RAL 84-104
c2
REPLACEMENT

Science and Engineering Research Council

Rutherford Appleton Laboratory

CHILTON, DIDCOT, OXON, OX11 0QX

RAL-84-104

RAL-84-104
BIBLIOTHEQUE
CERN

29 MARS 1985

Quantum Bound States where the Classical Motion is Unbounded

J M F Gunn

CERN LIBRARIES, GENEVA

CM-P00066725

December 1984

© Science and Engineering
Research Council 1984

The Science and Engineering Research Council does not
accept any responsibility for loss or damage arising from
the use of information contained in any of its reports or
in any communication about its tests or investigations.

QUANTUM BOUND STATES WHERE THE
CLASSICAL MOTION IS UNBOUNDED

J M F GUNN

Rutherford Appleton Laboratory
Chilton
Didcot
Oxon
OX11 0QX

Abstract

An example of bound quantum states occurring where the classical motion is unbounded is given. It consists of a void in an otherwise perfect array of hard sphere scattering centres. The Hamiltonian consists only of kinetic energy and an interpretation is that the particle is bound in order to lower its kinetic energy is given, contrary to usual intuition. The calculation is also an unusual solid state physics problem. The physical situations where this may be relevant are mentioned.

1. Introduction

There are two situations in which "bound" or localised states are normally expected in quantum mechanics: potential wells (which might include man-made solids where the effective mass of electrons is position dependent); more subtly due to interference as in the example of Von Neumann and Wigner (1929) (see also Stillinger and Herrick (1975)) where a decaying oscillatory, potential of wave vector k gives rise to a bound state at a positive energy which corresponds to the kinetic energy $\hbar^2 k^2 / 2m$. The latter interference type of localisation probably also occurs in Anderson Localisation. A third possibility arose recently in a paper by Simon (1983): the particle is trapped by its own zero point energy. In Simon's example, which is two dimensional, this is due to each having as equipotentials the four branches of a hyperbola which squash together in pairs as x or y approaches infinity; the particles transverse motion (with respect to the asymptotes) gets more and more constricted and so its zero point energy, associated with the localisation in the transverse direction, gets larger. It is this transverse zero point energy which makes it prohibitive for the wave functions to have a finite amplitude at spatial infinity. Simon in fact proved the interesting result that there is nothing but a discrete spectrum.

The idea of zero point localisation has also recently arisen in the interpretation of experiments on excitons in semiconductor heterostructures (Voos and Bastard, 1984). Here an exciton is trapped in a layer of a semiconductor sandwich; however the layer in reality fluctuates in thickness, this leading to localised states where the layer is thicker than average, as its wave function has to curve less in such regions. I also believe that analogous evanescent states must have been considered in wave guides, but have not been able to find an explicit reference, however this case is a little different due to the boundary conditions being more complicated than in ordinary quantum mechanics.

In this paper we will give another example, where the kinetic energy of the particle plays a crucial role, however without its motion being indefinitely constricted as in Simon's example. Almost all the classical motion is unbounded (except for a set of "measure zero") but we find bound states.

The problem is that of a void (which will be assumed to be spherical) in an otherwise perfect array of hard core scattering centres. Thus the Hamiltonian is just the kinetic energy operator, so there is no potential to trap the particle. There is no stochastic element in the problem to yield interference effects. Admittedly there could be interference due to coherent scattering from the hard spheres - in fact this leads to the band structure of a perfect array - but we will argue that the bound states are not due to this.

Physically the reason for the appearance of bound states is that if the wave function has a finite amplitude outside the void, it must have nodes on the surfaces of the hard cores. This enforces some curvature in the wave function, which increases its kinetic energy. However in the void itself the wave function is only forced to curve by the hard cores on its boundary. It is clear for a sufficiently large void, the particle's ground state will in fact be localised in the void. Thus the seemingly paradoxical situation of a particle localising to lower its kinetic energy occurs.

