The Effect of the Cusp on the Rate of Convergence of the Rayleigh-Ritz Method

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Abstract. This paper investigates how smoothing the Hamiltonian and the cusp of the corresponding eigenfunction affects the rate of convergence of the Rayleigh-Ritz method. A simple example from quantum mechanics is used, with a basis of harmonic oscillator functions.

1 Introduction

This study is motivated by a computational problem in the electronic molecular structure theory. It has been shown ([1]) that the variational energy error of a configuration interaction(CI), or any other orbital-based method is slow (of order $O(L^{-3})$ or greater, where L is the maximum angular momentum in the finite orbital basis). This behavior can be explained by the inability of the basis functions to describe the "electron correlation cusps" of the wavefunction introduced by the singularities of the Coulombic potential.

One possible approach that we are exploring is a perturbational one, in which the reference problem has a Hamiltonian free of such singularities, and for which the wavefunctions differ significantly from those of the true Hamiltonian only in the vicinity of such cusps. Traditional CI methods are used to solve the reference problem, and geminal-based methods are employed to solve the low-order Rayleigh-Schrödinger perturbation equations. The success of this approach is dependent upon finding a reference Hamiltonian for which the Rayleigh-Ritz (RR) method converges far more rapidly than for the true Hamiltonian (see [2]).

This paper illustrates how the convergence of the RR method is accelerating with the "smoothing" of the Hamiltonian and of the corresponding ground-state wavefunction for a simple example from quantum mechanics. The singular potential v used here is different from the usual potentials used in quantum chemistry, so we investigate whether the associated operator H is selfadjoint and the RR method for this operator using a basis of harmonic oscillator functions is convergent.

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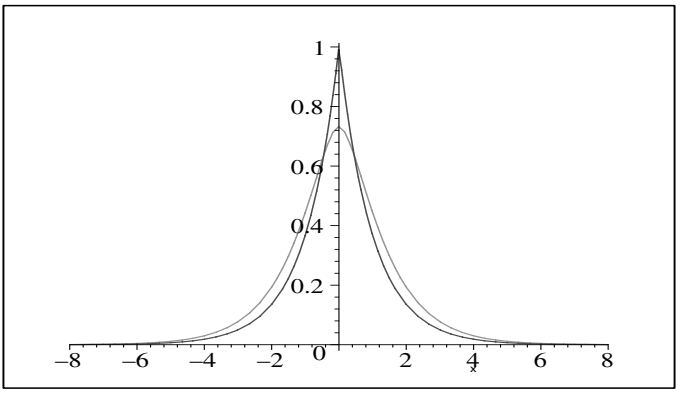

Fig. 1. The wavefunctions ψ and ψ_a for $a = 1$

2 The Model

Consider the one-dimensional Schrödinger equation

$$-\frac{1}{2}\frac{d^2\psi(x)}{dx^2} + v(x)\psi(x) = E\psi(x),\ x \in \mathbf{R} \tag{1}$$

With the potential $v(x) = -\delta(x)$ the equation (1) has the ground-state energy $E = -1/2$, with the normalized wavefunction $\psi(x) = exp(-|x|)$. With the smoothed potential

$$v_a(x) = -\frac{a + 1/2 + a(a+2)|x| + a^2x^2}{(1 + a|x|)^4} \tag{2}$$

the Schrödinger equation has ground-state wavefunction $\psi_a(x) = N_a exp\left(-\frac{ax^2}{1+a|x|}\right)$ with the same energy $E = -1/2$; N_a is the normalization constant. The function $\psi(x)$ is continuous, but has a cusp at the origin; the function $\psi_a(x)$ has continuous first and second derivatives and a discontinuous third derivative for any $a > 0$. Moreover, $\psi_a(x) \to \psi(x)$ pointwise as $a \to \infty$. $v_a(x) \to 0$ as $a \to \infty$ for any $x \neq 0$ and $v_a(0) = -a - 1/2 \to -\infty$ as $a \to \infty$.

3 The Expansion

Consider the expansion of the two wavefunctions, ψ and ψ_a

$$\psi(x) = \sum_{n=0}^{\infty} c_n\phi_n(x), \qquad \psi_a(x) = \sum_{n=0}^{\infty} c_n^a\phi_n(x) \tag{3}$$

in the orthonormal basis of harmonic oscillator functions

$$\phi_m(x) = N_m H_m(\lambda x) exp(-(\lambda x)^2/2), \tag{4}$$

where λ is a positive scaling factor and N_m is a normalization constant.

