On the Rayleigh-Ritz variational method

Francisco M. Fernández *
INIFTA, División Química Teórica,
Blvd. 113 S/N, Sucursal 4, Casilla de Correo 16,
1900 La Plata, Argentina.

Abstract

We give a simple proof of the well known fact that the approximate eigenvalues provided by the Rayleigh-Ritz variational method are increasingly accurate upper bounds to the exact ones. To this end, we resort to the variational principle, mentioned in most textbooks on quantum chemistry, and to a well known set of projection operators. We think that present approach may be suitable for an advanced course on quantum mechanics or quantum chemistry.

1 Introduction

The Rayleigh-Ritz variational method (RRVM) is discussed in most textbooks on quantum chemistry [1,2] but it is not so widely found in textbooks on quantum mechanics [3]. The reason is that this approach is most important for the study of the electronic structure of molecules [1,2]. The RRVM provides increasingly tighter upper bounds to all the eigenvalues of an Hermitian operator as proved long ago by MacDonald [4]. This property of the approach is invoked in many textbooks without proof [1]. Szabo and Ostlund [2] sketched an incomplete simple proof for the two lowest eigenvalues in Exercise 1.21 of page 36.

*E-mail: fernande@quimica.unlp.edu.ar
In this paper we generalize this result to all the eigenvalues of a given Hermitian operator in a way that may be suitable for a graduate course on quantum mechanics or quantum chemistry.

In section 2 we outline the variational principle already mentioned in most textbooks [1,3]. In section 3 we introduce some well known projection operators [1,3] that facilitate the derivation of the proof of the main property of the RRVM in section 4. In section 5 we apply the RRVM to a simple nontrivial example. Finally, in section 6 we summarize the main results and draw conclusions.

2 Variational principle

We are interested in the eigenvalue equation

\[ H \psi_n = E_n \psi_n, \quad n = 1, 2, \ldots, \]

\[ E_1 \leq E_2 \leq \ldots, \quad \langle \psi_i | \psi_j \rangle = \delta_{ij}, \]

for a Hermitian operator \( H \). If \( \psi \) belongs to the domain of \( H \) then

\[ \psi = \sum_j c_j \psi_j, \quad c_j = \langle \psi_j | \psi \rangle, \]

and

\[ \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_1. \]

If

\[ \langle \psi_j | \psi \rangle = 0, \quad j = 1, 2, \ldots, k - 1, \]

then the same argument leads to

\[ \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_k. \]

In general, this result may not be of practical utility because it requires some of the supposedly unknown eigenvectors \( \psi_j \) of \( H \). However, if we know the
symmetry of such eigenvectors we can construct a trial function $\varphi$ that satisfies the orthogonality condition (4) for some value of $k$. We will resort to equations (3-5) to derive the main results of this paper in section 4.

3 Projection operators

By means of an orthonormal basis set $\{|j\rangle, j = 1, 2, \ldots\}$, $\langle i | j \rangle = \delta_{ij}$, we can construct projection operators of the form [1–3]

$$P_N = \sum_{j=1}^{N} |j\rangle \langle j|, \ N = 1, 2, \ldots,$$

(6)

that are Hermitian ($P_N^\dagger = P_N$) and idempotent

$$P_N^2 = \sum_{i=1}^{N} \sum_{j=1}^{N} |i\rangle \langle i| \langle j| = \sum_{j=1}^{N} |j\rangle \langle j| = P_N.$$

(7)

Since $P_N = P_{N-1} + |N\rangle \langle N|$ and $|N\rangle \langle N| P_{N-1} = P_{N-1} |N\rangle \langle N| = 0$ then

$$P_N P_{N-1} = P_{N-1} P_N = P_N^2 = P_{N-1}.$$

(8)

4 The Rayleigh-Ritz variational method

If $S$ is the vector space on which $H$ operates then we can define the projected subspace $S_N = P_N S$ and the projection of $H$ on $S_N$ [1–3]

$$H_N = P_N HP_N.$$

(9)

The eigenvectors $|N, j\rangle$ of $H_N$,

$$H_N |N, j\rangle = E_j^{(N)} |N, j\rangle, \ j = 1, 2, \ldots, N,$$

$$E_1^{(N)} \leq E_2^{(N)} \leq \ldots \leq E_N^{(N)},$$

(10)

belong to $S_N$

$$|N, j\rangle = \sum_{i=1}^{N} c_{ij}^{(N)} |i\rangle.$$

(11)
These eigenvectors can be constructed orthonormal: \( \langle N,i |N,j \rangle = \delta_{ij} \). Obviously,
\[
P_N |N - 1, j \rangle = P_{N-1} |N - 1, j \rangle = |N - 1, j \rangle.
\] (12)

It is convenient to define the linear combination
\[
\varphi = \sum_{j=1}^{K} a_j |N - 1, j \rangle , \quad 1 \leq K \leq N - 1,
\] (13)
and choose the coefficients \( a_j \) so that
\[
\langle N, i | \varphi \rangle = \sum_{j=1}^{K} a_j \langle N, i | N - 1, j \rangle = 0, \quad i = 1, 2, \ldots, K - 1.
\] (14)

