5}$$

Then

$$\mu - (\langle u, A^2u\rangle - \mu^2)^{1/2} \leqslant \lambda_i. \tag{4.6}$$

Proof. A straightforward computation of the lower bound given by the preceding proposition for this particular choice of μ yields the desired result.

Observation 4.2.1. Both these lower bounds require a μ which is less than or equal to $(\lambda_i+\lambda_{i+1})/2$. Physicists usually get this number by using experimental values; this makes the lower bounds semi-empirical. By using the method of § 3 it is possible to find lower bounds to both λ_i and λ_{i+1} and the mean value of the two bounds may provide an upper bound which satisfies the requirements. One can make sure that this is so by ensuring that this mean value is greater than an upper bound found with the help of corollary 4.1.1 of I.

Proposition 4.2. (Temple 1928). Let A be an atomic Hamiltonian and let λ_i be its ith eigenvalue. Let unit vector $u \in \mathscr{D}_A$ and $\rho \in \mathbb{R}$ satisfy

$$\lambda_i < \langle u, Au\rangle < \rho \leqslant \lambda_{i+1}. \tag{4.7}$$

Then

$$\langle u, Au\rangle - \frac{\langle u, A^2u\rangle - \langle u, Au\rangle^2}{\rho - \langle u, Au\rangle} \leqslant \lambda_i. \tag{4.8}$$

Proof. From proposition 4.1 we have

$$\mu - \sigma \leqslant \lambda_i \leqslant \mu + \sigma.$$

Noting that σ depends on μ and taking a given $\rho \leqslant \lambda_{i+1}$ we find a μ such that

$$\sigma + \mu = \rho \tag{4.9}$$

or

$$(\mu - \rho)^2 = \sigma^2. \tag{4.10}$$

Simple computation now yields

$$\mu = \frac{\langle u, A^2u\rangle - \rho^2}{2(\langle u, Au\rangle - \rho)}. \tag{4.11}$$

In forming the squares in equation (4.10) we have lost the information implicit in equation (4.9) that μ is less than or equal to ρ. We must therefore impose this condition on μ found from equation (4.11). It is easy to show that this condition implies that $\langle u, Au\rangle < \rho$, for if we assume that $\langle u, Au\rangle > \rho$ with the help of the given condition we can readily deduce that

$$\langle u, (A-\rho)^2u\rangle < 0 \tag{4.12}$$

which is clearly impossible. This justifies the necessity of one of the assumptions in (4.7). With the μ given by equation (4.11) a computation of $\mu - \sigma$ together with proposition 4.1 finally yields Temple's lower bound (4.8). It is interesting to note that it is not necessary that $\langle u, Au\rangle > \lambda_i$ as assumed in (4.7), but if $\langle u, Au\rangle \leqslant \lambda_i$ then $\langle u, Au\rangle$ itself is a lower bound to λ_i which is considerably better than the one given by Temple's formula.

Observation 4.2.1. Proposition 3.2 enables one to find a ρ satisfying condition (4.7), thus making it possible to calculate a purely theoretical lower bound with the help of Temple's formula.

Observation 4.2.2. Purely theoretical lower bounds obtained with the help of any of the formulae of this section can themselves be used to obtain μ and ρ in starting iterative processes which progressively lead to increasingly better lower bounds.

Observation 4.2.3. $u \in \mathcal{D}_A$ does not necessarily imply that $Au \in \mathcal{D}_A$. Whenever we use $\langle u, A^2 u\rangle$, this should be taken to mean $\|Au\|^2$ which is well defined even if $Au \notin \mathcal{D}_A$.

5. Applications

Let H be the quantum Hamiltonian for the motion of the two electrons in helium. It can be written as

$$H = h \otimes I + I \otimes h + H_{12} = H_0 + H_{12} \tag{5.1}$$

where h is the Hamiltonian for the motion of the electron in a hydrogen atom with the appropriate nuclear charge and H_{12} is the interelectronic interaction. If the underlying Hilbert space is taken to be the configuration space $L^2(\mathbb{R}^3) \otimes L^2(\mathbb{R}^3)$, on the dense linear manifold of infinitely differentiable functions in $L^2(\mathbb{R}^3)$, h, or more precisely its restriction to the manifold, is a linear second-order differential operator. The eigenvalues and the eigenfunctions of h, and hence also of H_0, are exactly known from the theory of the hydrogen atom. In configuration space, H_{12} is simply $1/r_{12}$ where $r_{12} = \|\boldsymbol{r}_1 - \boldsymbol{r}_2\|$, $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ being the position vectors of the two electrons. H, H_0 and H_{12} satisfy all the properties required of A, B and C respectively in §§ 2 and 3. In order to find the lower bounds to the energies of, say, the lowest three singlet S states of helium, one takes the eigenfunctions Φ_1, Φ_2 and Φ_3 of H_0 belonging to the $1s^2\ {}^1S$, $1s2s\ {}^1S$ and $1s3s\ {}^1S$ states. $\mathcal{F}_3^{H_0}$ is the span of Φ_1, Φ_2 and Φ_3; $r_{12}^{1/2}(\mathcal{F}_3^{H_0})$ is the span of $r_{12}^{1/2}\Phi_1$, $r_{12}^{1/2}\Phi_2$ and $r_{12}^{1/2}\Phi_3$. By the Gram–Schmidt process the last three vectors of the preceding sentence can be orthonormalized to yield orthonormal functions Ψ_1, Ψ_2 and Ψ_3 which span the same subspace. Projection operator P_3 on $r_{12}^{1/2}(\mathcal{F}_3^{H_0})$ is now given by

$$P_3 = \sum_{i=1}^{3} \langle \Psi_i, \cdot \rangle \Psi_i. \tag{5.2}$$

It is now a simple computational exercise to determine the matrix of H_3 restricted to $\mathcal{F}_3^{H_0}$ and the corresponding eigenvalues. This has already been done by Bazley (1959) by an essentially equivalent procedure; he obtained the values (in natural atomic units) $-3{\cdot}063_7$, $-2{\cdot}165_5$ and $-2{\cdot}039_2$. These provide lower bounds to the energies of the $1s^2\ {}^1S$, $1s2s\ {}^1S$ and $1s3s\ {}^1S$ states of helium.

As far as we know, no actual application of the method described in § 4 has been made to obtain purely theoretical lower bounds with the help of the formulae of Stevenson and Crawford (1938), Weinstein (1932) and Temple (1928). However, the method is fairly straightforward and there can be little doubt that as the theory described here becomes better known and understood, it will become a normal tool of the trade for calculating lower bounds to eigenvalues of atomic Hamiltonians.

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