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Ritz energy minimization, Weinstein variance minimization and Hilbert subspace projection: an analytical case study

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Abstract

We show on a analytical case example how the projection method on full Hilbert space converges to Weinstein variance minimization and differs from Ritz variational method.

1 Introduction

In Quantum Physics, and in particular, in Quantum Chemistry, the minimization of the Rayleigh quotient of the Hamiltonian, which, in general, represents the energy expectation value of the system, has been arguably the most common variational method employed to calculate approximate energy eigenvalues, since its introduction by Ritz¹. However, other approaches have also been considered, and used advantageously. Weinstein variance minimization², or numerically more stable variants^{3,4}, have been extensively employed in Quantum Monte-Carlo (QMC)^{5,6}. Recently, Ye et al. have developed similar Weinstein variance

minimization techniques for Self-Consistent Field (SCF) wave-function methods to overcome the variational collapse of energy-based optimizations to the lowest solution of a given symmetry. Their method called the “ σ -SCF” method has been used by David et al.⁸ to calculate excited states in strong magnetic fields. Note also, that variance minimization has been extended to, and advocated for, non-linear Schrödinger equations⁹.

In the past, Weinstein’s idea has been implemented in various ways and investigated numerically for atomic and molecular systems by Frost^{10–12}, or Goodisman^{13,14}, and for nuclei by Satyan et al.¹⁵, to quote a few. Note also, the work of Messmer and collaborators^{16,17} related to Weinstein’s idea but oriented towards approximating the excited eigenfunctions rather than the eigenvalues. However, to our knowledge no author has compared variance minimization and energy minimization on an analytical example. The recent revival of variance-based variational methods prompts us to fill this gap. Furthermore, most implementations of coupled cluster methods as well as computer codes such as HORTON¹⁸ rely on Hilbert subspace projection to optimize variational parameters. Here, we point to the relationship between full Hilbert space projection and Weinstein minimization, which makes our comparison between Ritz and Weinstein methods also relevant to Hilbert space projection.

2 A toy-model

Let us consider a two-electron two-orbital system and the following Hamiltonian \hat{H} represented in an orthonormal basis of ($\hat{S}_z = 0$)-geminal functions $(\psi_1 \wedge \bar{\psi}_1, \psi_1 \wedge \bar{\psi}_2, \psi_2 \wedge \bar{\psi}_1, \psi_2 \wedge \bar{\psi}_2)$, by the matrix :

$$H = \begin{pmatrix} A & C & C & 0 \\ C & B & 0 & C \\ C & 0 & B & C \\ 0 & C & C & A \end{pmatrix}$$

,

where A, B, C are three scalar parameters. This Hamiltonian is invariant under permutation

of indices “1” and “2”, in order to have as simple as possible a model. The eigenpairs of the Hamiltonian are easily found. There is one triplet and three singlet eigenstates:

$$\begin{aligned}
& (B, \psi_1 \wedge \bar{\psi}_2 - \psi_2 \wedge \bar{\psi}_1), \\
& (A, \psi_1 \wedge \bar{\psi}_1 - \psi_2 \wedge \bar{\psi}_2), \\
& \left(\frac{A+B}{2} + \sqrt{\left(\frac{A-B}{2}\right)^2 + 4C^2}, 2C(\psi_1 \wedge \bar{\psi}_1 + \psi_2 \wedge \bar{\psi}_2) + \left(\frac{B-A}{2} + \sqrt{\left(\frac{B-A}{2}\right)^2 + 4C^2} \right) (\psi_1 \wedge \bar{\psi}_2 + \psi_2 \wedge \bar{\psi}_1) \right), \\
& \left(\frac{A+B}{2} - \sqrt{\left(\frac{A-B}{2}\right)^2 + 4C^2}, 2C(\psi_1 \wedge \bar{\psi}_1 + \psi_2 \wedge \bar{\psi}_2) + \left(\frac{B-A}{2} - \sqrt{\left(\frac{B-A}{2}\right)^2 + 4C^2} \right) (\psi_1 \wedge \bar{\psi}_2 + \psi_2 \wedge \bar{\psi}_1) \right).
\end{aligned}$$

