Comparison of the Richardson and BCS models of superconductivity based on calculations of ground state energies

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Abstract

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Superconductivity remains an active area of research because there still is no comprehensive understanding of the phenomenon despite all the possibilities it offers. In this thesis I go through the basics of two models for superconductivity, the BCS model and the Richardson model. The BCS theory is the first and most used successful microscopic theory of superconductivity. Richardson model is a less used model which gives the exact eigenstates of the reduced BCS Hamiltonian. I calculate the ground state energies for both the reduced and the full BCS Hamiltonian for both models. This is done for a general paired state with fixed number of electrons as well. For this state I find that the difference between the full and reduced Hamiltonian energies depends only on the number of electrons, and thus conclude that it does not matter for comparison between such states which Hamiltonian is used. I find that in a system with equally spaced energies and in the free-electron three-dimensional system the ground state energies are very close to each other, with the Richardson model ground state energy being lower. From this I infer that the BCS model is a good description of these systems. The ground state energies of a two-level system however differs considerably, with the Richardson model ground state energy being significantly lower. This is an indication that the BCS model is not suitable for describing this system.

Keywords: Thesis, master's thesis, superconductivity, Richardson model, ground state energy

Tiivistelmä

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Suprajohtavuuden Richardsonin ja BCS mallien vertailu perustilojen laskettujen
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Suprajohtavuus on edelleen aktiivinen tutkimuksen alue, koska sen tarjoamista mah-
dollisuuksista huolimatta sitä ei vielä ymmärretä kokonaisvaltaisesti. Tässä pro gradu
-tutkielmassa käyn läpi perusteet kahdelle suprajohtavuuden mallille, Richardsonin
ja BCS malleille. BCS teoria on ensimmäinen ja käytetyin mikroskooppinen supra-
johtavuuden teoria. Richardsonin malli on harvemmin käytetty malli, josta saadaan
redusoidun BCS Hamiltonin operaattorin tarkat ominaistilat. Lasken molempien
mallien perustilojen energiat sekä redusoidulle että täydelle BCS Hamiltonin operaat-
torille. Sama lasketaan myös yleiselle tarkan määrän vain pariutuneita elektroneja
sisältävälle tilalle. Tälle eri Hamiltonin operaattorien energioiden erotus riippuu
ainoastaan hiukkasmäärästä, ja siten ei ole merkitystä, kumpaa Hamiltonin operaat-
toria sellaisten tilojen energioiden vertailuissa käytetään. Energioiden vertailuista
huomaan, että tasavälisten energiatilojen systeemillä ja kolmiulotteisella vapaiden
elektronien systeemillä Richardsonin ja BCS mallien perustilojen energiat ovat lähellä
toisiaan, Richardsonin mallin antaessa matalamman perustilan energian. Tästä päät-
telen, että BCS malli kuvaa hyvin näitä systeemejä. Kaksitilasysteemillä energioiden
erotus on huomattava, Richardsonin mallin antaessa merkittävästi matalamman pe-
rustilan energian. Tämä on merkki siitä, että BCS malli ei kuvaa tällaista systeemiä
hyvin.

Avainsanat: Opinnäyte, pro gradu -tutkielma, suprajohtavuus, Richardsonin malli,
perustilan energia

Sisältö

1 Introduction

Superconductivity is the phenomenon of disappearance of electrical resistivity in a material below a critical temperature. This occurs in many materials, but still is not an effect seen in everyday life, since the critical temperatures below which different materials become superconducting are usually of the order of a few Kelvin or below. The highest temperature in which superconductivity has been observed so far is 203 K, which is the critical temperature for sulfur hydride at a pressure of approximately 90 GPa[1].

A material which is superconducting above or close to 0°C would no doubt be a major scientific discovery, since it would allow superconducting applications to run in a basic freezer instead of requiring cryostats. The most obvious benefits would be the possibility to decrease losses in electrical devices and possibly transmission lines, thus creating a more energy efficient society. A room temperature superconductor could be used for example to increase battery life of any portable device. Besides these a room temperature superconductor would open up opportunities for bringing into everyday use applications at the moment requiring cryostats. These applications could be versatile and new, because a superconducting state is a state with macroscopic coherence, and as such it exhibits some phenomena with no classical counterparts, such as the Josephson effect[2].

1.1 BCS theory

The first successful microscopic theory of superconductivity is the Bardeen-Cooper-Schrieffer (BCS) theory[3]. It seems to work well for most conventional superconductors, but there are also superconducting compounds which do not behave according to the BCS theory. Nevertheless it is widely used and the best understood theory about superconductivity so far.

The BCS theory assumes that there is an attractive interaction between the electrons in the system. It is worth noting here, that BCS theory can also be applied to systems containing other fermions, but in this study we are only interested in electrons. The BCS theory also assumes that, for the perspective of superconductivity, the relevant interactions of the electrons take place between the time-reversed electron pairs, i.e. electron pairs of the form $(\boldsymbol{k} \uparrow, -\boldsymbol{k} \downarrow)$, where $\boldsymbol{k}$ is the wave vector of the electron and $\uparrow$ and $\downarrow$ are the spins of the electrons. By leaving out all other interactions we get a Hamiltonian usually called the reduced BCS Hamiltonian.