The rest of the paper is devoted to working out this example in a more quantitative way. We need to calculate the low energy band structure of the perfect array of hard core centres, to determine the wave functions and energies outside the void to match to that inside. The calculation of $E(k)$ for small k (with respect to the reciprocal lattice vectors) is performed using the Wigner-Seitz approximation. This calculation is of interest in its own right - as a hard core lattice is the simplest solid one can think of - and the problem is of a novel effective mass impurity. In the last section the wave functions inside and outside the void are matched and conditions for a bound state to exist and, its binding energies are derived. The physical motivation for the problem is briefly considered at the end.

2. Calculation of Low Energy $E(k)$ for a Regular Array of Hard Spheres

In this section we will calculate the approximate form of the lowest band in a regular array of hard spheres. We will only calculate the energy of the band minimum and the coefficient of k^2 in the expansion of $E(k)$ about $k = 0$, to get the effective mass. If we are only dealing with weakly bound states, this information should be sufficient, as the envelope of

the bound state wave function will vary slowly on the scale of a lattice parameter, in which case its behaviour should be determined by $E(k)$ near $k = 0$.

Of course it is not possible to calculate the bandstructure exactly in an analytic fashion, even for this simplest of solids, but for $(a/r_s) \ll 1$, where a is the hard sphere radius and r_s the radius of the Wigner-Seitz sphere of the same volume as the unit cell, some progress can be made. We will use the Wigner-Seitz cellular method, approximating the real Wigner-Seitz unit cell by a sphere. This approximation should be a good one for highly coordinated lattices, as then the number of faces of the Wigner-Seitz cell is large and hence the difference between the minimum and maximum distances of the surface of the cell from the centre is small. More formally, if the Wigner-Seitz cell surface is expressed as $r = r(\theta, \phi)$ where θ, ϕ are polar angles and expanded in terms of spherical harmonics, then neglecting all but the first term leads to the spherical approximation, the magnitude of the remaining coefficients being of the order of the difference of maximum and minimum distances, or in general smaller. A review article on the cellular method (although not discussing the last point) is Altmann (1974).

The energy of the bottom of the band is easy to find, assuming that it is at $k = 0$. There are two ingredients: that the particle is always in free space so the wave function is $j_0(kr) + \alpha_0 y_0(kr)$ where $j_0(z)$ and $y_0(z)$ are spherical Bessel functions which are regular and irregular at the origin (terminology as in Abramowitz and Stegun (1965)); the boundary conditions that the wave function must vanish on the boundary of the hard sphere, at the centre of the Wigner-Seitz sphere (which determines α_0 , say) and the boundary condition on the edge of the Wigner-Seitz sphere, (which determines k) which will be discussed later.

At this point we should notice that it is not an assumption (within the Wigner-Seitz approximation) that the ground state has $\ell = 0$. For a central potential it can be proved that one of the ground states must be s-like (Downs 1963), and in our case, it is clear that the ground state is non-degenerate, as higher ℓ -values push the maximum in the cellular wave function farther out, meaning that it must curve more to obey the boundary conditions, and so pay a price in terms of kinetic energy.

We shall now discuss the boundary conditions. The one on the boundary of the hard core, at $r = a$, namely:

$$\psi(r = a) = 0 \quad (2.1)$$

is obvious, and immediately leads to the coefficient α_0 :

$$\alpha_0 = \tan \kappa a \quad (2.2)$$

However the boundary conditions on the Wigner-Seitz sphere require a little more thought (see Ashcroft and Mermin 1976, p210). Since the wave functions obey the Bloch condition, they must be of the form:

$$\underline{\psi}_k(\underline{x}) = e^{i\underline{k}\underline{x}} \underline{U}_k(\underline{x}) \quad (2.3)$$

where $\underline{U}_k(\underline{x})$ is periodic with period equal to the lattice parameter. This periodicity guarantees that the wave functions on neighbouring cells having matching amplitudes. Across a given Wigner-Seitz sphere it implies (for $\underline{r}$ on the boundary):

$$\underline{U}_k(\underline{r}) = \underline{U}_k(-\underline{r}) \quad (2.4)$$

This is automatically obeyed for the even part of the function $\underline{U}_k(\underline{r})$, but implies that $\underline{U}_k(\underline{r}) = 0$ for the odd part, on the boundary. The second boundary condition is that the derivatives of the wave functions in neighbouring cells match on the boundary. The only part of the derivative matching not implied by (2.4) is that of the normal derivative (Ashcroft and Mermin 1976, p210). Thus ($\hat{n}(\underline{r})$ is the normal to the Wigner-Seitz sphere at $\underline{r}$, $\underline{R}$ is the lattice parameter):

$$\hat{n}(\underline{r}) \cdot \nabla \underline{\psi}_k(\underline{r}) = -\hat{n}(\underline{r}-\underline{R}) \cdot \nabla (e^{-i\underline{k} \cdot \underline{R}} \underline{\psi}_k(\underline{r})) \quad (2.5)$$