3 Hartree-Fock solution

The expectation value of this Hamiltonian for a general wave function

$\Psi = a\psi_1 \wedge \bar{\psi}_1 + b\psi_1 \wedge \bar{\psi}_2 + c\psi_2 \wedge \bar{\psi}_1 + d\psi_2 \wedge \bar{\psi}_2$ is

$$\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{(a^2 + d^2)A + (b^2 + c^2)B + 2(a + d)(b + c)C}{a^2 + b^2 + c^2 + d^2} \quad (1)$$

Let us find the restricted Hartree-Fock (RHF) solution for this Hamiltonian, that is the single determinantal, singlet wave function that minimizes this expression. From the exact singlet eigenstate expressions, we see that we can safely assume $a \neq 0$ for general Hamiltonian parameter values i.e. provided $C \neq 0$. Then it is convenient to factor out a as a normalization and phase factor, and to define three new coefficients $\beta = \frac{b}{a}$, $\gamma = \frac{c}{a}$, $\delta = \frac{d}{a}$, and because we are looking for a singlet, we have to impose $\beta = \gamma$. Equation (1) becomes,

$$\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{(1 + \delta^2)A + 2\beta^2 B + 4(1 + \delta)\beta C}{1 + 2\beta^2 + \delta^2}. \quad (2)$$

The wave function Ψ will be a Slater determinantal function if and only if it satisfy the Plücker relation $ad - bc = 0$, that is to say, in terms of the new coefficients, $\delta = \beta^2$. So,

finding the RHF solution amounts to minimizing the function,

$$f(\beta) = \frac{(1 + \beta^4)A + 2\beta^2 B + 4(1 + \beta^2)\beta C}{1 + 2\beta^2 + \beta^4} = \frac{A + 4C\beta + 2B\beta^2 + 4C\beta^3 + A\beta^4}{1 + 2\beta^2 + \beta^4}. \quad (3)$$

Its derivative is,

$$f'(\beta) = \frac{4C(1 + \beta^2 - \beta^4 - \beta^6) + 4(A - B)(\beta^5 - \beta)}{(1 + 2\beta^2 + \beta^4)^2} = \frac{4(1 + \beta^2)(\beta - 1)(\beta + 1)((A - B)\beta - C(\beta^2 + 1))}{(1 + \beta^2)^4}. \quad (4)$$

This shows that unless $|A - B| \geq 2|C|$, stationary states will only be obtained for $\beta = \pm 1$ (the Hamiltonian being real, we consider only real coefficients). When $|A - B| > 2|C|$ two additional solutions show up, $\beta = \frac{A-B}{2C} \pm \frac{\sqrt{(A-B)^2 - 4C^2}}{2C}$. For a give value of β , the (unnormalized) corresponding Slater determinantal function is

$$\Psi(\beta) = (\psi_1 + \beta\psi_2) \wedge (\bar{\psi}_1 + \beta\bar{\psi}_2).$$

The energy expectation values corresponding to the RHF stationary solutions are ($f(\beta)$ can be reexpressed as $f(\beta) = A + 4C\frac{\beta}{1+\beta^2} + 2(B - A) \left(\frac{\beta}{1+\beta^2}\right)^2$:

$$f(\pm 1) = \frac{A + B}{2} \pm 2C \quad (5)$$

and

$$f\left(\frac{A - B}{2C} \pm \frac{\sqrt{(A - B)^2 - 4C^2}}{2C}\right) = A + \frac{2C^2}{A - B}. \quad (6)$$

The latter value will possibly be a ground state energy approximation in the ‘‘small coupling’’ case $|A - B| > 2|C|$, when $A < B$. The two β -values give the same energy and correspond to either doubly-occupied ψ_1 dominant, mono-excitations negligible, doubly-occupied ψ_2 super-negligible or the reverse doubly-occupied ψ_2 dominant, doubly-occupied ψ_1 super-negligible. One of the values $\beta = \pm 1$ will give a ground state energy approximation in the ‘‘strong coupling regime’’ or when $A > B$, depending on the sign of C .