For this Hamiltonian we can find an approximate ground state or other eigenstates by applying a mean-field theory. This approximation should hold at least with weak enough coupling. The mean-field theory results in a model Hamiltonian which does not conserve the particle number. The average number of particles can still be regulated by using a chemical potential, meaning essentially just that all energies are expressed with respect to a Fermi level instead of the vacuum. It is also possible to project the BCS state into a fixed particle-number state.

The order parameter for superconductivity in the BCS theory is the energy gap Δ, sometimes also called the pair potential, and it can be solved self-consistently in the BCS framework. By solving it for different temperatures we can get the critical temperature T_c above which the order parameter vanishes and the material ceases to be superconducting. The critical temperature is usually one of the most important quantities we want to know about a material considering superconductivity.

Because the mean-field approximation is used in the BCS theory it is not expected to work well for small particle number or strong coupling. Because of that we are interested in other models to describe superconductivity. In this thesis I consider the Richardson model as an alternative approach to the BCS model to avoid these restrictions.

1.2   Flat-band superconductors

One group of superconductors that are not always described well by the BCS model are the flat-band superconductors. The name flat-band superconductor refers to the dispersion relation of the system, which is approximately flat on some interval near zero momentum. This can be achieved for example with a dispersion proportional to k^n, where n is a large constant.

What originally made these superconductors interesting is that the BCS model predicts high temperature superconductivity for some flat-band systems[4]. Since then it has been shown that the mean-field approximation used in the BCS model is not valid for some of the flat-band systems, for example the surface states of rhombohedral graphite[5]. However, for some flat-band systems there has also been other evidence pointing towards the possibility of high temperature superconductivity[6][7], so the systems remain an active area of interest.

There are several different approaches that could be taken in order to approach the problem of non-linear fluctuations, i.e. failure of the mean field approximation. One possibility is to add some correction terms to the original theory. There are also a number of different models that usually have a different perspective on the system (for example [8][9]). One of these alternatives is the Richardson model[10], which is studied in this thesis.

In the Richardson model we begin with the reduced BCS Hamiltonian and make an ansatz state parametrized by the pair energies. It can be shown that, if and only

if the parameters satisfy the resulting Richardson equations, the ansatz state is an eigenstate of the reduced BCS Hamiltonian. The Richardson equations are a set of M non-linear algebraic equations, where M is the number of electron pairs in the system. Solving this system of equations is usually done numerically, because in most cases no analytical solutions are known. It is worth noting, however, that the eigenstates of the system could be solved numerically even without the Richardson model, but the Richardson equations are computationally much more efficient to solve than the original eigenvalue problem with eigenvalue solving algorithms.

In this thesis I first go through the basic procedures of the BCS theory and find the BCS ground state using the Bogoliubov transformation, after which I explain the basics of the Richardson model and how to find the Richardson model ground state. I continue to calculate the ground state energies with respect to the full BCS Hamiltonian and the reduced BCS Hamiltonian introduced in section 2. Once comparing numerical calculations of these values in different systems we learn that in some systems the BCS model gives almost the same ground state energies even with a strong coupling and with only few dozens of particles, whereas in other systems the Richardson model gives considerably lower ground state energies with stronger couplings no matter what the system size is. It would be interesting to apply the Richardson model to a flat-band system, because it does not have the same restrictions as the BCS model, and so could describe the flat-band system better.

2 BCS theory

In this section I go through the basics of the BCS theory starting from specifying the interactions and formulating the relevant Hamiltonians to finding the ground state by using the Bogoliubov transformation. The energy of this ground state is calculated in section 4 and then compared with the Richardson model ground state energy in section 5.

The BCS theory assumes that there exists an attractive interaction between the charge carriers, which are throughout this thesis electrons. The origin of such an interaction is not trivial, as the electrons in free space normally have a repulsive Coulombic interaction. Usually the attractive interaction arises from the background lattice of positive ions. In that case we get coupling between phonons and electrons, which can result in an effective attractive interaction between the electrons. Classically this is understood as the moving electron attracting the lattice ions thus resulting in increased positive charge density, which then attracts the other electrons once the first electron has moved away.

2.1 Interaction Hamiltonian

Let us start by defining the system and forming the relevant Hamiltonians. We start with a quite general system with a given set of single particle energies and a given translation invariant two-body interaction potential. Along the way we restrict the potential to be a contact potential and make some other approximations to get the full and reduced BCS Hamiltonians and the model Hamiltonian.

Once we take the attractive interaction as given with the two-body potential function $U(\boldsymbol{r} - \boldsymbol{r}')$ we can then write the interaction part of the Hamiltonian as

$$H_I = \frac{1}{2} \sum_{\sigma\sigma'} \int d\boldsymbol{r} d\boldsymbol{r}' U(\boldsymbol{r} - \boldsymbol{r}') \Psi_\sigma^\dagger(\boldsymbol{r}) \Psi_{\sigma'}^\dagger(\boldsymbol{r}') \Psi_{\sigma'}(\boldsymbol{r}') \Psi_\sigma(\boldsymbol{r}), \tag{1}$$

where the integrals are over the whole space, the sums are over spins up and down and Ψ_σ is the second quantized field operator for the electrons. Now we can transform this into the momentum space.

