A Comparative Study of Variational Techniques for Schrödinger Equations. Pointwise Quality Criteria

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Different variational schemes for solving the Schrödinger equation are tested for the model potential of Kratzer-Fues. Wavefunctions are analyzed in terms of their global (expectation values) and local properties which are expressed as functions of coordinates. The Rayleigh-Ritz variation almost uniformly produces the most accurate expectation values. However the point properties show qualitatively different behaviour for different regions of the coordinate space. To define the local quality, a set of criteria is proposed.

Key words: Eigenvalue problem, quality of solution, local properties.

Introduction

There are usually two general approach of obtaining eigenvalues and eigenfunctions of Schrödinger equations for the bound states of small systems. Either the equations are solved numerically or some trial functions are assumed and their parameters are optimized. According to the problem in hand and the type of the properties to be studied one or the other approach can be selected. In this study we would like to focus on the choise of trial functions as linear combinations of basis functions and discuss several techniques of obtaining unknown linear coefficients.

The computational techniques can be compared either by their numerical aspects, that is, the ease of calculations, required hardware and the computer time and/or by the quality of the wavefunctions produced. The tremendous developments in the computers seem to be eliminating most of the technological difficulties and very accurate wavefunctions are now being obtained. Still the definition of the quality is not clearly established.

The most common measure of the wavefunction is the expectation value of the Hamiltonian. The Rayleigh-Ritz variational principle states that for the ground state

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geqq E_0 \qquad (1)$$

and the interleaving theorem of Hylleraas-Undheim-MacDonald [1, 2] provides similar upper bounds to the higher eigenvalues. Then by virtue of these theorems one can argue that the lower the eigenvalue(s) the better the quality of solutions. However this widely accepted criterion alone is not sufficient. The upper and lower bounds to the other expectation values should be computed and their convergence behaviour should be studied. This is not always possible as the lower bound formulas may not be trivial to define and compute for every operator. They also tend to give a meaningful analysis only when highly accurate wavefunctions are used. A detailed study of different definitions of upper and lower bounds is given by Weinhold [3]. A simpler general bound can be obtained from Eckart's inequality [4].

$$\langle \psi | \psi_{\mathrm{exa}} \rangle^2 \geqq \frac{E_1 - \langle \psi | H | \psi \rangle}{E_1 - E_0}. \qquad (2)$$

ψ and ψ_{exa} correspond to the approximate and the exact eigenfunctions for the ground state, and E_1, E_0 are the exact energies of the two lowest states of the same symmetry. The right hand side of (2) can be assumed as a global measure of the approximate function because it is a lower bound to the overlap with the exact solution. Still this overlap cannot be an

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absolute measure since the contributions from different regions of the coordinate space would be greatly different. That is to say that (2) would underestimate the errors where the absolute value of the wavefunction is small. To overcome this arbitrariness in the selection of measures one can combine a number of different properties [5], or simply one compares the computed expectation values with the observed quantities, however the latter method is a rather subjective one as normally the true values are not known. Then one has to use chemical/physical experience and intuition to decide on how accurate answers are to be expected.

All the methods of solution of eigenvalue equations are based on some requirements that wavefunctions are supposed to fulfil. Even though these requirements may involve expectation values which are global properties, they still emphasize certain regions of the coordinate space. For example the Rayleigh-Ritz method would optimize the wavefunction most effectively around the maxima of the functional $\psi H \psi$. Then any physical observable obtained from such computations would have a larger error if different regions play an important role for that observable. One example for this is the cusp condition [6, 7] which should be satisfied by the electronic wavefunctions. The variationally minimized solutions do not necessarily give the correct cusp which is a point property at the origin. In fact only by the proper choice of the basis functions this requirement can be met [8] even though good approximations to the energy are usually obtained by any basis set.

In this study we would like to show that different methods for the Schrödinger equation produce different quality wavefunctions. The quality criteria based on the expectation values do not necessarily guarantee better wavefunctions over all coordinate space. Therefore two new point-criteria for the wavefunctions are defined, and the differences between these methods are analyzed.