Since both ψ and ψ_a are even functions, $c_{2k+1} = c^a_{2k+1} = 0$ for all integers k. For even integers we have $c_{2k} = C_{2k}$ and $c^a_{2k} = C^a_{2k}$, where

$$C_n = \frac{2N_n}{\lambda} \int_0^\infty exp\left(-\frac{x}{\lambda} - \frac{x^2}{2}\right) H_n(x)dx \tag{5}$$

$$C^a_n = \frac{2N_n N_a}{\lambda} \int_0^\infty exp\left(-\frac{x^2}{2} - \frac{ax^2}{\lambda^2 + a\lambda x}\right) H_n(x)dx \tag{6}$$

The coefficients C_n can be computed using an exact recurrence formula which can be obtained integrating (5) by parts. To compute C^a_n an approximate quadrature formula is used for the function $f(x) = exp\left(-\frac{x^2}{2} - \frac{ax^2}{\lambda^2+\lambda ax}\right) H_n(x)$, where the roots x_j and weights w_j are for polynomials orthogonal with respect to the weight function $w(x) = exp(-x^2)$ on the interval $(0, \infty)$.

Once the expansion coefficients c_n and c^a_n are computed, one can define the projection of the wavefunctions ψ and ψ_a on the $n+1$-dimensional space W_n spanned by $\phi_0, \phi_1, \ldots, \phi_n$:

$$\psi_n(x) = \sum_{i=0}^{n} c_i \phi_i(x), \qquad \psi^a_n(x) = \sum_{i=0}^{n} c^a_i \phi_i(x). \tag{7}$$

$$H = -\frac{1}{2}\frac{d^2}{dx^2} + v(x), \qquad H^a = -\frac{1}{2}\frac{d^2}{dx^2} + v_a(x). \tag{8}$$

Next, let us define E_n and E^a_n as the lowest eigenvalue of the Hamiltonian matrix $(< \phi_i|H|\phi_j >)_{0\le i,j\le n}$ and of $(< \phi_i|H^a|\phi_j >)_{0\le i,j\le n}$, respectively. For each n, the norm of the projection $\|\psi_n\|$ is maximized as a function of λ and E_n is computed for this λ. Values of E_n are reported in Table 1 and E^a_n are reported in Table 2 for two different values of the smoothing parameter a. Also

Table 1. λ and the energies E^1_n and E_n for $\psi(x)$

ψ				
n	λ	(ψ_n, ψ_n)	E^1_n	E_n
8	1.300	.997350	-.405894	-.409083
16	1.450	.999183	-.433470	-.435312
24	1.575	.999629	-.447763	-.448960
32	1.675	.999795	-.456453	-.457308
40	1.750	.999873	-.462174	-.462830
64	1.975	.999955	-.472857	-.473204
80	2.125	.999973	-.477236	-.477483
104	2.275	.999986	-.481202	-.481372
120	2.375	.999990	-.483174	-.483311

Table 2. λ and the energies $E_n^{1,a}$ and E_n^1 for $\psi_a(x)$for $a = 4$ and $a = 1$

	ψ_a for $a = 4$				ψ_a for $a = 1$			
n	λ	(ψ_n^a, ψ_n^a)	$E_n^{1,a}$	E_n^a	λ	(ψ_n^a, ψ_n^a)	$E_n^{1,a}$	E_n^a
8	1.125	.999051	-.485252	-.485353	.875	.999811	-.498480	-.498483
16	1.225	.999824	-.494604	-.494620	.950	.999979	-.499683	-.499684
24	1.300	.999947	-.497446	-.497450	1.00	.999995	-.499891	-.499891
32	1.375	.999979	-.498464	-.498467	1.05	.999998	-.499975	-.499975
40	1.400	.999989	-.498934	-.498938	1.075	.999999	-.499975	-.499997
64	1.550	.999998	-.499752	-.499752				
80	1.625	.999999	-.499869	-.499869				

reported in these tables are energies E_n^1 and $E_n^{1,a}$ computed for ψ_n and ψ_n^a, the projections of the true wavefunctions on the subspace.

$$E_n^1 = \frac{<\psi_n|H|\psi_n>}{(\psi_n, \psi_n)}, \qquad E_n^{1,a} = \frac{<\psi_n^a|H^a|\psi_n^a>}{(\psi_n^a, \psi_n^a)}. \tag{9}$$

Note that $E_n \leq E_n^1$ and $E_n^a \leq E_n^{1,a}$. Figures 2 and 3 illustrate the beneficial effects of smoothing.