The field operator Ψ can be written in terms of the plane waves as

$$\Psi_\sigma(\boldsymbol{r}) = \sum_{\boldsymbol{k}} \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} c_{\boldsymbol{k}\sigma}, \tag{2}$$

where now $c_{k\sigma}$ is the annihilation operator of an electron with wave vector $\boldsymbol{k}$ and spin σ, and V is the volume of the system. By substituting this into the interaction Hamiltonian (1) we get

$$H_I = \frac{1}{2V^2} \sum_{\sigma\sigma'} \sum_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3,\boldsymbol{k}_4} \int d\boldsymbol{r} d\boldsymbol{r}' U(\boldsymbol{r}-\boldsymbol{r}') e^{i((\boldsymbol{k}_4-\boldsymbol{k}_1)\cdot\boldsymbol{r}+(\boldsymbol{k}_3-\boldsymbol{k}_2)\cdot\boldsymbol{r}')} c^\dagger_{\boldsymbol{k}_1\sigma} c^\dagger_{\boldsymbol{k}_2\sigma'} c_{\boldsymbol{k}_3\sigma'} c_{\boldsymbol{k}_4\sigma}. \quad (3)$$

Now the exponential factor can be reformulated as

$$e^{i((\boldsymbol{k}_4-\boldsymbol{k}_1)\cdot\boldsymbol{r}+(\boldsymbol{k}_3-\boldsymbol{k}_2)\cdot\boldsymbol{r}')} = e^{\frac{i}{2}(\boldsymbol{k}_4-\boldsymbol{k}_3+\boldsymbol{k}_2-\boldsymbol{k}_1)\cdot(\boldsymbol{r}-\boldsymbol{r}')} e^{\frac{i}{2}(\boldsymbol{k}_4+\boldsymbol{k}_3-\boldsymbol{k}_2-\boldsymbol{k}_1)\cdot(\boldsymbol{r}+\boldsymbol{r}')}$$

$$= e^{\frac{i}{2}(\boldsymbol{k}_4-\boldsymbol{k}_3+\boldsymbol{k}_2-\boldsymbol{k}_1)\cdot\Delta\boldsymbol{r}} e^{i(\boldsymbol{k}_4+\boldsymbol{k}_3-\boldsymbol{k}_2-\boldsymbol{k}_1)\cdot\boldsymbol{R}}, \quad (4)$$

where on the second line we introduce new variables $\Delta\boldsymbol{r} = \boldsymbol{r}-\boldsymbol{r}'$ and $\boldsymbol{R} = (\boldsymbol{r}+\boldsymbol{r}')/2$. By changing the integration over these new variables, the interaction Hamiltonian (3) becomes

$$H_I = \frac{1}{2V^2} \sum_{\sigma\sigma'} \sum_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3,\boldsymbol{k}_4} \int d(\Delta\boldsymbol{r}) U(\Delta\boldsymbol{r}) e^{\frac{i}{2}(\boldsymbol{k}_4-\boldsymbol{k}_3+\boldsymbol{k}_2-\boldsymbol{k}_1)\cdot\Delta\boldsymbol{r}}$$
$$\times \int d\boldsymbol{R} e^{i(\boldsymbol{k}_4+\boldsymbol{k}_3-\boldsymbol{k}_2-\boldsymbol{k}_1)\cdot\boldsymbol{R}} c^\dagger_{\boldsymbol{k}_1\sigma} c^\dagger_{\boldsymbol{k}_2\sigma'} c_{\boldsymbol{k}_3\sigma'} c_{\boldsymbol{k}_4\sigma}. \quad (5)$$

Here we notice that the second integral yields a delta function

$$\int d\boldsymbol{R} e^{i(\boldsymbol{k}_4+\boldsymbol{k}_3-\boldsymbol{k}_2-\boldsymbol{k}_1)\cdot\boldsymbol{R}} = V\delta(\boldsymbol{k}_4+\boldsymbol{k}_3-\boldsymbol{k}_2-\boldsymbol{k}_1). \quad (6)$$

Let us now define some new variables in order to get rid of the delta function: $\boldsymbol{k} = \boldsymbol{k}_4$, $\boldsymbol{k}' = \boldsymbol{k}_3$ and $\boldsymbol{q} = (-\boldsymbol{k}_4+\boldsymbol{k}_3-\boldsymbol{k}_2+\boldsymbol{k}_1)/2 = \boldsymbol{k}_1-\boldsymbol{k}_4 = \boldsymbol{k}_3-\boldsymbol{k}_2$, where the equalities hold whenever $\boldsymbol{k}_4+\boldsymbol{k}_3-\boldsymbol{k}_2-\boldsymbol{k}_1 = 0$. Now we may notice that the first integral in the interaction Hamiltonian (3) is the Fourier transform of the interaction potential

$$\tilde{U}(\boldsymbol{q}) = \int d(\Delta\boldsymbol{r}) U(\Delta\boldsymbol{r}) e^{-i\boldsymbol{q}\cdot\Delta\boldsymbol{r}}. \quad (7)$$

By using these we get the interaction Hamiltonian

$$H_I = \frac{1}{2V} \sum_{\sigma\sigma'} \sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}} \tilde{U}(\boldsymbol{q}) c^\dagger_{(\boldsymbol{k}+\boldsymbol{q})\sigma} c^\dagger_{(\boldsymbol{k}'-\boldsymbol{q})\sigma'} c_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}\sigma}. \quad (8)$$

Now we can write the full Hamiltonian of the system by adding the single particle energies of the particles

$$H = \sum_{\boldsymbol{k},\sigma} \epsilon_{\boldsymbol{k}} c^\dagger_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \frac{1}{2V} \sum_{\sigma\sigma'} \sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}} \tilde{U}(\boldsymbol{q}) c^\dagger_{(\boldsymbol{k}+\boldsymbol{q})\sigma} c^\dagger_{(\boldsymbol{k}'-\boldsymbol{q})\sigma'} c_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}\sigma}, \quad (9)$$

where $\epsilon_{\boldsymbol{k}}$ is the single-particle energy of an electron with wave vector $\boldsymbol{k}$.