Methods of Computation

We choose the Kratzer-Fues potential [9, 10] for the test problem. The Schrödinger equation in one-dimension is defined by

$$\left[-\frac{1}{2} \frac{d^2}{dx^2} + V_0 \left(\frac{a_0^2}{x^2} - 2 \frac{a_0}{x} \right) \right] \psi(x) = E \psi(x) \qquad (3)$$

with parameters $V_0 = 25.0$ au and $a_0 = 1.0$ au. This potential has analytical solutions [11] in terms of associated Laguerre polynomials, so the exact bounds can be computed for comparison. The Kratzer-Fues potential is generally used to describe vibrational potentials of diatomic molecules and is a specific case of a general class of functions which are used for the atom-surface interactions [12]. The trial wavefunction is expanded as a linear combination of the basis functions of the form

$$\psi(x) = \sum_{p=0}^{n-1} C_p \phi_p; \quad \phi_p = x^{p+s} e^{-\alpha x}. \qquad (4)$$

By setting $s = 1/2(1 + (1 + 8 V_0 a_0^2)^{1/2})$ and $\alpha = 2 V_0 a_0/s$ we observe that ϕ_0 corresponds to the exact ground state function with eigenvalue $E_0 = -\alpha^2/2$. Then the higher eigenfunctions can used for comparison.

The first method chosen is the standard Rayleigh-Ritz variation in which the linear coefficients are varied until the minimum in the expectation value of the Hamiltonian is reached. The basis chosen is not orthonormal so it is transformed by the Gram-Schmidt procedure to an orthonormal basis, and the standard techniques are used to solve $HC = EC$. For the second method we use the name "fluctuation", and it is also known as the least squares method [13, 14]. For the exact solutions

$$\langle \sigma^2 \rangle = \langle H^2 \rangle - \langle H \rangle^2 = 0. \qquad (5)$$

Hence the approximate wavefunction can be optimized by minimizing the quantity $\langle \sigma^2 \rangle$. This procedure has the advantage that it is valid also for the resonance states [15, 16], however more difficult integrations than within the variational techniques have to be performed. The resulting equations to be solved are written in Gram-Schmidt orthonormalized basis as

$$(H^2 - 2 \langle H \rangle H) C = EC. \qquad (6)$$

The third method is based on a different philosophy [17, 18]. For the exact solution the eigenvalue is a constant, hence

$$\left[\frac{d^k E}{dq^k} \right] = 0 \quad \text{for} \quad k = 1, 2, \dots, \infty, \qquad (7)$$

where q is the general coordinate. However for the trial function, the Schrödinger equation in one dimension is written as

$$H \psi(x) = \mu \psi(x), \qquad (8)$$

and μ must be a function of only the coordinate as $\psi(x)$ is defined in coordinate space. Then the condition (7) do not apply. Still it is possible to obtain functions which satisfy the condition (7) for a finite number of derivatives at a given point X_0 by differentiating (8) k times

$$\left| \frac{d^k}{dx^k} \cdot \sum_{p=1}^{n} C_p H \phi_p \right|_{x=x_0}$$

$$= \sum_{p=1}^{k} C_p \sum_{l=0}^{k} \binom{k}{l} \left| \frac{d^l \mu}{dx^l} \right|_{x=x_0} \left| \frac{d^{k-1} \phi_p}{dx^{k-1}} \right|_{x=x_0} ; \quad (9)$$

then by setting all the derivatives of $\mu(x)$ equal to zero we obtain

$$\sum_{p=1}^{n} C_p \left| \frac{d^k(H \phi_p)}{dx^k} \right|_{x=x_0} = \sum_{p=1}^{n} C_p \mu \left| \frac{d^k \phi_p}{dx^k} \right|_{x=x_0} . \quad (10)$$

Equation (10) is a general eigenvalue problem $AC = \mu BC$, where A and B are unsymmetric Wronskian matrices of $(H\phi_p)$ and ϕ_p at $x = x_0$. This method is called Wronskian and has the advantage that it does not require any integration. Therefore any complicated functional form can be chosen for the basis functions. But the resulting eigenvalues do not have theoretical bounds, and they can be studied only by their convergence behaviour. They also tend to optimize the functions in a given region rather than around x_0.

Criteria for the Wavefunction

Since the exact solutions are available for the Kratzer-Fues problem, the expectation values for several operators can be used for comparison as well as the eigenvalues themselves. The operators x, x^2, $1/x$ and $1/x^2$ are chosen for comparison in addition to the previously defined quantity $\langle \sigma^2 \rangle$, which is also a measure of the wavefunction [19], and the overlap with the exact eigenfunction. This list of global measurements can be extended to include more operators.