The minus sign on the right comes from the antiparallelism of normals on opposite sides of the sphere. This condition is automatically obeyed for odd component of a state, but for even part implies that

$$\hat{n}(\underline{r}) \cdot \nabla \underline{U}_k(\underline{r}) = 0 \quad (2.6)$$

For $\underline{k} = 0$ (the bottom of the band) $\underline{\psi}_k = \underline{U}_k$ and the boundary condition implies ((2.4) is irrelevant as the lowest state is even):

$$\kappa \approx \frac{1}{r_s} \left(\frac{3a}{r_s} \right)^{\frac{1}{2}} \quad (2.7)$$

where $(a/r_s) \ll 1$. The reason why κ tends to zero as a , the hard core radius, tends to zero is that the maximum in ψ which occurs at the boundary (to give $\partial\psi/\partial n = 0$) is associated with the maximum of $j_0(z) = 0$, which has been pushed out to finite z , by the addition of a little $y_0(z)$ (which is negative) to obey $\psi(r = a) = 0$. As a tends to zero a smaller and smaller amount of $y_0(z)$ is required, as y_0 is singular at $z = 0$.

Thus, at fixed radius, the effect of the admixture of y_0 vanishes as a tends to zero, thus letting the maximum of ψ move back towards $z = 0$ and hence require κ to tend to zero to keep it at finite r , r_s to be precise.

Given κ , by (2.7), the energy of the $k = 0$ state can immediately be written down:

$$E(k = 0) \approx \frac{\hbar^2}{2mr_s^2} \left(\frac{3a}{r_s} \right) \quad (2.8)$$

This expression is interesting, particularly in the context of what happens in lower dimensions. Note that the energy tends to zero as $a \rightarrow 0$, thus approaching its free space value. The curious point is that the wave functions still have enforced nodes at each lattice site, albeit only at a point, as the volume of the hard spheres tends to zero. Thus the wave functions are affected, although the energy is not. In the analogous situation in one dimension a periodic enforced node in a wave function certainly affects its energy, even when $a = 0$, namely:

$$E(k = 0) = \frac{\hbar^2}{2m} \left(\frac{\pi}{2r_s} \right)^2 \quad (2.9)$$

where only point "hard lines" have been considered (i.e. $a = 0$). In two dimensions the energy does go to zero as a tends to zero, as in three dimensions, but in a more abrupt way:

$$E(k = 0) \approx \frac{\hbar^2}{2mr_s^2} \frac{1}{|\ln(r_s a)|^2} \quad (2.10)$$

The other piece of information that we need is the effective mass (or curvature of the band. For finite $\underline{k}$, the Schrodinger equation for $U_{\underline{k}}(\underline{r})$ is (substituting the Bloch form (2.7) into the equation):

$$\left(-\frac{\hbar^2}{2m} (\nabla^2 + 2i\underline{k} \cdot \nabla - k^2) - E\right) U_{\underline{k}}(\underline{r}) = 0 \quad (2.11)$$

This is a simple equation except for the second term on the left hand side. It can be treated perturbatively, a second order calculation being sufficient for the correction to $E(k) = \hbar^2 k^2 / 2m$:

$$E(k) = E_0 + k^2 E_2 \quad (2.12)$$

and the wave function is:

$$\psi_n(\underline{r}) = e^{i\underline{k} \cdot \underline{r}} (U_{k=0}(\underline{r}) + k U_1(\underline{r})) \quad (2.13)$$