Next we want to simplify the situation a little bit and assume that the interaction potential is a contact interaction potential, i.e.,

$$U(\boldsymbol{r} - \boldsymbol{r}) = G\delta(\boldsymbol{r} - \boldsymbol{r}'), \tag{10}$$

where G is a coupling constant describing the strength of the interaction. It is worth noting here that for the attractive interaction $G < 0$. Using the definition of the Fourier transform we then get

$$\tilde{U}(\boldsymbol{q}) = G. \tag{11}$$

With this simplification we get a Hamiltonian below referred to as the full BCS Hamiltonian

$$H = \sum_{\boldsymbol{k},\sigma} \epsilon_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^\dagger c_{\boldsymbol{k}\sigma} + \frac{G}{2V} \sum_{\sigma\sigma'} \sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}} c_{(\boldsymbol{k}+\boldsymbol{q})\sigma}^\dagger c_{(\boldsymbol{k}'-\boldsymbol{q})\sigma'}^\dagger c_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}\sigma}. \tag{12}$$

With the full BCS Hamiltonian we are able to do some calculations already, but often it is necessary to further simplify the situation. The key element in the whole BCS theory is the pairing of electrons, and with this in mind we want to consider only interactions affecting the time-reversed pairs, i.e. state pairs of the form $(\boldsymbol{k}, \sigma)$ and $(-\boldsymbol{k}, \bar{\sigma})$. Here $\bar{\sigma}$ is the spin opposite to σ. When leaving all other interactions out, we can redefine the summation variables to get

$$H = \sum_{\boldsymbol{k},\sigma} \epsilon_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^\dagger c_{\boldsymbol{k}\sigma} + \frac{G}{V} \sum_{\boldsymbol{k},\boldsymbol{k}'} c_{\boldsymbol{k}'\uparrow}^\dagger c_{-\boldsymbol{k}'\downarrow}^\dagger c_{-\boldsymbol{k}\downarrow} c_{\boldsymbol{k}\uparrow}. \tag{13}$$

This is the reduced BCS Hamiltonian, also sometimes called the pairing Hamiltonian.

2.2 Finding the ground state

Now that we have a Hamiltonian for the system, next we would like to see what kind of eigenstates it has. As far as the ground state is concerned, the conventional BCS treatment gives us a widely used approximation. This can be obtained for example by using the original BCS ansatz ground state

$$|\Psi_G\rangle = \prod_{\boldsymbol{k}} \left(u_{\boldsymbol{k}} + v_{\boldsymbol{k}} c_{-\boldsymbol{k}\downarrow}^\dagger c_{\boldsymbol{k}\uparrow}^\dagger \right), \tag{14}$$

where $u_{\boldsymbol{k}}$ and $v_{\boldsymbol{k}}$ are variationally determined constants. However, usually the approximate ground states are found by applying mean-field theory, and that is what we do here also. Note that the results are the same either way.

Let us start with the reduced BCS Hamiltonian (13). We want to do mean-field theory regarding the electron pairs, so let us denote

$$d_{\boldsymbol{k}} = \langle c_{-\boldsymbol{k}\downarrow} c_{\boldsymbol{k}\uparrow} \rangle. \tag{15}$$

Now we can define the fluctuation of the pair of operators $\delta d_{\boldsymbol{k}}$ (which is an operator itself) such that

$$c_{-\boldsymbol{k}\downarrow}c_{\boldsymbol{k}\uparrow} = d_{\boldsymbol{k}} + \delta d_{\boldsymbol{k}}. \tag{16}$$

From this it trivially follows that

$$\langle \delta d_{\boldsymbol{k}} \rangle = 0. \tag{17}$$

Let us now substitute our mean-field definition (16) into the pairing Hamiltonian (13), and we get

$$H = \sum_{\boldsymbol{k},\sigma} \epsilon_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} + \frac{G}{V} \sum_{\boldsymbol{k},\boldsymbol{k}'} \left(d_{\boldsymbol{k}'}^{*} d_{\boldsymbol{k}} + d_{\boldsymbol{k}'}^{*} \delta d_{\boldsymbol{k}} + \delta d_{\boldsymbol{k}'}^{\dagger} d_{\boldsymbol{k}} + \delta d_{\boldsymbol{k}'}^{\dagger} \delta d_{\boldsymbol{k}} \right). \tag{18}$$

Now we assume that the fluctuations of the operator pairs are small, which means that we can neglect the $\delta d_{\boldsymbol{k}'}^{\dagger} \delta d_{\boldsymbol{k}}$ term since it is bilinear in small quantities. Thus we get the model Hamiltonian

$$H = \sum_{\boldsymbol{k},\sigma} \epsilon_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} + \frac{G}{V} \sum_{\boldsymbol{k},\boldsymbol{k}'} \left(d_{\boldsymbol{k}'}^{*} d_{\boldsymbol{k}} + d_{\boldsymbol{k}'}^{*} \delta d_{\boldsymbol{k}} + \delta d_{\boldsymbol{k}'}^{\dagger} d_{\boldsymbol{k}} \right). \tag{19}$$

At this point it is worth noting that the model Hamiltonian does not conserve particle number. However, for bulk metals with a large number of particles this should not pose a problem, as the relative violation usually gets smaller with increasing particle number, although this seems not to be the case for all systems, as we find out in section 5. The BCS ground state can also be projected to a fixed electron number state[3], to solve this problem, but this also complicates the calculations quite a bit, and so the unprojected state is often used instead.

