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On the application of the Rayleigh-Ritz method to a projected Hamiltonian

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Abstract

We apply the well known Rayleigh-Ritz method (RRM) to the projection of a Hamiltonian operator chosen recently for the extension of the variational principle to ensemble states. By means of a toy model we show that the RRM eigenvalues approach to those of the projected Hamiltonian from below.

1 Introduction

The Rayleigh-Ritz method (RRM) is one of the most widely used approaches for the study of the electronic structure of atoms and molecules [1,2]. One of its main advantages is that the RRM eigenvalues converge from above towards the exact energies of the physical system [3] (see also [4] and references therein).

In their introduction to the Rayleigh-Ritz variational principle Ding et al [5] resorted to a most curious Hamiltonian operator on a D-dimensional Hilbert space. Although such an operator is quite unrealistic for the treatment of actual physical problems, it seems to be worth further investigation.

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2 The Rayleigh-Ritz method

The RRM applies to any Hermitian operator H with eigenvalues E_k and eigenvectors $|\psi_k\rangle$

$$H\,|\psi_k\rangle = E_k\,|\psi_k\rangle\,,\ k = 0, 1, \ldots. \tag{1}$$

If we have a complete set of non-orthogonal vectors $|u_i\rangle$, $i = 0, 1, \ldots$, then the approximate RRM eigenvalues W_n are roots of the secular determinant [1,2,6]

$$|\mathbf{H} - W\mathbf{S}| = 0, \tag{2}$$

where $\mathbf{H}$ and $\mathbf{S}$ are $N \times N$ matrices with elements $H_{ij} = \langle u_i|\,H\,|u_j\rangle$ and $S_{ij} = \langle u_i\,|u_j\rangle$, $i, j = 0, 1, \ldots N-1$, respectively. It is well known that $W_k \geq E_k$ for all $k = 0, 1, \ldots, N-1$ [1–4,6].

2.1 Projected Hamiltonian

In their introduction to the Rayleigh-Ritz variational principle, Ding et al [5] considered the projection

$$H_D = \sum_{k=0}^{D-1} E_k\,|\psi_k\rangle\,\langle\psi_k|\,, \tag{3}$$

of H on a subspace $\mathcal{H}_D$ of dimension D spanned by the set of eigenvectors $\mathcal{S}_D = \{|\psi_k\rangle\,,\ k = 0, 1, \ldots, D-1\}$. They correctly stated that

$$\frac{\langle\psi|\,H_D\,|\psi\rangle}{\langle\psi\,|\psi\rangle} \geq E_0\ \forall\psi \in \mathcal{H}_D. \tag{4}$$

This introduction of the variational principle is rather unrealistic and of scarce utility because in practical applications we do not know $\mathcal{H}_D$. If we already know $\mathcal{H}_D$ then we can choose a complete basis set $\mathcal{B} = \{|i\rangle\,,\ i = 0, 1, \ldots, D-1\}$ of orthonormal vectors and, consequently, the diagonalization of the matrix of H_D in such a basis is a trivial problem. For this reason, in what follows we assume that $\mathcal{H}_D$ is unknown. Typically, we have to deal with a Hamiltonian operator H defined on an infinite-dimensional Hilbert space $\mathcal{H}$ and we do not know its eigenvalues and eigenvectors. However, we can try and do something interesting with the unrealistic scheme of Ding et al by simply assuming that $\mathcal{H} \subset \mathcal{H}_D$.

If we assume that H_D is also defined on $\mathcal{H}$ we can apply the RRM to this projected Hamiltonian. In such a case, the matrix elements are given by

$$(H_D)_{ij} = \sum_{k=0}^{D-1} E_k \langle u_i | \psi_k \rangle \langle \psi_k | u_j \rangle , \tag{5}$$

where $\{|u_j\rangle , \ j = 0, 1, \ldots\}$ spans the Hilbert space $\mathcal{H}$. We do not assume the vectors $|u_j\rangle$ to be orthonormal.