For the pointwise properties one could study the difference between the exact and approximate functions. This is unfortunately only possible in a very limited number of cases. Here we propose two different criteria, which are easily applicable whether or not the exact solutions are known. The first one is the fluctuations of the wavefunction, which is defined in the one-dimensional case as

$$\sigma^n = \left[\frac{H^n \psi(x)}{\psi(x)} \right] - \left[\frac{H \psi(x)}{\psi(x)} \right]^n . \quad (11)$$

For simplicity $n = 2$ is used. The other criterion is based on the idea of the Wronskian method and includes the derivatives of the wavefunction with respect to the coordinate,

$$\mu^k(x) = \frac{d^k}{dx^k} \mu(x) . \quad (12)$$

Both of these quantities should be zero for all values of the coordinate x, and deviations from zero can be taken as local measures.

Results and Discussion

Since the basis set includes the exact state already, we start the analysis from the second eigenvalue. In Table 1 the energies of the second eigenvalue from different methods are given. The same basis set is used in all computations, so the lowest energies are obtained from variational calculations as they should be. It is also observed that the semi-variational fluctuation method produces high quality results. This fact has also been observed before, however the difficulties in obtaining matrix elements of H^2 in general have been discouraging for further studies. The next three columns in Table 1 are the results of Wronskian calculations. The first set are the direct solutions μ of the generalized eigenvalue equation $AC = \mu BC$. The eigenvalues can also be computed as expectation values from the Wronskian eigenfunctions. However in the Wronskian method the orthonormality conditions are not implicitly included. Hence the expectation values may be calculated directly from the solutions or from the orthonormalized vectors. Although for the lower eigenvalues no significant changes are

Table 1. Second eigenvalue of the Kratzer-Fues potential from different methods*.

Basis	I	II	III	IV	V
3	0.6761631	0.6759995	0.6766298	0.6752224	0.6304324
4	0.8777403	0.6777287	0.6773840	0.6772938	0.6659274
5	0.6778151	0.6778146	0.6777518	0.6777481	0.6746749
6	0.6778174	0.6778174	0.6778104	0.6778103	0.6770931
7	0.6778175	0.6778175	0.6778169	0.6778169	0.6776682
8	0.6778175	0.6778175	0.6778175	0.6778175	0.6777900

Exact value = 0.6778175

I: Variation; II: Fluctuation; III: Wronskian expectation values; IV: Orthogonalized Wronskian expectation values; V: Results of the generalized eigenvalue equations. * In units of (-25.0) au.
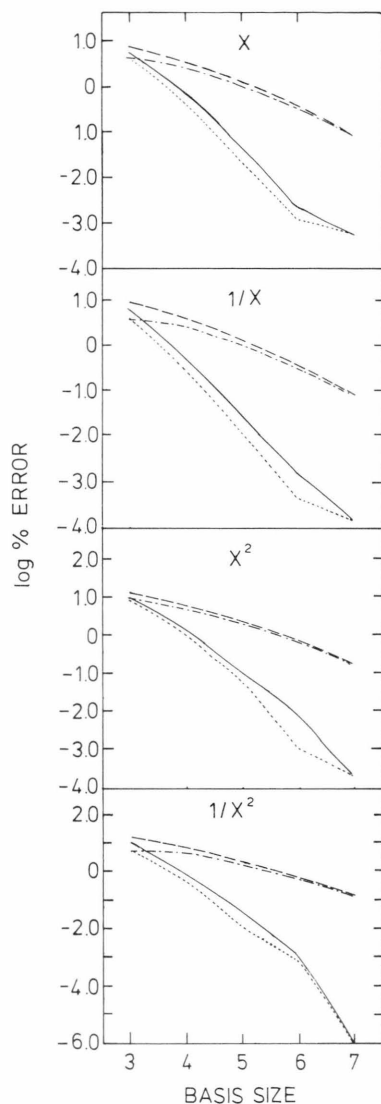
Fig. 1. The logarithmic errors for the expectation values of several operators of the second eigenvalue. ⋯⋯⋯ Variation; ———— fluctuation; –·–·–·– nonorthogonal Wronskian; – – – – orthogonal Wronskian.

Table 2. $\langle \sigma^2 \rangle$ and $\langle \psi | \psi_{exa} \rangle$ for the third eigenfunction for different methods.