In order to set the average particle number of the system we introduce a chemical potential μ, which is defined as the derivative of the energy of the system with respect to the average particle number of the system. Choosing a chemical potential fixes the average particle number of the ground state, when we take it into account in our Hamiltonian. Thus we will consider a Hamiltonian

$$H = \sum_{\boldsymbol{k},\sigma} \epsilon_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} + \frac{G}{V} \sum_{\boldsymbol{k},\boldsymbol{k}'} \left(d_{\boldsymbol{k}'}^{*} d_{\boldsymbol{k}} + d_{\boldsymbol{k}'}^{*} \delta d_{\boldsymbol{k}} + \delta d_{\boldsymbol{k}'}^{\dagger} d_{\boldsymbol{k}} \right) - \mu \hat{N}, \tag{20}$$

where

$$\hat{N} = \sum_{\boldsymbol{k},\sigma} c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} \tag{21}$$

is the particle-number operator. Now we can define

$$\xi_{\boldsymbol{k}} = \epsilon_{\boldsymbol{k}} - \mu \tag{22}$$

in order to change the model Hamiltonian into its final form

$$H = \sum_{\boldsymbol{k},\sigma} \xi_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} + \frac{G}{V} \sum_{\boldsymbol{k},\boldsymbol{k}'} \left(d_{\boldsymbol{k}'}^{*} d_{\boldsymbol{k}} + d_{\boldsymbol{k}'}^{*} \delta d_{\boldsymbol{k}} + \delta d_{\boldsymbol{k}'}^{\dagger} d_{\boldsymbol{k}} \right). \tag{23}$$

We may now notice, that introducing the chemical potential actually corresponds to simply changing the zero of the energy by μ. However, this achieves the desired effect of setting the average particle number, as the occupation probability of any state depends on its energy or, when the chemical potential is introduced, on the difference between the energy of the state and the chemical potential.

Next we define the pair potential

$$\Delta = -\sum_{\boldsymbol{k}} \frac{G}{V} d_{\boldsymbol{k}}, \tag{24}$$

which is also called the energy gap, superconducting gap or simply the gap because in the BCS theory it is directly related to the energy gap in the excitation spectrum of the superconducting state, as we will see in the end of this section. By using this definition the model Hamiltonian can be written as

$$H = \sum_{\boldsymbol{k},\sigma} \xi_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} - \sum_{\boldsymbol{k}} \left(d_{\boldsymbol{k}}^{*} \Delta + \Delta^{*} \delta d_{\boldsymbol{k}} + \delta d_{\boldsymbol{k}}^{\dagger} \Delta \right). \tag{25}$$

Now we can diagonalize this Hamiltonian by using the Bogoliubov transformation, which is of the form

$$\begin{aligned} c_{\boldsymbol{k}\uparrow} &= u_{\boldsymbol{k}}^{*} \gamma_{\boldsymbol{k}\downarrow} + v_{\boldsymbol{k}} \gamma_{\boldsymbol{k}\uparrow}^{\dagger} \\ c_{-\boldsymbol{k}\downarrow}^{\dagger} &= -v_{\boldsymbol{k}}^{*} \gamma_{\boldsymbol{k}\downarrow} + u_{\boldsymbol{k}} \gamma_{\boldsymbol{k}\uparrow}^{\dagger}, \end{aligned} \tag{26}$$

where $u_{\boldsymbol{k}}$ and $v_{\boldsymbol{k}}$ are constants satisfying $|u_{\boldsymbol{k}}|^2 + |v_{\boldsymbol{k}}|^2 = 1$. This transformation is unitary, so it preserves commutation relations, and thus in this case the operators $\gamma_{\boldsymbol{k}\sigma}$ are fermionic operators, sometimes called the bogoliubon operators. Now by substituting these definitions into the model Hamiltonian (19) we get a lengthy expression containing different combinations of the γ operators. In order to do the substitution we need to write the $\delta d_{\boldsymbol{k}}$ operators as a function of the fermionic operators using (16).

