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The Gaussian Potential: Bound States in the Continuum?*

Nimrod Moiseyev and Jacob Katriel

Department of Chemistry, Technion, Israel Institute of Technology, Haifa

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Simple variational solutions to the problem of a single particle in a Gaussian potential well in N dimensions, N being positive and real, are investigated. The system exhibits locally bound states in the continuum, which are demonstrated to be artifacts of the variational procedure. The relevance of the conclusions to recent studies of the possible existence of bound states in the continuum is discussed.

Key words: Bound states – Continuum – Gaussian Potential

1. Introduction

The existence and physical significance of bound as well as quasi-bound (resonance) states in the continuum has long been considered. Hamiltonians having bound states embedded in a continuum in a trivial manner are easily constructed for systems possessing non-interacting degrees of freedom one of which, at least, has a continuous as well as a discrete spectrum. Well known examples are doubly excited configurations of non-interacting electrons, or molecules in a Born-Oppenheimer excited electronic state embedded in the nuclear motion continuum of a lower electronic state. In these two cases the coupling between the different degrees of freedom (interelectronic repulsion in the first instance and nuclear-electronic coupling, breaking the Born-Oppenheimer approximation, in the second) mixes the bound with continuum states. What would be more interesting is the possible existence of Hamiltonians in which all degrees of freedom are coupled, yet possessing bound states degenerate with a continuum but non-interacting with it. Some nontrivial examples in which a bound state moves into the continuum while rigorously remaining a square integrable steady-state solution of the Schroedinger equation, are discussed by Stillinger and Herrick [1]. Some rigorous theorems are available, which exclude the occurrence of bound states embedded in the continuum for certain types of potentials [2].

It would, however, be much more significant to establish the existence of bound states embedded in the continuum for systems which can conceivably be realized

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experimentally. Negative as well as multiply excited atomic and molecular species are probably the most likely candidates to investigate with this aim in mind.

These systems, which include the two electron atoms, are beyond the scope of the presently known rigorous theorems and analytical treatments, and can therefore be studied only by means of approximate methods such as variational computations.

The use of variational methods has long been known to exhibit a large variety of non-physical characteristics which can be traced back to the restrictions imposed on the space in which the variations are carried out [3]. These characteristics are usually associated with the existence of more than one solution to the variational problem. The types of situations hitherto discussed in this connection involve two solutions for both of which some extremum condition is satisfied (a first derivative or a first variation of some energy type quantity vanishes). An additional class of complications can arise if the absolute minimum is obtained on the boundary of the range of the variational parameters involved, rather than satisfy an extremum condition within the range. The simplest example involves some exponential parameter which characterizes the long range fall-off of the variational wavefunction, and which obtains the value zero. This implies a state becoming unbound, but does not preclude the existence of a local minimum of the variational problem which does possess an energy value higher than the one corresponding to the free state. Such a bound state is necessarily embedded in a continuum of free states.

In the present communication a model system which possesses bound variational approximations embedded in the continuum is investigated. This system is separable, but not in the sense leading to trivial degeneracies between bound states and an unrelated continuum. Moreover, the rigorous theorems which exclude the existence of bound states in the continuum in fact apply to this system. The nature of its variational solutions and their detailed behaviour are therefore directly relevant to the understanding of the power and limitations of using the variational method to establish the existence of bound states in the continuum.

The variational solutions of the model system here studied share some characteristics with the two electron atom studied by Stillinger and Stillinger [4] in spite of certain obvious differences.

2. The Gaussian Potential: A Qualitative Analysis

Given the N-dimensional Hamiltonian

$$\mathscr{H} = -\frac{1}{2}\sum_{i=1}^{N}\frac{d^2}{dx_i^2} - 2Z\cdot\exp(-\beta\cdot r^2) \tag{1}$$

where

$$r^2 = \sum_{i=1}^{N} x_i^2,$$

we first consider the variational function $\psi = \exp(-\alpha\cdot r^2)$. The energy is given by $E = n\alpha - 2Z\cdot(2\alpha/(2\alpha+\beta))^n$, where $n = N/2$. In order to obtain a normalizable (bound) wavefunction one has to require $\alpha>0$. Furthermore, at $\alpha=0$ one obtains $E=0$, provided that $n>0$. The variational parameter α is determined by solving the equation

$$\frac{\partial E}{\partial \alpha}=n\left[1-4Z\beta\cdot\frac{(2\alpha)^{n-1}}{(2\alpha+\beta)^{n+1}}\right]=0. \tag{2}$$

The nature of the solution is determined by the sign of

$$\frac{\partial^2 E}{\partial \alpha^2}=8Z\beta n\frac{(2\alpha)^{n-2}}{(2\alpha+\beta)^{n+2}}[4\alpha-\beta\cdot(n-1)]. \tag{3}$$

One should note, however, that Eq.(2) does not necessarily possess a (real) positive solution. Furthermore, a solution of Eq.(2), even if it is a local minimum by the criterion provided by Eq.(3), may actually correspond to an energy value $E>0$. In this case the variational solution is embedded in the continuum of positive energy states.