4 Solution by projection on the whole Hilbert space and least square minimization

It can be seen that solving the projected eigenvalue equation on the full Hilbert space by least square fitting amounts to minimizing the dispersion, since for Ψ_K 's running over a complete set, we have:

$$\sum_K \|\langle \Psi_K | H - E | \Psi(\vec{p}) \rangle\|^2 = \langle \Psi(\vec{p}) | (H - E)^2 | \Psi(\vec{p}) \rangle \quad (7)$$

and for a stationary solution $E_0, \Psi(\vec{p}_0)$, the stationnarity with respect to E will give

$$E_0 = \langle \Psi(\vec{p}_0) | H | \Psi(\vec{p}_0) \rangle. \quad (8)$$

We can study within the same model the function

$$g(\beta) = \langle \Psi(\beta) | H^2 | \Psi(\beta) \rangle - |\langle \Psi(\beta) | H | \Psi(\beta) \rangle|^2. \quad (9)$$

The square of the Hamiltonian is

$$H^2 = \begin{pmatrix} A^2 + 2C^2 & (A+B)C & (A+B)C & 2C^2 \\ (A+B)C & B^2 + 2C^2 & 2C^2 & (A+B)C \\ (A+B)C & 2C^2 & B^2 + 2C^2 & (A+B)C \\ 2C^2 & (A+B)C & (A+B)C & A^2 + 2C^2 \end{pmatrix}$$

For a normalized $\Psi(\beta)$ we get

$$\langle \Psi(\beta) | H^2 | \Psi(\beta) \rangle = A^2 + 2C^2 + 4(A+B)C \frac{\beta}{1+\beta^2} + 2(B^2 - A^2 + 4C^2) \left(\frac{\beta}{1+\beta^2} \right)^2$$

$$|\langle \Psi(\beta) | H | \Psi(\beta) \rangle|^2 = A^2 + 8AC \frac{\beta}{1+\beta^2} + 4(4C^2 + (B-A)A) \left(\frac{\beta}{1+\beta^2} \right)^2 + 16(B-A)C \left(\frac{\beta}{1+\beta^2} \right)^3 + 4(B-A)^2 \left(\frac{\beta}{1+\beta^2} \right)^4.$$

Setting $\theta = \frac{\beta}{1+\beta^2}$, the g -function in terms of this new θ parameter is:

$$g(\theta) = 2C^2 + 4(B - A)C\theta + (2(A - B)^2 - 8C^2)\theta^2 - 16(B - A)C\theta^3 - 4(B - A)^2\theta^4 \quad (10)$$

For $A = B$, the RHF solutions $\beta = \pm 1$ (depending on the sign of C , one will be the ground state and the other and excited eigenstate) is exact and you do retrieve it by minimizing g , because actually for exact eigenstates the dispersion is minimal and equal to 0. For $A \neq B$, the exact eigenstates cannot be condensed into a single determinantal function, as can be seen from the Plücker relation, then the RHF solution is only approximate. The derivative of g is

$$g'(\theta) = 4(B - A)C + 4((A - B)^2 - 4C^2)\theta - 48(B - A)C\theta^2 - 16(B - A)^2\theta^3 \quad (11)$$

For the RHF solutions in the low coupling regime, $\theta = \frac{C}{A-B}$. Inserting this value into g' we can check that it does not correspond to a stationary point of the dispersion. We calculate:

$$g'\left(\frac{C}{A-B}\right) = \frac{16C^3}{A-B}, \quad (12)$$

So cancellation can occur only for $C = 0$.

5 Comparison on a numerical example

Let us set $A = 0, B = 2, C = -0.5$. The exact eigenvalues are: 2.41421, 2, 0, -0.414214. There are two equivalent optimal β -values: $\beta \approx 0.267949$ and $\beta \approx 3.73205$ which give an RHF energy of $E_{RHF} = -0.25$ to be compared with $E_{FCI} = -0.414214$. The optimal β -value in the same range is: $\beta \approx 0.218032$ which gives a complete Hilbert space projected energy of $E_{CHSP} = -0.24299$ quite close to E_{RHF} .

See more examples at the end: **there is always a relative minimum of the disper-**