Basis	Variation	Fluctuation	Orthonormalized Wronskian
$\langle \sigma^2 \rangle$			
3	0.395 (-1) [a]	0.397 (-1)	0.402 (-1)
4	0.877 (-2)	0.595 (-2)	0.515 (-2)
5	0.216 (-2)	0.122 (-2)	0.171 (-2)
6	0.421 (-3)	0.221 (-3)	0.561 (-3)
7	0.592 (-4)	0.300 (-4)	0.195 (-3)
8	0.618 (-5)	0.305 (-5)	0.625 (-4)
$\langle \psi | \psi_{exa} \rangle$			
3	0.68611	0.68372	0.67965
4	0.91230	0.89948	0.88641
5	0.98428	0.97938	0.94159
6	0.99818	0.99735	0.97586
7	0.99585	0.99977	0.99062
8	0.99999	0.99998	0.99682

[a] The numbers inside parenthesis show the power of 10.

detected, it may be necessary to study the effects of the nonorthogonal orbital set on the computed properties. All three sets of calculations show fairly rapid convergence. In Fig. 1 the logarithmic errors of the expectation values of some operators are shown as functions of the basis size. For the Wronskian approach these matrix elements cannot be directly obtained, as they are global properties. Again normalized and orthonormalized vectors are used to com-

pute these results. For the operators studied, the best results are from variational calculations. Here the best is defined simply as having the lowest error. The results for the fluctuation method are somewhat worse than the variational ones but in general the differences are very small. The Wronskian method gives uniformly poorer results with again slow but smooth convergences being observed. In Table 2 $\langle \sigma^2 \rangle$ and the overlap between the approximate and the exact functions is given. These results are for the third eigenfunction as the differences corresponding to the second eigenfunction are too small to be meaningful. Naturally the lowest $\langle \sigma^2 \rangle$ are in the fluctuation method. It is also clear that this quantity is a more sensitive measure. Even for the cases where reasonable eigenvalues are obtained, $\langle \sigma^2 \rangle$ may be very large, showing that the wavefunction is far from accurate. The study of the overlap does not really bring out any new information. The Eckart condition in a way shows that the largest overlaps would be obtained for those with the lowest energy expectation values.

So far the results follow the known trends. Variational methods focus on the quality of the wavefunction in a global way with the special emphasize on the regions where energy is most important. Since most of the potentials can be written as power series of the coordinate x, the optimization of the energy E almost guarantees optimization of expectation values of operators which are powers of x. However the "quality" of the wavefunction may not be uniform for all regions of the coordinate space. In Fig. 2 several "pointwise
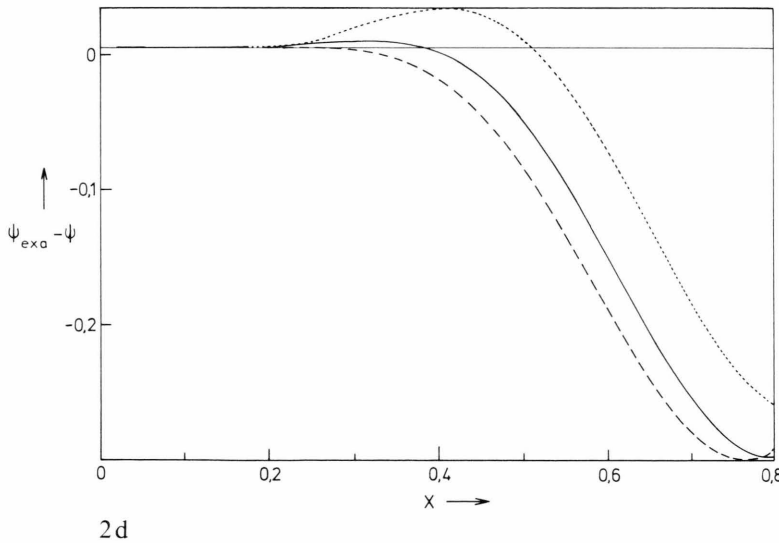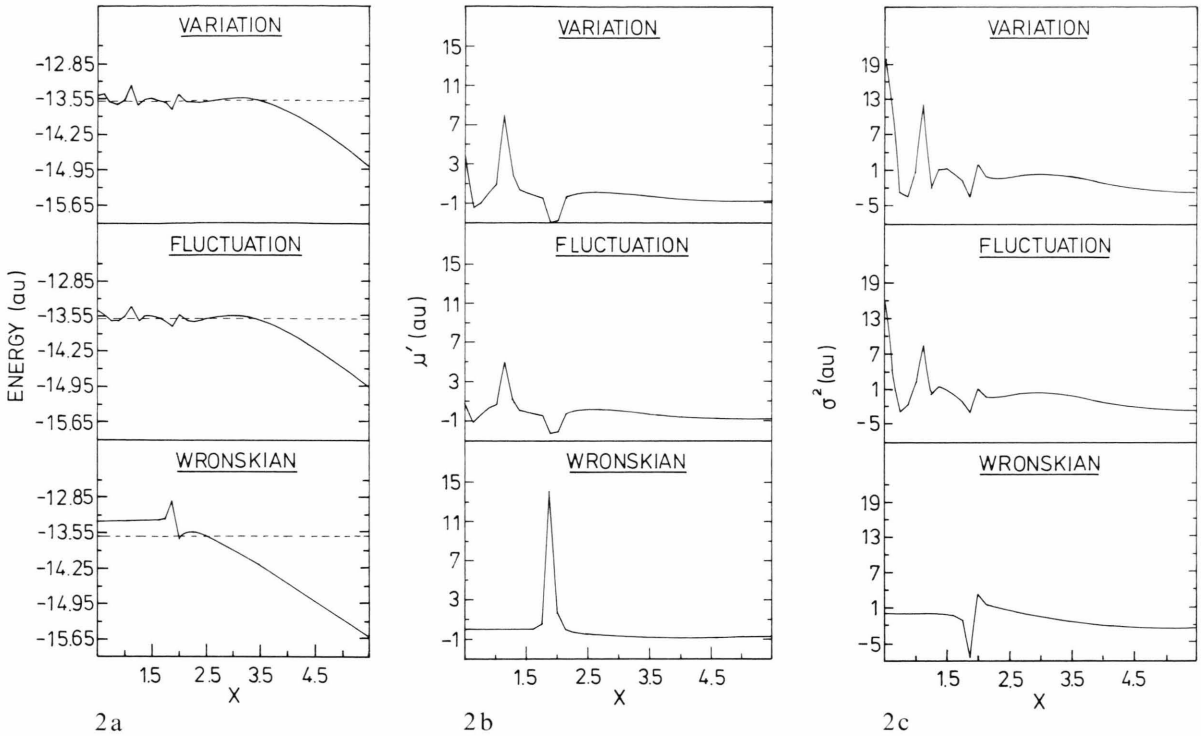
2a