Inspecting the form of Eq.(3) one easily realizes that for $N<2$, only a minimum can exist for non-negative α, and for $N>2$, both a minimum and a maximum can exist.

The following special cases are particularly simple:

a) $\alpha\gg\beta$:

In this case

$$\frac{\partial E}{\partial \alpha}\simeq n\cdot[1-Z\beta/\alpha^2]=0$$

so that

$$\alpha\simeq\sqrt{\beta Z};\quad E\simeq n\sqrt{\beta Z}-2Z;\quad \lim_{Z\to\infty}\frac{E}{Z}=-2$$

and

$$\frac{\partial^2 E}{\partial \alpha^2}=[4\alpha-\beta(n-1)]\cdot n/(2\beta Z).$$

The initial assumption $\alpha\gg\beta$ is satisfied provided that $Z\gg\beta$. The solution is a minimum if $\alpha=\sqrt{\beta Z}>\beta/4(n-1)$. This is true for any positive α if $N<2$, but for $N>2$ only if $Z>\beta/16(n-1)^2$. However, as here we also require $Z\gg\beta$, the above condition becomes relevant only for $N>10$. For large Z the ground state solution becomes identical to that of a harmonic oscillator with a force constant equal to $k=\partial^2 V/\partial x^2|_{\circ}=4\beta Z$, which is a Gaussian with $\alpha=\frac{1}{2}\sqrt{k}=\sqrt{\beta Z}$, in agreement with the result just established.

b) $\alpha\ll\beta$:

Here

$$E\simeq n\cdot\alpha-2Z\cdot(2\alpha/\beta)^n$$

$$\frac{\partial E}{\partial \alpha}\simeq n\cdot\left[1-4Z\beta\cdot\frac{(2\alpha)^{n-1}}{\beta^{n+1}}\right]=0$$

$$\frac{\partial^2 E}{\partial \alpha^2}\simeq-8Z\beta n(n-1)\cdot\frac{(2\alpha)^{n-2}}{\beta^{n+1}}.$$

Hence, a solution is obtained for $\alpha \simeq \frac{1}{2} \cdot (\beta^n/4Z)^{1/(n-1)}$.

For $N<2$ this low α solution is a minimum, but for $N>2$ it is a maximum. Furthermore,

$$\frac{\partial \alpha}{\partial Z} \simeq [(\beta/Z)^n/4]^{1/(n-1)}/[2 \cdot (1-n)]$$

so that α increases with Z if $N<2$ and decreases with Z if $N>2$.

The low α maximum and the high α minimum merge into one another when the two conditions $\partial E/\partial \alpha = 0$ and $\partial^2 E/\partial \alpha^2 = 0$, (Eqs.(2), (3)) are simultaneously satisfied.

This gives for the values of α and Z at which the merging occurs

$$\alpha_c = \frac{\beta}{4}(n-1) \quad \text{and} \quad Z_c = \frac{\beta}{16} \frac{(n+1)^{n+1}}{(n-1)^{n-1}}.$$

A neighbourhood of considerable interest is that associated with the vanishing of the energy. This occurs when the two conditions $E=0$ and $\partial E/\partial \alpha = 0$ are satisfied. From these two equations one obtains

$$\alpha_0 = \frac{\beta}{2} \cdot (n-1) \quad \text{and} \quad Z_0 = \frac{\beta}{4} \cdot \frac{n^{n+1}}{(n-1)^{n-1}}.$$

The nature of the intersection of the energy curve with the $E=0$ axis can be studied by evaluating

$$\left. \frac{\partial (E/Z)}{\partial Z} \right|_{Z_0} = -\frac{8}{\beta} \cdot \frac{(n-1)^{N-1}}{n^{N+1}}.$$

This quantity vanishes for $N=2$, in which case the bound energy merges into the bottom of the continuum in a tangential manner, thus exhibiting a second order discontinuity. However, for $N>2$ the bound state energy penetrates into the continuum as Z is lowered below Z_0. This is also reflected by the behaviour of α_0, which vanishes for $N=2$, but obtains a positive value for any higher dimensionality.