It is clear that this set of \( K - 1 \) equations with \( K \) unknowns \( a_j \) will always have nontrivial solutions. According to equation (15) we have
\[
\frac{\langle \varphi | H_N | \varphi \rangle}{\langle \varphi | \varphi \rangle} \geq E_K^{(N)}.
\] (15)

On the other hand, since \( P_N \varphi = P_{N-1} \varphi = \varphi \) it follows that
\[
\langle \varphi | H_N | \varphi \rangle = \langle \varphi | P_{N-1} H_N P_{N-1} | \varphi \rangle
= \langle \varphi | H_{N-1} | \varphi \rangle = \sum_{j=1}^{K} |a_j|^2 E_j^{(N-1)} \leq E_K^{(N-1)} \langle \varphi | \varphi \rangle,
\] (16)
or
\[
\frac{\langle \varphi | H_N | \varphi \rangle}{\langle \varphi | \varphi \rangle} \leq E_K^{(N-1)}.
\] (17)

It follows from equations (15) and (17) that \( E_K^{(N)} \leq E_K^{(N-1)} \).

We next choose another linear combination
\[
\psi = \sum_{j=1}^{K} b_j |N,j \rangle , \quad 1 \leq K \leq N - 1,
\] (18)
and require that the coefficients \( b_j \) satisfy
\[
\langle \psi_i | \psi \rangle = \sum_{j=1}^{K} b_j \langle \psi_i | N,j \rangle = 0, \quad i = 1, 2, \ldots, K - 1.
\] (19)

Then, according to equation (5) we have
\[
\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_K.
\] (20)
On the other hand, it follows from
\[ \langle \psi | H | \psi \rangle = \langle \psi | P_N H P_N | \psi \rangle = \langle \psi | H_N | \psi \rangle = \sum_{j=1}^{K} |b_j|^2 E_j^{(N)} \]
that
\[ \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \leq E_K^{(N)}. \] (22)
It follows from equations (20) and (22) that \( E_K \leq E_K^{(N)} \). We thus derive the main property of the RRVM:
\[ E_K^{(N-1)} \geq E_K^{(N)} \geq E_K, \quad 1 \leq K \leq N - 1. \] (23)

It is important to realize that it is not necessary to know the eigenvectors \( \psi_i \) of \( H \) explicitly in order to derive equation (20). We merely assume the existence of such eigenvectors and prove that the trial function \( \psi \) already exists. From a practical point of view, the upper bounds in equation (23) are given by the eigenvectors of \( H_N \) that we can easily obtain as argued below.

Any eigenvector \( \varphi \) of \( H_N \) can be written as
\[ \varphi = \sum_{j=1}^{N} c_j |j\rangle. \] (24)
Therefore, it follows from \( (H_N - E) \varphi = 0 \) that
\[ \langle k | (H_N - E) \varphi \rangle = \langle k | (P_N H P_N - E) \varphi \rangle = \langle k | (H_N - E) \varphi \rangle \]
\[ = \sum_{j=1}^{N} (H_{k,j} - E \delta_{kj}) c_j = 0, \quad k = 1, 2, \ldots, N, \]
\[ H_{k,j} = \langle k | H | j \rangle. \] (25)
There are nontrivial solutions to this equation if \( E \) is a root of \([1, 2]\)
\[ |H_N - EI| = 0, \] (26)
where \( H_N \) is the \( N \times N \) matrix with elements \( H_{ij}, i, j = 1, 2, \ldots, N, \) and \( I \) is the \( N \times N \) identity matrix. We conclude that the roots \( E_n^{(N)}, n = 1, 2, \ldots, N, \)
of the secular determinant (or characteristic polynomial) \( (26) \) satisfy the
inequalities \( (23) \) for \( N = 2, 3, \ldots \). In other words, the solutions of the RRVM,
given by equations \( (25) \) and \( (26) \), approach the corresponding eigenvalues of
\( H \) from above. For a given eigenvalue \( E_n^{(N)} \) of \( H_N \) we obtain the coefficients
\( c_{jn}^{(N)} \) from equation \( (25) \) and then the eigenvectors \( |N, j\rangle \) shown in equation \( (11) \)
(after suitable normalization) \( [1, 2] \).

More details about the convergence of the RRVM in the case of the Hamiltonian operators that appear in molecular physics and quantum chemistry were given by Klahn and Bingel \( [5] \) some time ago.

5 Example

As an example we consider a simple model given by a particle of effective mass \( m^* \) and charge \( e \) in an infinite square well of length \( L \) under the effect of an electric field of intensity \( F \) \( [6] \). The Hamiltonian operator reads

\[
H = -\hbar^2 \frac{d^2}{2m^* dz^2} + |e|Fz,
\]

and its eigenfunctions \( \psi_n(z) \) satisfy \( \psi_n(0) = \psi_n(L) = 0 \).