2b

2c

2d

Fig. 2a. The function μ as a function of the coordinate x (au). All the plots are for the third eigenvalue.

Fig. 2b. The first derivative of μ as a function of x (au).

Fig. 2c. The quantity σ^2 as a function of x (au).

Fig. 2d. Difference between the exact and approximate solutions as a function of x (au).
· · · · · Variation,
——— fluctuation,
– – – Wronskian.

quality criteria" are plotted as functions of the coordinate x. These results are for the third eigenvalue and are obtained from matrix equations of equal sizes. Fig. 2a depicts the function $\mu(x)$. For the very accurate solutions, $\mu(x)$ should be a flat function which coincides with the eigenvalue. Then all the derivatives

of $\mu(x)$ should be zero, independent of the position of the eigenvalue and the coordinate. In Fig. 2b the first derivatives with respect to x are plotted for different methods. In Fig. 2c we plot σ^2 again as a function of the coordinate. This quantity should also be zero for bound states. In all three sets of graphs the common

trend is that the variation and fluctuation eigenfunctions satisfy the quality criteria mostly in the region of a potential minimum. The curves for $\mu(x)$ tend to deviate from the actual energy at large distances since the contribution from these regions to the energy is very small. One pronounced difference of the quality of the solutions is detected near the origin. Both the derivative of $\mu(x)$ and σ^2 for the Wronskian approach behave correctly where the variation-like methods have comparatively larger errors. This difference can also be observed by plotting $(\psi_{exa} - \psi)$. Fig. 2d shows that the variational method has larger errors close to the origin but gets "better" in the energetically important regions. One would expect that in any calculation where the wavefunction's behaviour around the origin is important, the Wronskian approach should give more reliable results. We also note a number of sharp peaks which are due to the functional forms of $\mu(x)$ and σ^2. For the basis chosen, they are expressed as

ratios of polynomials, hence for small size calculations they tend to become very large around zeros of the denominator. This effect is subdued upon enlarging the basis size.

In conclusion we would like to point out that the quality of the wavefunction is a rather subjective measure. Most of the efforts in the past have been towards comparing energies where there is a theoretical bound or comparing the results with experimental data, which is statistically very inconsistent. We have presented several new criteria which are based on the point properties of the wavefunction, and they should give an idea about the quality of the results in regions of interest. Of course these guidelines alone are not deterministic and they are thought as an additional measure to the well-established rules.

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