3. Computed Results

The results presented in Figs. 1 and 2 are in complete agreement with the above discussion. They exhibit the penetration into the continuum of the quasi-bound ground state on decreasing the depth of the Gaussian potential well, for a dimensionality greater than two. They also exhibit the merging of the local minimum with the maximum which separates it from the zero energy absolute minimum at $\alpha = 0$.

In order to further investigate the problem the two-Gaussian variational wavefunction was studied in detail. The results, shown in Figs. 3 and 4, indicate an (expected) improvement over the one-Gaussian results as far as the energy is concerned. The most significant feature of these results is, however, the fact that the behaviour is still very similar to that of the single Gaussian wavefunction: Penetration of the bound state into the continuum is still observed. Moreover, the

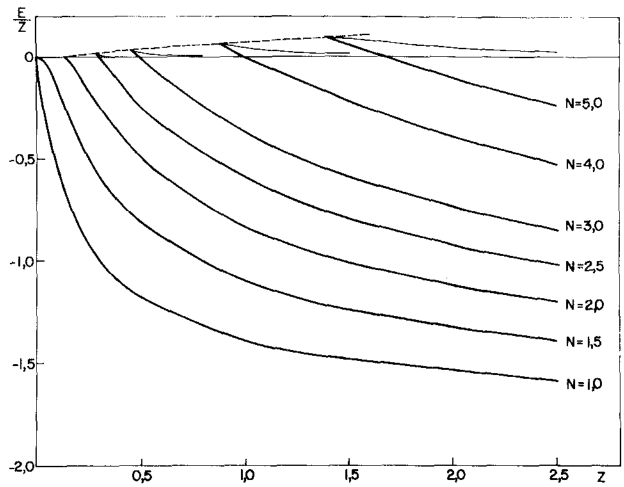

Fig. 1. Energy *vs.* well depth for the one Gaussian wavefunction

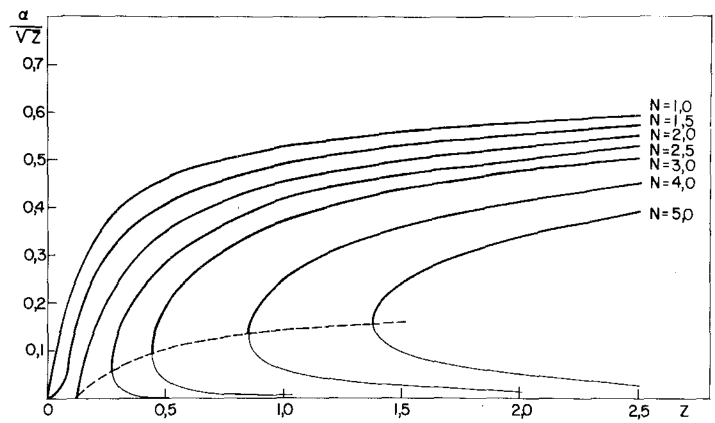

Fig. 2. The variational parameter for the one Gaussian wavefunction

existence of the bound state in the continuum is again terminated by merging with a maximum which, in parameter space, lies between the local minimum corresponding to the bound state discussed and the zero energy absolute minimum corresponding to an unbound particle. Further computations with basis sets of 3, 4 and 5 Gaussians have confirmed the main conclusions presented. The range of existence of the positive energy bound solution, $Z_0 - Z_c$, where Z_0 is the value of Z for which $E = 0$ and Z_c the value for which the minimum and maximum merge, is plotted vs. the basis set size, for different dimensionalities, in Fig. 5. The curves indicate that for a sufficiently large basis set the penetration into the continuum disappears altogether, as one expects.

The Gaussian wavefunction does not have the correct exponential asymptotic decay. One might expect that this deficiency would be particularly severe for