Under the conditions given above the results may be unexpected. For example, if $\psi \in \mathcal{H} \subset \mathcal{H}_D$ and $\langle \psi_k | \psi \rangle = 0, \ k = 0, 1, \ldots, n-1, n+1, \ldots, D-1$, then

$$\frac{\langle \psi | H_D | \psi \rangle}{\langle \psi | \psi \rangle} = E_n \frac{|\langle \psi_n | \psi \rangle|^2}{\langle \psi | \psi \rangle} \leq E_n \frac{\langle \psi_n | \psi_n \rangle \langle \psi | \psi \rangle}{\langle \psi | \psi \rangle} = E_n, \tag{6}$$

where we have used the Cauchy-Schwartz inequality [7]. We appreciate that it is possible to obtain lower bounds instead of upper ones.

2.2 Simple example

A suitable toy model is given by

$$H = -\frac{1}{2} \frac{d^2}{dx^2}, \tag{7}$$

with the boundary conditions $\psi(0) = \psi(1) = 0$. This example was chosen in recent discussions of the RRM [4, 6]. The exact eigenvalues and eigenfunctions are

$$E_k = \frac{k^2 \pi^2}{2}, \ \psi_k(x) = \sqrt{2} \sin(k\pi x), \ k = 1, 2, \ldots. \tag{8}$$

For simplicity, we choose the non-orthogonal basis set

$$u_i(x) = x^i (1-x), \ i = 1, 2, \ldots, \tag{9}$$

already used earlier [6]. Table 1 shows that the RRM eigenvalues W_k converge from above towards the exact eigenvalues E_k as expected [1–4, 6].

Tables 2, 3 and 4 show the RRM results for the projected Hamiltonian H_D with $D = 1$, $D = 2$ and $D = 3$, respectively (note that $k = 1, 2, \ldots, D$ in this example). We appreciate that there are D meaningful eigenvalues $W_k \neq 0$,

$k = 1, 2, \ldots, D$, and the remaining roots vanish $W_k = 0$, $D < k \leq N$. A most curious fact is that the RRM eigenvalues W_k converge towards the exact ones E_k from below. The well known proofs for the upper bounds mentioned above [3,4] (and references therein) do not apply here because the functions $u_i(x)$ cannot be expressed in terms of the finite set $\{\psi_k(x),\ k = 1, 2, \ldots, D\}$.

For every RRM eigenvalue W_k we obtain an approximate solution [1,2,6]

$$\left|\varphi_k\right\rangle = \sum_{j=1}^{N} c_{jk} \left|u_j\right\rangle , \tag{10}$$

and we choose such solutions to be orthonormal $\left\langle \varphi_k \right| \left.\varphi_n \right\rangle = \delta_{kn}$. The results of tables 2, 3 and 4 suggest that

$$\sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \varphi_i \right| H_D \left|\varphi_j\right\rangle \left|\varphi_i\right\rangle \left\langle \varphi_j\right| = \sum_{i=1}^{D} W_i \left|\varphi_i\right\rangle \left\langle \varphi_i\right| , \tag{11}$$

because $\left\langle \varphi_i \right| H_D \left|\varphi_j\right\rangle = W_i \delta_{ij}$ [1,2,6].

2.3 Arbitrary example

We can extend the results of the preceding subsection to a more general case based on the same toy model. Suppose that we have a set of orthonormal vectors $\left|\psi_k\right\rangle$, $k = 1, 2, \ldots, D$ and construct the projected Hamiltonian operator

$$H_D = \sum_{k=1}^{D} \alpha_k \left|\psi_k\right\rangle \left\langle \psi_k\right| , \tag{12}$$

where α_k are arbitrary real numbers. We can obviously apply the RRM as in the preceding example. Table 5 shows RRM eigenvalues for the case $D = 3$ and $\alpha_k = k$.