We want to diagonalize the Hamiltonian, so we fix coefficients $u_{\boldsymbol{k}}$ and $v_{\boldsymbol{k}}$ such that only constants and terms with $\gamma_{\boldsymbol{k}\sigma}^{\dagger} \gamma_{\boldsymbol{k}\sigma}$ remain. With a straightforward calculation using the fermionic anticommutation relations of the bogoliubon operators we then get as condition for the diagonalization

$$2\xi_{\boldsymbol{k}} u_{\boldsymbol{k}} v_{\boldsymbol{k}} + v_{\boldsymbol{k}}^2 \Delta^* - u_{\boldsymbol{k}}^2 \Delta = 0. \tag{27}$$

With coefficients satisfying this condition we get a Hamiltonian

$$\begin{aligned} H = \sum_{\boldsymbol{k}} \Bigg[&\xi_{\boldsymbol{k}} \left(2|v_{\boldsymbol{k}}|^2 + \left(|u_{\boldsymbol{k}}|^2 - |v_{\boldsymbol{k}}|^2 \right) \left(\gamma_{\boldsymbol{k}\uparrow}^{\dagger} \gamma_{\boldsymbol{k}\uparrow} + \gamma_{\boldsymbol{k}\downarrow}^{\dagger} \gamma_{\boldsymbol{k}\downarrow} \right) \right) \\ &- \Delta^* \left(u_{\boldsymbol{k}}^* v_{\boldsymbol{k}} - u_{\boldsymbol{k}}^* v_{\boldsymbol{k}} \gamma_{\boldsymbol{k}\uparrow}^{\dagger} \gamma_{\boldsymbol{k}\uparrow} - v_{\boldsymbol{k}} u_{\boldsymbol{k}}^* \gamma_{\boldsymbol{k}\downarrow}^{\dagger} \gamma_{\boldsymbol{k}\downarrow} \right) \\ &- \Delta \left(v_{\boldsymbol{k}}^* u_{\boldsymbol{k}} - v_{\boldsymbol{k}}^* u_{\boldsymbol{k}} \gamma_{\boldsymbol{k}\uparrow}^{\dagger} \gamma_{\boldsymbol{k}\uparrow} - u_{\boldsymbol{k}} v_{\boldsymbol{k}}^* \gamma_{\boldsymbol{k}\downarrow}^{\dagger} \gamma_{\boldsymbol{k}\downarrow} \right) + d_{\boldsymbol{k}} \Delta^* \Bigg], \end{aligned} \tag{28}$$

which is indeed diagonal.

At the moment we are more interested in the condition (27) diagonalizing the Hamiltonian than we are in the Hamiltonian itself, since from the condition we can calculate the values of the constants $u_{\bm{k}}$ and $v_{\bm{k}}$. We first multiply the condition (27) by $\Delta^*/u_{\bm{k}}^2$ to get

$$\frac{2\xi_{\bm{k}}\Delta^* v_{\bm{k}}}{u_{\bm{k}}} + \frac{(v_{\bm{k}}\Delta^*)^2}{u_{\bm{k}}^2} - |\Delta|^2 = 0. \tag{29}$$

This is now a quadratic equation in $(v_{\bm{k}}\Delta^*)/u_{\bm{k}}$ and can be solved as such. We get

$$\frac{v_{\bm{k}}\Delta^*}{u_{\bm{k}}} = -\xi_{\bm{k}} \pm \sqrt{\xi_{\bm{k}}^2 + |\Delta|^2}. \tag{30}$$

Let us then define $E_{\bm{k}} = \pm\sqrt{\xi_{\bm{k}}^2 + |\Delta|^2}$, to get a nice form

$$\frac{v_{\bm{k}}\Delta^*}{u_{\bm{k}}} = E_{\bm{k}} - \xi_{\bm{k}}. \tag{31}$$

There is a choice in the sign of $E_{\bm{k}}$, because we can diagonalize the Hamiltonian by creating either electron-like or hole-like quasiparticles. Here we only consider the case $E_{\bm{k}} > 0$ meaning that we have electron-like bogoliubons.

By squaring (31) and using the condition $|u_{\bm{k}}|^2 + |v_{\bm{k}}|^2 = 1$ we get

$$|v_{\bm{k}}|^2 = \frac{1}{2}\left(1 - \frac{\xi_{\bm{k}}}{E_{\bm{k}}}\right). \tag{32}$$

For $u_{\bm{k}}$ we get

$$|u_{\bm{k}}|^2 = \frac{1}{2}\left(1 + \frac{\xi_{\bm{k}}}{E_{\bm{k}}}\right). \tag{33}$$

Now that our Hamiltonian is diagonalized by the Bogoliubov transformation, we can find its eigenstates and especially the ground state with a little bit of work.

Let us first examine the Hamiltonian (28) and using equations (31) and (33) write it in the form

$$H = \sum_{\bm{k}}\left[\xi_{\bm{k}} - E_{\bm{k}} + d_{\bm{k}}\Delta^* + E_{\bm{k}}\left(\gamma_{\bm{k}\downarrow}^\dagger\gamma_{\bm{k}\downarrow} + \gamma_{\bm{k}\uparrow}^\dagger\gamma_{\bm{k}\uparrow}\right)\right]. \tag{34}$$

Now the Hamiltonian consists of a constant part and a weighed sum of different bogoliubon number operators. Moreover we see that a bogoliubon excitation created with $\gamma_{\bm{k}\sigma}$ contributes an energy of $E_{\bm{k}}$ to the system. As we chose that all $E_{\bm{k}}$ are positive, we can infer that the ground state of the system is the vacuum with respect to the bogoliubon operator. As $E_{\bm{k}}$ is now the excitation energy, we see from its definition that Δ is the minimum excitation energy, so it is the energy gap between the ground state and the excited state with the lowest energy. Usually non-zero Δ is found only in superconducting systems [11], so it is often an interesting parameter to study.