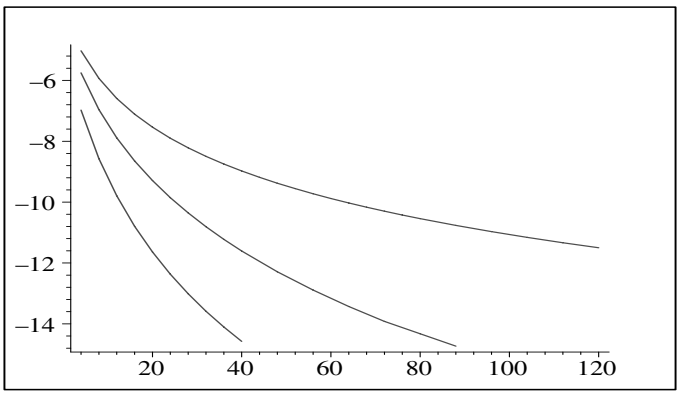

Fig. 2. The norm errors $ln(1 - (\psi_n, \psi_n))$ (top curve) and $ln(1 - (\psi_n^a, \psi_n^a))$ for $a = 1$ (lowest curve) and $a = 4$ (middle curve)

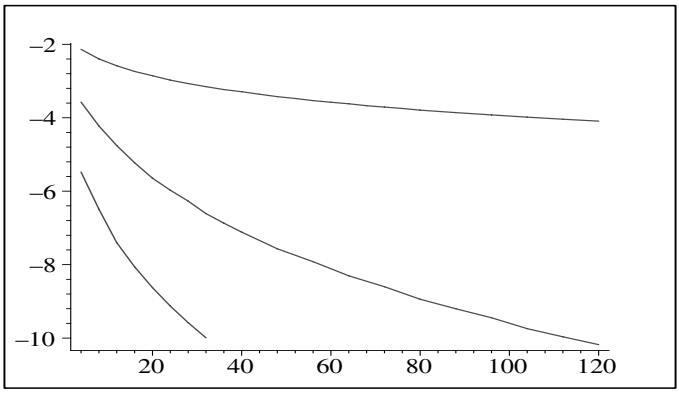

Fig. 3. The energy errors $ln(1/2 + E_n)$ (top curve) and $ln(1/2 + E_n^a)$ for $a = 1$ (lowest curve) and and $a = 4$ (middle curve).

4 The Convergence of the RR Method

For eq. (1) with $v(x) = -\delta(x)$ the behavior of the energy error exhibited in Figure 3 raises a serious question whether the method is just slowly convergent or not convergent at all. In fact, convergence can be established by rigorous mathematics outlined below.

A theorem in Michlin [6] (see also [5]) says that for a positive definite and selfadjoint operator B with the domain $D_B \subset L^2$ dense in L^2 the RR method converges to the lowest exact eigenvalue E_0 of the operator B provided that the basis used $\{\phi_m\}_{m=0,1,2,\ldots}$ is complete in the energy space H_B. The energy space H_B is the closure of D_B in the B-norm:

$$\|f\|_B = (f, Bf)^{1/2}. \tag{10}$$

Let t be the form defined by

$$t(u,v) = \frac{1}{2}\int u^{'}(t)\overline{v^{'}(t)}dt + \left(\frac{1}{2} + \delta_0\right)\int u(t)\overline{v(t)}dt - u(0)\overline{v(0)} \tag{11}$$

for functions $u, v \in H^1$,where $\delta_0 > 0$. The Sobolev space $H^1 = \{f \in L^2, f^{'} \in L^2\}$ (the derivatives are in the generalized sense), is the closure of $C_0^\infty(\mathbf{R})$ in the H^1-norm: $\|f\|_{H^1}^2 = \int |f(t)|^2 dt + \int |f^{'}(t)|^2 dt$. For any $f \in C_0^\infty(\mathbf{R})$ and $\epsilon > 0$

$$|f(0)|^2 \leq \frac{1}{2\epsilon}\int |f(t)|^2 dt + \frac{\epsilon}{2}\int |f^{'}(t)|^2 dt \tag{12}$$