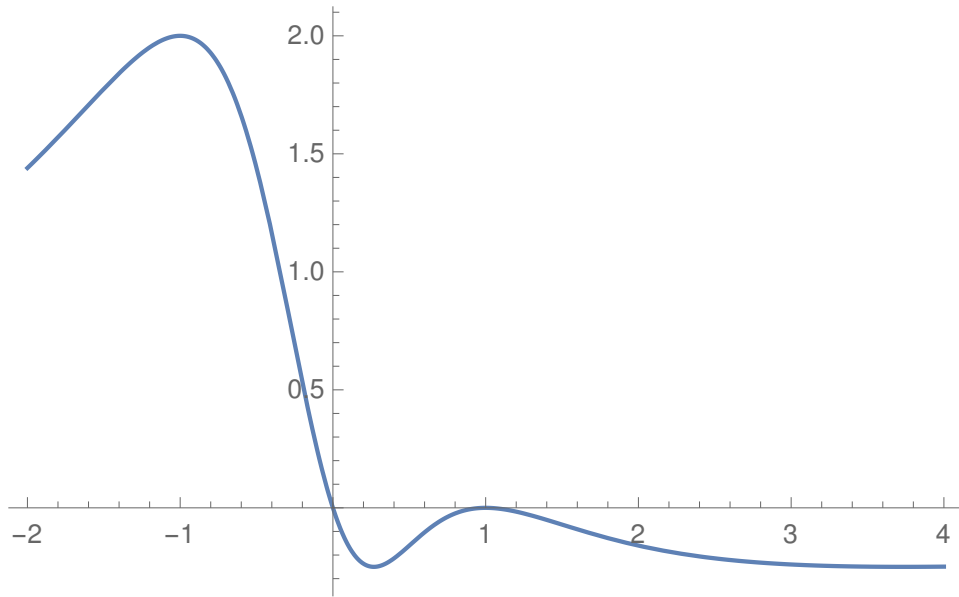


Figure 1: The f -function (expectation value of the Slater determinant) as a function of β

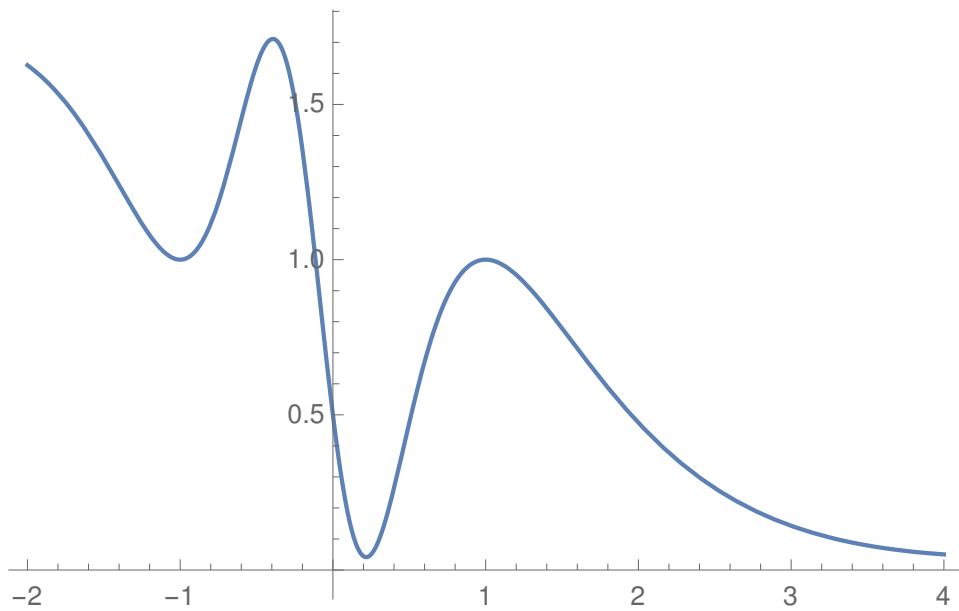


Figure 2: The g -function (dispersion value of the Slater determinant) as a function of β

sion near the absolute minimum of the expectation value, but it is not always the absolute minimum of the dispersion.

6 Solution by projection on Slater determinants

We can also project the eigenvalue equation on a few Slater determinants. The four single determinantal functions $(\psi_1 \wedge \bar{\psi}_1, \psi_1 \wedge \bar{\psi}_2, \psi_2 \wedge \bar{\psi}_1, \psi_2 \wedge \bar{\psi}_2)$ give the following projected equations:

$$a(A - E) + (b + c)C = 0 \quad (13)$$

$$b(B - E) + (a + d)C = 0 \quad (14)$$

$$c(B - E) + (a + d)C = 0 \quad (15)$$

$$d(A - E) + (b + c)C = 0. \quad (16)$$

Looking for a singlet single determinantal solution, these equations reduce to

$$A - E + 2\beta C = 0 \quad (17)$$

$$\beta(B - E) + (1 + \beta^2)C = 0 \quad (18)$$

$$\beta^2(A - E) + 2\beta C = 0. \quad (19)$$

Two at least are needed to determine the two unknowns E and β .