3 Richardson model

For the reduced BCS Hamiltonian (13) it is also possible to find exact eigenstates. This was first demonstrated by R. W. Richardson in 1964, as he used an ansatz state which yields the exacts eigenstates[10]. This method has no limitations regarding the particle number of the considered system or the strength of the coupling as the BCS treatment does. However, many calculations become very complicated or unsolvable using the Richardson model, and so the BCS theory is more often used instead.

Let us now consider a system with M pairs of charge carriers. In the Richardson model we begin with an ansatz of the form

$$|\Psi\rangle = \prod_{l=1}^{M} S_l^\dagger |0\rangle, \tag{35}$$

where $|0\rangle$ is the vacuum and

$$S_l^\dagger = \sum_{\boldsymbol{k}} \frac{1}{2\epsilon_{\boldsymbol{k}} - E_l} b_{\boldsymbol{k}}^\dagger. \tag{36}$$

Here $b_{\boldsymbol{k}}^\dagger = c_{\boldsymbol{k}\uparrow}^\dagger c_{-\boldsymbol{k}\downarrow}^\dagger$ and E_l are complex parameters. There are as many parameters as there are electron pairs in the system, and they are sometimes referred to as the pair energies, since their sum gives the energy of the state $|\Psi\rangle$.

By using the fermionic commutation relations of the creation and annihilation operators of the electrons, it can be shown that whenever the parameters satisfy the Richardson equations

$$1 + \frac{G}{V} \sum_{\boldsymbol{k}} \frac{1}{2\epsilon_{\boldsymbol{k}} - E_l} + \frac{2G}{V} \sum_{i(\neq l)=1}^{M} \frac{1}{E_l - E_j} = 0, \qquad \forall l = 1, \dots M \tag{37}$$

the ansatz state $|\Psi\rangle$ is an eigenstate of the reduced BCS Hamiltonian [12]. Equation (37) constitutes of as system of M distinct equations to be solved in order to get the parameters.

The Richardson model can be applied also to systems where there are unpaired electrons occupying known states. In order to handle those, we just need to change the vacuum in (35) into the state containing the unpaired electrons. An unpaired electron with momentum and spin $\boldsymbol{k}\sigma$ blocks the $\boldsymbol{k}\sigma$ state so that an electron pair cannot occupy the related pair state $(\boldsymbol{k}\sigma, -\boldsymbol{k}\bar{\sigma})$. Hence in (37) we also have to leave those states out of the sum over all momenta. Below we assume that there are no unpaired electrons in the system.

Solving the Richardson equations can be a difficult task, depending on the system. Analytical solutions are not known for any practical systems and are likely not to exist. With the calculational power of computers this is usually not a problem, but solving the Richardson equations numerically also requires a surprising amount of work, even though they are a fairly simple looking algebraic system of equations.

Most numerical solving algorithms require a fairly decent initial guess for the solution of the Richardson equations in order to actually converge. I have tested solving the system with Levenberg-Marquardt[13], Newton-Krylov[14] and MATLABs trust-region based [15] algorithms, and none of them performed consistently better than the others. Moreover, the different sets of solutions of the Richardson equations describe different eigenstates. Usually we would like to have a certain state, e.g. the ground state, and this poses some additional work to make sure that the solution found actually describes the desired state.

In order to tackle these problems it is customary to turn on the coupling G adiabatically starting from a very small value. With $G = 0$ it is clear that the solution is not well-defined. With small values of G, however, the solutions exist and are known, as in the limit of $G \to 0$ the pair energies $E_l \to 2\epsilon_{\boldsymbol{k}}$ for some $\boldsymbol{k}$. There is also an additional constraint that no more pair energies can converge towards a single value of $\epsilon_{\boldsymbol{k}}$ than the degeneracy of that energy state is.

This procedure gives us also a way to characterize the state we are solving, assuming there are no crossings in the energies as a function of the coupling. With that assumption the configuration with small G determines also the final state when G is increased adiabatically. Especially the ground state can then be easily found, as we place the pair energies close to as low energies $2\epsilon_{\boldsymbol{k}}$ as possible. This is very similar to filling the lowest states when creating a Fermi sea.

3.1   Electrostatic analogy

To help visualising the behaviour of the parameters E_l in the complex plane in our minds, there is a useful electrostatic analogy with the Richardson equations [16]. This analogy is often used also when considering the limit $M \to \infty$. Let us consider a two-dimensional classical system consisting of M free positive charges called pairons, and N fixed negative charges called orbitons, where N is the number of different energy states in the original system. We position the N orbitons on points $(2\epsilon_{\boldsymbol{k}}, 0)$, each of them having the charge of $-d_{\boldsymbol{k}}$, with $d_{\boldsymbol{k}}$ being the degeneracy of the state with momentum $\boldsymbol{k}$ (excluding spin degeneracy). The M pairons all have the same charge of one unit. We also add a static constant electric field pointing towards negative x-axis and having a magnitude of $1/(4G)$.

If we now consider the equilibrium configurations of this system, they can be found by expressing the electric potential of the system and then finding the zeros of the derivatives. Let us then define a new quantity in this system $E_l = x_l + iy_l$, where

(x_l, y_l) is the position of the l:th pairon. With this definition the equation for the zeros of the derivatives coincides perfectly with the Richardson equation [16]. So we know that any solution for the Richardson equations corresponds to an equilibrium configuration in the aforementioned electrostatic system.