The inequality (12) with $\epsilon = 1$ makes it possible to define $f(0)$ for any $f \in H^1$ and to prove that the symmetric form t is positive definite ($t(u,u) \geq \delta_0\|u\|^2 \; \forall \; u \in$

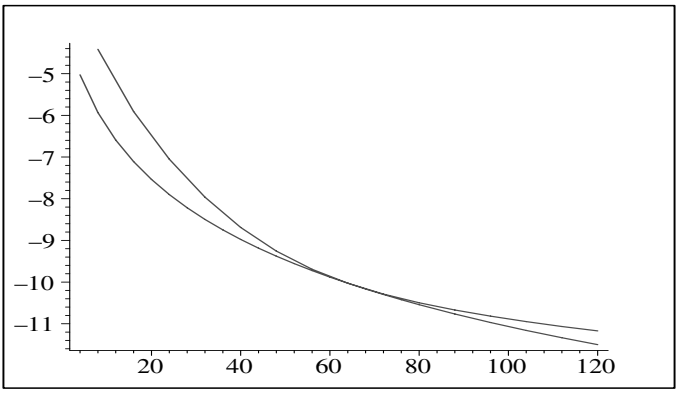

Fig. 4. Norm errors for $\psi(x)$ for $\lambda = 2$(top curve) and optimized λ(lower curve)

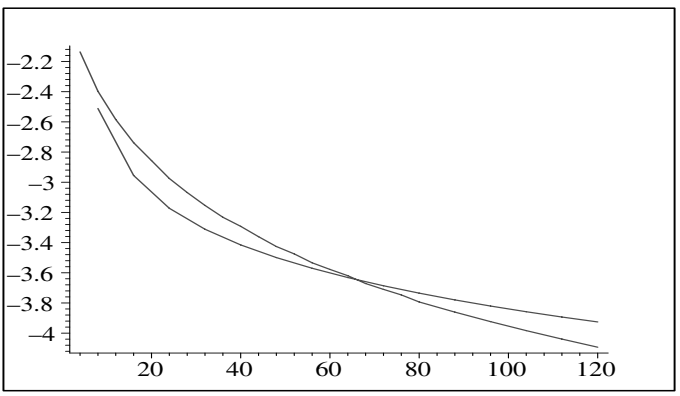

Fig. 5. Energy errors for $\psi(x)$ for xed $\lambda = 2$ (upper right) and optimized λ (lower right)

$H^1,\ \delta_0 > 0$). In its general form, (12) is the main ingredient in proving that the form t is closed. By a representation theorem (see [3]) there exists a selfadjoint operator $T : D(T) \subset H^1 \subset L^2 \to L^2$, positive definite (with the same lower bound δ_0 as the form t) defined by the relation $(Tu, v) = t(u, v)\ \forall u \in D(T),\ \forall v \in H^1$. Moreover, its domain $D(T)$ is dense in the Hilbert space H^1 with the norm $\| \ \|_{H_t} = t(\ ,\ )^{1/2}$.

This implies that H_T-the closure of $D(T)$ in the norm $\| \ \|_{H_t}$-is H^1, since the norms $\| \ \|_{H_t}$ and $\| \ \|_{H^1}$ are equivalent. The basis $\{\phi_m(x)\}_{m=0,1,\ldots}$ is complete in H^1 for any $\lambda > 0$ (see [4]) so the RR method is convergent for the operator T and also for $T - 1/2 - \delta_0$, which is the operator from eq. (1) with $v(x) = -\delta(x)$. These considerations are for a fixed λ, while the results from Figure 2 and 3 are for a λ varied to optimize (ψ_n, ψ_n) for each n. The difference between the results for a fixed λ and λ optimized in the sense above can be seen in Figures 4 and 5. As shown in Table 2, $\lambda = 2$ maximizes the norm of ψ_n for $n \approx 70$, so

the curves in Figures 4 and 5 coincide at this point. The norm error for optimal λ is smaller than that for $\lambda = 2$ for all n, as expected, while the energy error is lower for $\lambda = 2$ for small values of n (λ was optimized with respect to the norm). After $n \approx 70$ the energy error for fixed λ is greater than that for optimized λ. So the method is convergent both for fixed and optimized λ, but the convergence is very slow due to the inability of the basis functions to describe the cusp $\psi(x)$.

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