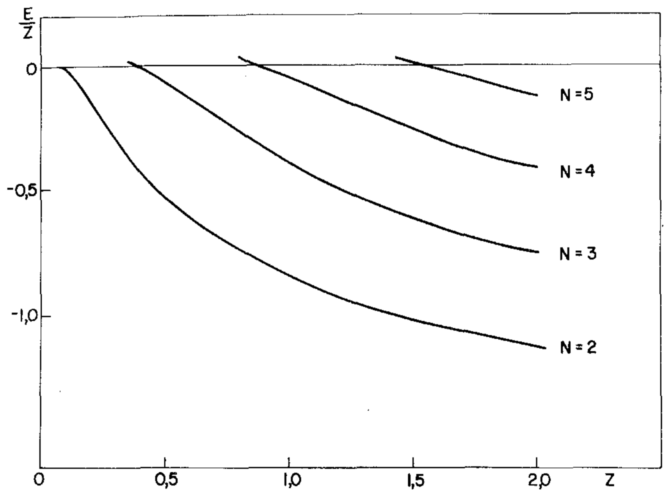

Fig. 3. Energy *vs.* well depth for the two Gaussian wavefunction

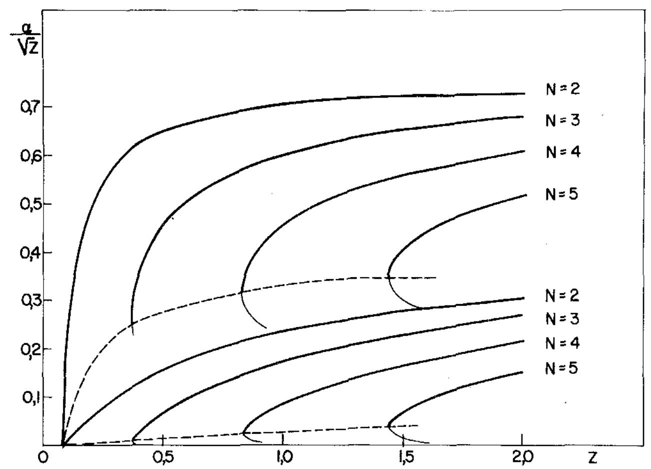

Fig. 4. The variational parameters for the two Gaussian wavefunction

states with energy very near the continuum threshold, as the energetic distance from this threshold determines the rate of exponential decrease of the exact wavefunction. In order to check the possible connection between this deficiency of the variational wavefunction used and the penetration into the continuum, a series of variational computations with an exponential (Slater) wavefunction, $\psi = e^{-\alpha r}$, was carried out for the three dimensional case.

The energy expression is

$$E = \beta \cdot \mu^2/2 - 2Z \cdot \mu^3 \cdot [\sqrt{\pi} \exp(\mu^2) \cdot \operatorname{erfc}(\mu) \cdot (1 + 2\mu^2) - 2\mu]$$

where

$$\mu = \alpha/\sqrt{\beta}.$$

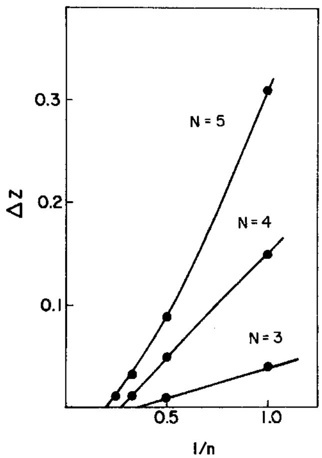

Fig. 5. Extrapolation of the penetration range to large basis sets

The results obtained are qualitatively identical with those obtained for the Gaussian variational wavefunction, indicating that ascertaining the correct asymptotic behaviour is not sufficient to eliminate the penetration into the continuum.

4. Discussion

The existence of bound states in the continuum of the two electron atom has been argued by Stillinger and co-workers on the basis of $1/Z$ perturbation theory [5] and variational computations [4, 6].

The presently reported results cannot, of course, claim to characterize and exhaust all the possible situations which can give rise to bound states in the continuum. They do, however, point out the possible existence of variational solutions exhibiting bound states in the continuum which are, manifestly, artifacts of the restricted space within which the variation is carried out. Although these results cannot and are not intended to rule out the possible existence of real bound states in the continuum of the two electron atom, they indicate that variational computations within a restricted space cannot provide an unequivocal foundation for the existence of such states. The case for (or against) stable bound atomic states in the continuum is still not settled.

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References

1. Stillinger,F.H., Herrick,D.R.: Phys. Rev. A **11**, 446 (1975)
2. Simon,B.: Comm. Pure Appl. Math. **22**, 531 (1967)
3. Paldus,J., Čižek,J.: Phys. Rev. A **2**, 2268 (1970), and references therein

4. Stillinger,F.H., Stillinger,D.K.: Phys. Rev. A **10**, 1109 (1974)
5. Stillinger,F.H.: J. Chem. Phys. **45**, 3623 (1966)
6. Stillinger,F.H., Weber,T.A.: Phys. Rev. A **10**, 1122 (1974)

Dr. J. Katriel
Technion, Israel Institute of Technology,
Department of Chemistry,
Haifa, Israel