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► **To cite this version:**

Patrick Cassam-Chenai. Projection of the Eigenvalue Equation for a Given Wave Function Ansatz on Full Hilbert Space. 2018. hal-01756443v1

HAL Id: hal-01756443

<https://hal.univ-cotedazur.fr/hal-01756443v1>

Preprint submitted on 19 Apr 2018 (v1), last revised 1 May 2023 (v2)

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Projection of the Eigenvalue Equation for a Given Wave Function Ansatz on Full Hilbert Space

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Abstract

We show on a counter example that the projection method on full Hilbert space is not equivalent to the variational method

Let us consider the following Hamiltonian H represented in the basis $(\psi_1 \wedge \bar{\psi}_1, \psi_1 \wedge \bar{\psi}_2, \psi_2 \wedge \bar{\psi}_1, \psi_2 \wedge \bar{\psi}_2)$, by a matrix parametrized by 3 scalars A, B, C :

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

Its 4 eigenpairs are easily found. There is a triplet and three singlet states:

$$(B, \psi_1 \wedge \bar{\psi}_2 - \psi_2 \wedge \bar{\psi}_1),$$

$$(A, \psi_1 \wedge \bar{\psi}_1 - \psi_2 \wedge \bar{\psi}_2),$$

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

1 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 $|A - B| \geq 2|C|$, stationnary 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 .

2 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 stationarity 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 $C = 0$.

3 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

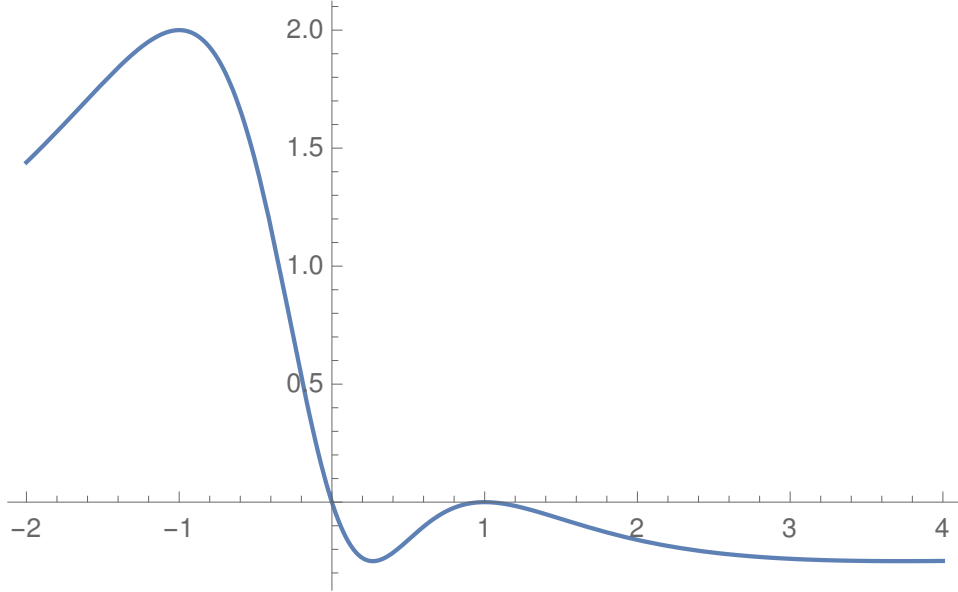


Figure 1: The f -function (expectation value of the Slater determinant) as a function of β

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

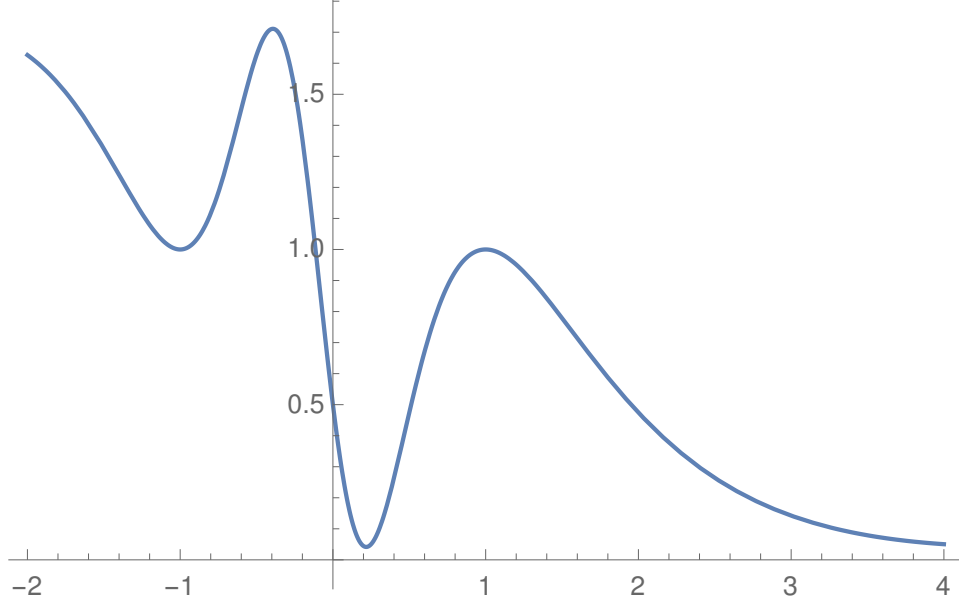


Figure 2: The g -function (dispersion value of the Slater determinant) as a function of β

of $E_{CHSP} = -0.24299$ quite close to E_{RHF} .

See more examples at the end: **there is always a relative minimum of the dispersion near the absolute minimum of the expectation value, but it is not always the absolute minimum of the dispersion.**

4 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:

$$a(A - E) + (b + c)C = 0 \tag{13}$$

$$b(B - E) + (a + d)C = 0 \tag{14}$$

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

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

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.