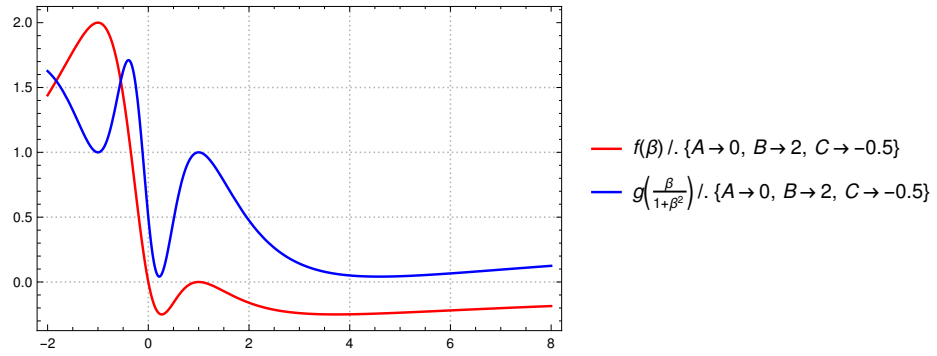
Choosing the first and the last, we find either $\beta = 0, E = A$ or $\beta = \pm 1, E = A \pm 2C$. The latter are RHF stationary solutions.

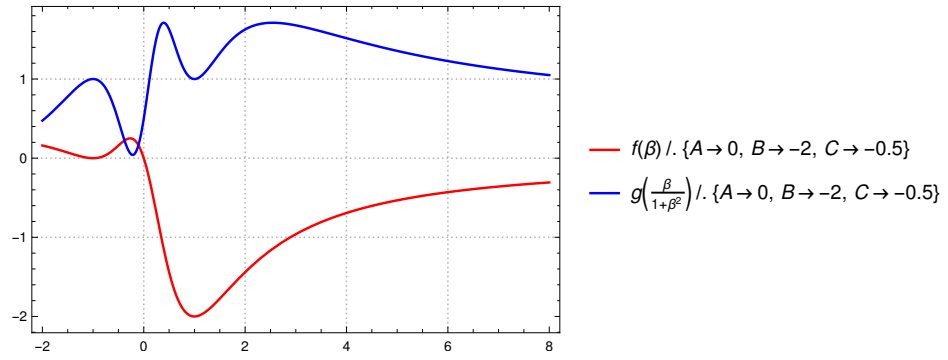
Choosing the first and the second, we find $\beta = \frac{B-A}{2C} \pm \frac{\sqrt{(A-B)^2 + 4C^2}}{2C}, E = B \pm \sqrt{(A-B)^2 + 4C^2}$.

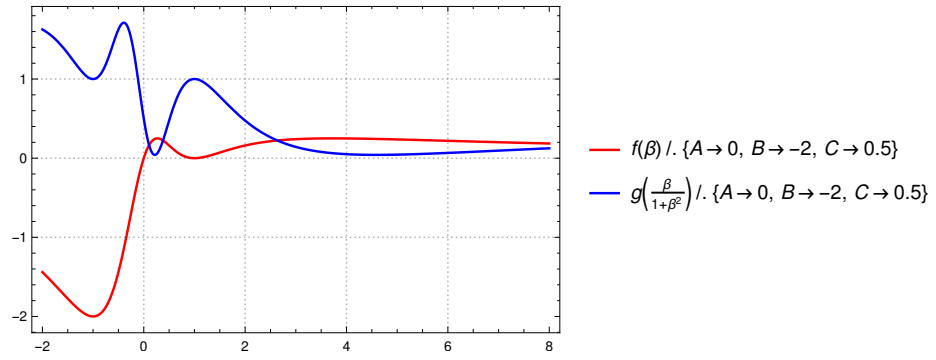
Choosing the second and the third, we find $\beta = \frac{A-B}{2C} \pm \frac{\sqrt{(A-B)^2 + 4C^2}}{2C}, E = B \pm \sqrt{(A-B)^2 + 4C^2}$.

These choices lead to identical energies for different β -values.

Note that, there is no solution to the 3 equations taken together, in general. Hence the least mean square procedure.







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