The result of the second order calculation for the energy is (to lowest order in (a/r_s)):

$$k^2 E_2 = \frac{\hbar^2 k^2}{2m} \left[1 - \left(\frac{a}{r_s}\right)^2 C \right] \quad (2.14)$$

where:

$$C = \sum_{n=1}^{\infty} [N_{n,1} \int_0^1 2r^2 dr (r - 1/r^2) U_{n,1}(r)]^2 / \epsilon_{n,1} \quad (2.15)$$

where $U_{n,1}(r)$ is the radial part of the n th p -wave, $k=0$, solution to the Schrodinger equation, with no hard core, obeying Wigner-Seitz boundary conditions, $\epsilon_{n,1}$ is the energy and $N_{n,1}$ its radial normalisation. Only p -wave states occur in the sum, due to the scalar product form of the perturbation. We should note that C is a pure number.

It should be noted that (2.14) can be written in a physically more illuminating way; by defining an effective mass m^* :

$$k^2 E_2 = \frac{\hbar^2 k^2}{2m^*} \quad ; \quad m^* = m \left(1 + \left(\frac{a}{r_s}\right)^2 C \right) \quad (2.16)$$

Finally for reference in the next section the first order correction to the wave function is:

$$kU_1(\underline{r}) = (ika) \tilde{U}_1(\underline{r})$$

$$\tilde{U}_1(\underline{r}) = 2 \sum_{n=1}^{\infty} [N_{n,1} \int_0^1 2r^2 (r - 1/r^2) U_{n,1}(r) dr / \epsilon_{n,1}] U_{n,1}(\underline{r}) \quad (2.17)$$

where the symbols have the same meanings as in (2.15). Note that the correction to $U_{k=0}$, U_1 , vanishes as a tends to zero.

3. Construction of Bound States and Discussion

To find bound states we need to match the wave functions inside and outside the void. If we were dealing with a standard potential well problem this would present no difficulty. However in the case to be discussed here the states outside the void are Bloch functions (or rather their analytic continuations to imaginary $\underline{k}$) and how to match the states at the boundary is not obvious. We will argue that in fact the procedure is the same as usual.

Firstly a few reminders about the normal case. In three dimensions a factor of $1/r$ can be factorised from the radial wave function ($\psi = \chi/r$). Then for $\ell = 0$, the radial Schrodinger equation for a square well of radius r_v is:

$$\left(\frac{-\hbar^2}{2m} \frac{d^2}{dr^2} - V\theta(r_v - r) - E \right) \chi = 0 \quad (3.1)$$

where $\theta(x)$ is the step function. In both $r > r_v$ and $r < r_v$ the equation is that of a classical harmonic oscillator. For $r < r_v$, only $\sin \kappa r$ is acceptable as a solution, as $\cos \kappa r$ leads to a divergent kinetic energy expectation value (although it would still be normalisable). Now if we want the condition for a bound state "just" to exist, i.e. the energy is zero, then the wave function for $r > r_v$ is a constant (zero kinetic energy) and this must match onto a portion of $\sin \kappa r$, for some κ . It is clear that the smallest κ is such that $\kappa r_v = \pi/2$, that is there is a quarter wavelength in the well. Then $\sin \kappa r$ is flat at the boundary, matching the flat wave function outside. (Higher bound states "about to be bound" correspond to $\kappa r_v = \pi/2 + n\pi$).

The critical point in the above discussion is that the wave function is flat at the boundary of the well when binding is about to occur. We will argue that this feature has an analogue in the void case.

Consider $E = 0$ "bound state" for the void. The wave function on the outside is the $\underline{k} = 0$ Bloch state. The gradient of this wave function vanishes on the boundary of each unit cell, in particular on the boundaries of those unit cells adjoining the void. Thus this will match onto the quarter wavelength of the wave function inside the void (which is just $\sin \kappa r / \kappa r$ as the void is free space), at it has zero gradient on the boundary of the void. Thus the condition to bind a state in the case of the void is the same as in a normal square well, in the sense that a quarter wavelength is fitted in the void, although $E(k = 0)$ replaces the well depth.

