Upper Bounds to Excited-State Energies

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Abstract. Variational techniques for the calculation of upper bounds to excited-state energies are proposed. Further, upper bounds can be obtained by means of lower bounds to the energies of the low-lying states.

1 Introduction

From the point of view of spectral analysis the problem of the calculation of excited-state energies was solved by Fischer [1] in 1905 establishing the min-max principle. In this paper we want to add some remarks on problems occurring in the application of this principle in physics and quantum chemistry.

As it is well known the ground-state energy \( E_1 \) of a Hamiltonian \( \mathcal{H} \) is given by

\[
E_1 = \inf_{f \in K, \|f\| = 1} \langle f, \mathcal{H}f \rangle,
\]

where \( K \) denotes the Hilbert space containing only wave functions with the correct statistics. Practically the infimum cannot be taken over an infinite-dimensional set; hence only an approximate ground-state energy \( E_1^a \) is calculated by

\[
E_1^a = \inf_{f \in M, \|f\| = 1} \langle f, \mathcal{H}f \rangle,
\]

where \( M \subset K \) is an appropriate set with a finite number of (linear or non-linear) variational parameters. It immediately follows that

\[
E_1^a \geq E_1.
\]

For the energies of excited states \( E_j \) it holds that

\[
E_1 + \cdots + E_j = \inf_{\{f_j\} \subset K, \langle f_j, f_j \rangle = \delta_k} (\langle f_1, \mathcal{H}f_1 \rangle + \cdots + \langle f_j, \mathcal{H}f_j \rangle).
\]

If \( \mathcal{H} \) has only \( l \) eigenvalues below the essential spectrum, then per definition \( E_{l+1} = E_{l+2} = \cdots = \inf_{\text{ess}(\mathcal{H})} \) [2]. (By a physical argument [3] Eq. (4) can easily be reduced to (1): Build up a new system consisting of \( j \) copies of the system considered, which do not interact with one another but to which the Fermi statistics applies. Then the ground-state energy of the whole system equals the sum of the first \( j \) eigenvalues of the original system. Remembering that the corresponding ground state is a Slater determinant built up by the orthonormal functions \( f_1, \ldots, f_j \) one gets (4).)
But usually the j-th eigenvalue $E_j$ itself is of interest. For it the min-max principle (strictly speaking it is an “inf-max principle”) holds:

$$E_j = \inf_{K_j} \max_{f \in K_j, \|f\| = 1} \langle f, H f \rangle,$$

where $K_j \subset K$ are j-dimensional subspaces. The straightforward application of this principle is not convenient for practical calculations, even if the variation is restricted to some subspaces $K_j$, since, e.g., every vector $f$ can lie in many subspaces $K_j$ and hence the same expectation values have to be considered several times.

If we restrict ourselves to subspaces $K_j(f^0)$, containing the exact eigenfunctions $g_1, \ldots, g_{j-1}$ and an arbitrary vector $f^0 \perp g_1, \ldots, g_{j-1}$ ($\|f^0\| = 1$) then

$$\max_{f \in K_j(f^0), \|f\| = 1} \langle f, H f \rangle = \langle f^0, H f^0 \rangle.$$  

(The choice $f^0 = g_j$ shows that the restriction to the spaces $K(f^0)$ is not a real one.) Thus (5) can be replaced by

$$E_j = \inf_{f^0 \perp g_1, \ldots, g_{j-1}, \|f^0\| = 1} \langle f^0, H f^0 \rangle.$$  

But unfortunately the exact eigenfunctions are in general not known. Therefore, a variational technique is often applied, which defines $E_j^a$ — the approximate $(j - 1)$-st excited-state energy — by

$$E_j^a = \inf_{f^0, f^1, \ldots, f_{j-1}} \langle f^0, H f^0 \rangle.$$  

Let the infimum in (8) be reached for $f^0_j$, that means $f^0_j$ is the $(j - 1)$-st excited state approximately determined by this technique. In order to ensure a good convergence of the variational principle (8), sometimes [4, 5] a set $M$ with a finite number of non-linear variational parameters is chosen. As already mentioned by Faulkner [6] then one cannot expect $E_j^a \geq E_j$ analogously to (3). The reason is that (6) holds no longer, if instead of $K_j(f^0)$ the space $K_j^a(f^0) := \{l_1 f^0_1 + \cdots + l_{j-1} f^0_{j-1} + l_j f^0, l_k \in \mathbb{C}\}$ is used.

But Faulkner did not search for other bounds $E_j^a$ satisfies. We prove in the next section that the variational method (8) in general only yields

$$E_j^a \geq (E_1 + \cdots + E_j)/j,$$  

and we modify this method in order to get modified approximate energies $E_j^{ma}$ satisfying $E_j^{ma} \geq E_j$.

In the last chapter upper bounds to $E_j$ are expressed by means of lower bounds to $E_1, \ldots, E_{j-1}$.

2 Modifications of Eq. (8)

First it is proven that the energies $E_j^a$ defined recursively by (8) satisfy only the inequality (9), which cannot be sharpened in general:

**Proof of (9).** Since for increasing $j$ the variation in (8) is performed over a decreasing set of vectors, it obviously holds that

$$E_j^a \geq E_k^a \quad \text{for} \quad j > k.$$