3 Conclusions

It is not clear to us why Ding et al [5] introduced the variational principle by means of an unrealistic projected Hamiltonian because this principle as well as the properties of the RRM have already been proved for the kind of operators commonly found in actual physical problems [3,4]. However, when the projected Hamiltonian is treated by the RRM in the usual way, one obtains some curious results as shown above. One of them is the occurrence of null eigenvalues and the other is the appearance of lower bounds instead of upper ones (compare table 1 with tables 2, 3 and 4).

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Table 1: Lowest RRM eigenvalues for the Hamiltonian (7)

N	W_1	W_2	W_3	W_4
4	4.934874810	19.75077640	51.06512518	100.2492235
5	4.934802217	19.75077640	44.58681182	100.2492235
6	4.934802217	19.73923669	44.58681182	79.99595777
7	4.934802200	19.73923669	44.41473408	79.99595777
8	4.934802200	19.73920882	44.41473408	78.97848206
9	4.934802200	19.73920882	44.41322468	78.97848206
10	4.934802200	19.73920880	44.41322468	78.95700917
11	4.934802200	19.73920880	44.41321981	78.95700917
12	4.934802200	19.73920880	44.41321981	78.95683586
13	4.934802200	19.73920880	44.41321980	78.95683586
14	4.934802200	19.73920880	44.41321980	78.95683521
15	4.934802200	19.73920880	44.41321980	78.95683521
16	4.934802200	19.73920880	44.41321980	78.95683520
17	4.934802200	19.73920880	44.41321980	78.95683520
18	4.934802200	19.73920880	44.41321980	78.95683520
19	4.934802200	19.73920880	44.41321980	78.95683520
20	4.934802200	19.73920880	44.41321980	78.95683520

Table 2: RRM for the projected Hamiltonian with $D = 1$

N	W_1	$W_k,\ 1 < k \leq N$
1	4.927671482	0
2	4.927671482	0
3	4.934799721	0
4	4.934799721	0
5	4.934802200	0
6	4.934802200	0

Table 3: RRM for the projected Hamiltonian with $D = 2$

N	W_1	W_2	$W_k,\ 2 < k \leq N$
2	4.927671482	19.40270646	0
3	4.934799721	19.40270646	0
4	4.934799721	19.73799899	0
5	4.934802200	19.73799899	0
6	4.934802200	19.73920734	0
7	4.934802200	19.73920734	0
8	4.934802200	19.73920880	0
9	4.934802200	19.73920880	0
10	4.934802200	19.73920880	0

Table 4: RRM for the projected Hamiltonian with $D = 3$

N	W_1	W_2	W_3	$W_k,\ 3 < k \leq N$
3	4.934799541	19.40270646	41.72191568	0
4	4.934799541	19.73799899	41.72191568	0
5	4.934802200	19.73799899	44.37877225	0
6	4.934802200	19.73920734	44.37877225	0
7	4.934802200	19.73920734	44.41306667	0
8	4.934802200	19.73920880	44.41306667	0
9	4.934802200	19.73920880	44.41321950	0
10	4.934802200	19.73920880	44.41321950	0
11	4.934802200	19.73920880	44.41321980	0
12	4.934802200	19.73920880	44.41321980	0
13	4.934802200	19.73920880	44.41321980	0

Table 5: RRM for the arbitrary Hamiltonian (12) with $D = 3$ and $\alpha_k = k$

N	W_1	W_2	W_3	$W_k,\ 3 < k \leq N$
4	0.9999994479	1.999877421	2.818209291	0
5	0.9999999999	1.999877421	2.997673155	0
6	0.9999999999	1.999999852	2.997673155	0
7	0.9999999999	1.999999852	2.999989656	0
8	0.9999999999	1.999999999	2.999989656	0
9	0.9999999999	1.999999999	2.999999979	0
10	0.9999999999	1.999999999	2.999999979	0
11	0.9999999999	1.999999999	2.999999999	0
12	1.0000000000	1.999999999	2.999999999	0
13	1.0000000000	1.999999999	2.999999999	0
14	1.0000000000	1.999999999	2.999999999	0