Thus the condition for a bound state in the void is:

$$\kappa r_v = \pi/2 \quad (3.2)$$

where r_v is the void radius. This yields a condition on the ratio (a/r_s) via:

$$\frac{\hbar^2 k^2}{2m} = E(\kappa = 0) \quad (3.3)$$

which is just that energy inside the void (left hand side) equals energy outside the void (right hand side). It determines the critical value that r_v must exceed to yield a bound state:

$$r_v > \frac{\pi}{2} r_s \left(\frac{r_s}{3a} \right)^{\frac{1}{2}} \quad (3.4)$$

Thus as a tends to zero, the required void size tends to infinity, by analogy with a shallow potential well needing to be large spatially to trap a state.

For a square well, in the limit of small binding energy, we can derive an expression (by approximately solving the equations matching amplitudes and derivatives across its boundary) linking the size, r_v , and depth, V , of a square well and the binding energy of its ground state, E_b :

$$E_b \approx -\frac{1}{4} \frac{2mr_v^2}{\hbar^2} \left(V - \frac{\hbar^2}{2m} \left(\frac{\pi}{2r_v} \right)^2 \right)^2 \quad (3.5)$$

In the case of the void, there is the complication - compared to the square well - that the wave function outside the void is a product of two parts: an envelope, $\exp(-\lambda r)$, where $\lambda = \{(2m^*/\hbar^2)(E(k=0) - E_B)\}^{\frac{1}{2}}$, and $U_\lambda(\underline{r})$; these being the continuation, to imaginary k , of the two parts of $\psi_k(\underline{r})$. Thus when matching derivatives at the boundary of the void, there will be two contributions from the wave function outside the void. We expect the contribution due to differentiating $U_\lambda(\underline{r})$ to be small, as it will come from the term which is first order in λ , and so in (a/r_s) . We find:

$$E_b \approx -\frac{1}{4} \frac{2m r_v^2}{\hbar^2} \left(\frac{\hbar^2}{2mr_s^2} \left(\frac{3a}{r_s} \right) - \frac{\hbar^2}{2m} \left(\frac{\pi}{2r_v} \right)^2 \right)^2 \left(1 - \left(\frac{a}{r_s} \right) \tilde{U}'_1(r_s) / U_{k=0}(r_s) \right) \quad (3.6)$$

where $\tilde{U}'_1(r_s)$ is defined by the derivative of the function in (2.17), and is a dimensionless constant we should note that V , the depth in the normal case is replaced by $E(k=0)$, as expected from (3.3) and more interestingly, m^* replaces m outside the brackets. This is because m^* partly controls the fall-off in the envelope function. The final factor is due to the derivative of U_k entering the matching process, as well as the envelope function.

At this point it is suitable to mention the physical problem which lead to the quantum problem considered in this paper. The problem was of the spectrum of excitations in solid Helium, in particular the bound states of vacancies and interstitials, which are assumed to be mobile at low temperatures, in a coherent manner. Of course the above calculation omits many important aspects of the problem: vacancy motion relaxation of the lattice around the vacancy and interstitial and the softer core of the

potentials. The last point is probably not a serious difficulty. The value of the above calculation is to point out the curious role of kinetic energy in making the energy of the bound state lower. There are other cases where the calculation may have relevance, such as the trapping of positrons or positive muons in voids or vacancies.

To conclude, we have presented an example where the Hamiltonian consists solely of kinetic energy, which would give classical unbound motion, but has bound quantum states. It is not due to an interference effect, but strangely due to the particle's zero point energy being minimised by forming a bound state, in contradiction to normal intuition.

Acknowledgements

The author would like to thank M Warner and R Williams for useful discussions and J Ryan for informing him of the experiments on excitons in heterostructures.

References

Abramowitz M and I A Stegun, 1965, "Handbook of Mathematical Functions", Dover.

Altmann S L, 1974, in "Orbital Theories of Molecules and Solids", ed. N H Marsh, O.U.P.

Ashcroft N W and N D Mermin, 1976, "Solid State Physics", Holt, Rinehart and Winston.

Downs B W, 1963, Am. J. Phys. 31, 277.

Simon B, 1983, Ann. Phys. 146, 209.

Stillinger F H and D R Herrick, 1975, Phys. Rev. A11, 446.

Von Neumann J and E Wigner, 1929, Phys. Z. 30, 465.

Voos J and G Bastard, to be published.