In order to facilitate the calculation it is convenient to convert the Schrödinger equation into a dimensionless eigenvalue equation. To this end, we define the dimensionless coordinate \( \tilde{z} = z/L \) and Hamiltonian (see \( [7] \) for more details and examples)

\[
\tilde{H} = \frac{m^* L^2}{\hbar^2} H = -\frac{1}{2} \frac{d^2}{dz^2} + \lambda \tilde{z}, \quad \lambda = \frac{m^* |e| FL^3}{\hbar^2}.
\]

The eigenvalues \( E_n \) and \( \tilde{E}_n \), \( n = 1, 2, \ldots \), of \( H \) and \( \tilde{H} \), respectively, are related by \( E_n(m^*, e, F, L) = \hbar^2 \tilde{E}_n(\lambda) / (m^* L^2) \). Notice that the dimensionless constant \( \lambda \) is the most relevant parameter of the model. The eigenfunctions \( \tilde{\psi}_n \) of \( \tilde{H} \) satisfy the boundary conditions \( \tilde{\psi}_n(0) = \tilde{\psi}_n(1) = 0 \).

A suitable orthonormal basis set of functions for the application of the RRRVM is

\[
u_j(\tilde{z}) = \sqrt{2} \sin(j \pi \tilde{z}), \quad j = 1, 2, \ldots,
\]
that satisfy the required boundary conditions. The matrix elements of $\tilde{H}$ can be obtained analytically

$$
\tilde{H}_{i,j} = \begin{cases} 
\frac{\pi z_i^2 + \lambda}{4i(-1)^{i+j-1}} z_i, & i = j \\
\frac{\pi z_i^2 - \lambda}{\pi z_i^2 - j^2}; & i \neq j 
\end{cases}, \quad i, j = 1, 2, \ldots 
$$ (30)

Table 1 shows the rate of convergence of the first four eigenvalues $\tilde{E}_n$ for $\lambda = 1$. It is clear that the sequence $\tilde{E}_n^{(N)}$, $N = 2, 3, \ldots$, converges from above as proved in section 4.

The eigenvalue equation

$$
\psi''(\tilde{z}) + 2 \left( \tilde{E} - \lambda \tilde{z} \right) \psi(\tilde{z}) = 0, 
$$ (31)

can be transformed into the Airy equation [8]

$$
y''(q) - qy(q) = 0, 
$$ (32)

by means of the change of variables

$$
q = (2\lambda)^{1/3} \left( \tilde{z} - \frac{\tilde{E}}{\lambda} \right). 
$$ (33)

The solution to equation (31) can therefore be written as

$$
\tilde{\psi}(\tilde{z}) = c_1 Ai(q) + c_2 Bi(q), 
$$ (34)

where $A_i(q)$ and $B_i(q)$ are the Airy functions of the first kind [8]. The boundary conditions $\tilde{\psi}(0) = \tilde{\psi}(1) = 0$ lead to a linear system of two equations with two unknowns, $c_1$ and $c_2$, with nontrivial solutions only for those values of $\tilde{E} = \tilde{E}_n$ that are roots of the equation

$$
Ai(q_L) Bi(q_R) - Ai(q_R) Bi(q_L) = 0, 
$$

$$
q_L = -(2\lambda)^{1/3} \frac{\tilde{E}}{\lambda}, \quad q_R = (2\lambda)^{1/3} \left( 1 - \frac{\tilde{E}}{\lambda} \right). 
$$ (35)

One can easily verify that the exact eigenvalues obtained in this way agree with those provided by the RRVM.
6 Conclusions

In this paper we have derived an important property of the RRVM in a way that may be suitable for an advanced course on quantum chemistry or quantum mechanics. Present approach illustrates the utility of a widely used kind of projection operators [1][2]. It is worth noticing that the arguments based on the vectors (13) and (18) are almost identical, the only difference being that we compare the eigenvalues of $H_N$ and $H_{N-1}$ with the former and the eigenvalues of $H$ and $H_N$ with the latter. We think that our strategy, which generalizes the exercise proposed by Szabo and Ostlund [2], is simpler than the one developed by MacDonald [4] several years ago. As stated above, Klahn and Bingel [5] discussed the convergence of the RRVM in the case of the Hamiltonian operators that commonly appear in molecular physics and quantum chemistry. Here, we illustrated the performance of the method by means of a simple one-dimensional model suitable for an advanced course on quantum mechanics or quantum chemistry.

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Table 1: Convergence of the RRVM for the first eigenvalues of the dimensionless Hamiltonian (28) with $\lambda = 1$.

| $N$ | $\tilde{E}_1$   | $\tilde{E}_2$   | $\tilde{E}_3$   | $\tilde{E}_4$   |
|-----|----------------|----------------|----------------|----------------|
| 2   | 5.432610908    | 20.24140099    | -              | -              |
| 4   | 5.432607957    | 20.23986646    | 44.91361286    | 79.45797872    |
| 6   | 5.432607865    | 20.23986320    | 44.91360984    | 79.45707684    |
| 8   | 5.432607857    | 20.23986306    | 44.91360969    | 79.45707417    |
| 10  | 5.432607855    | 20.23986304    | 44.91360967    | 79.45707402    |
| 12  | 5.432607855    | 20.23986304    | 44.91360966    | 79.45707400    |
| 14  | -              | -              | 44.91360966    | 79.45707400    |

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