This gives us some intuition on how the pair energies have to be positioned on the complex plane. It is worth noting though, that the equilibrium point of the system is not a stable minimum of the potential, but an unstable maximum. With small coupling G the static electric field strength approaches infinity. Thus in order to get an equilibrium, all the pairons, which have positive charges, have to get infinitesimally close to the fixed orbitons with negative charges in order to be able to cancel the static electric field. Increasing the coupling G decreases the electric field strength, thus forcing the equilibrium position of the pairons away from the orbitons.

We know that the solutions of Richardson equations come in complex conjugate pairs whenever they are not real [17]. This transforms into the electrostatic analogy as a symmetry with respect to x-axis. This on the other hand means that when we turn on the coupling, a pairon on the x-axis cannot exit the x-axis except when meeting another pairon. Because the pairons have the same positive charge they repel each other and cannot meet unless there is a negative charge in between them. So when we turn on the coupling G continuously and adiabatically, we encounter points where at least three charges occupy the same point in the two-dimensional space. This point is then singular, and makes the numerical calculations troublesome.

There are some papers featuring different variable changes in order to get rid of these singularities [18][12][19]. Using these many systems can be solved using the basic equation solving algorithms mentioned above. Let us next consider shortly a couple of examples.

3.2   Example systems

A two-state system with degeneracy of d for both states is one of the simplest systems concerning solving the Richardson equations. Let the state energies be $\pm\epsilon$. With small coupling G the pair energies gather in clusters forming arcs around values $\pm 2\epsilon$. Increasing the coupling G widens the clusters and eventually makes the initially two clusters join into a single arc. In the ground state of a half-filled system all the pair energies start from around the energy -2ϵ. The ground-state solutions for a system with $M = d = 30$ are shown in figure 1. These results are consistent with the ones in ref. [20]. One of the excited-state solutions for the same system is shown in figure 2 showing the two arcs around the values $\pm 2\epsilon$.

Another system considered here is the system with equally spaced energy levels. Let us define it so that we have N energy states equally distributed on the interval $[0, 2\omega]$. Here we consider half filling, so that there are $M = N/2$ electron pairs. The solutions of an example system for different couplings are shown in figure 3.
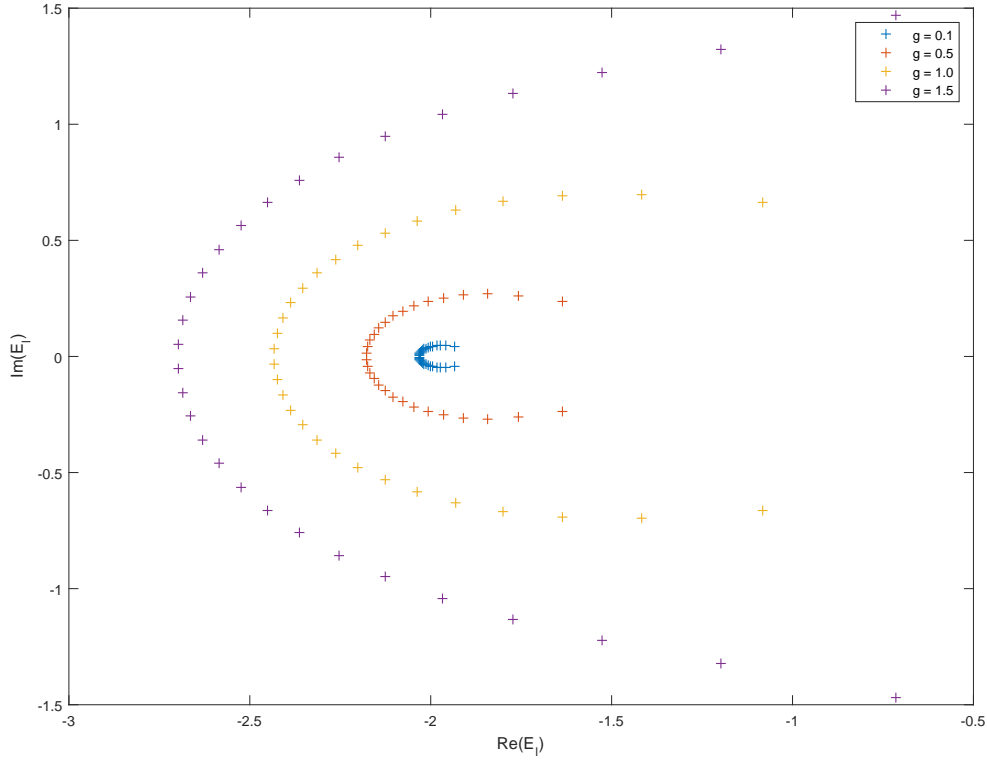
Figure 1. Ground state solutions of Richardson equations in a two level system with state energies ± 1 and degeneracies $d = 30$ containing $M = 30$ pairs of electrons. The solutions are shown with four different couplings $g = -GM$.

Excitations of this system are considered in ref [21]. The Richardson equations can be also solved for a three-dimensional box-normalized system with free electron dispersion $\epsilon_{\boldsymbol{k}} = \hbar^2 k^2/(2m)$. The results are shown in figure 4.

It can be shown that in the thermodynamic limit the solutions form arcs very similar as seen in the examples, but continuous. Furthermore, the endpoints of the arc can be shown to be $2\mu \pm i2\Delta$, where μ is the chemical potential and Δ is the superconducting gap of the system [20]. Using this feature it is easy to recognize superconducting states once the Richardson equations are solved.
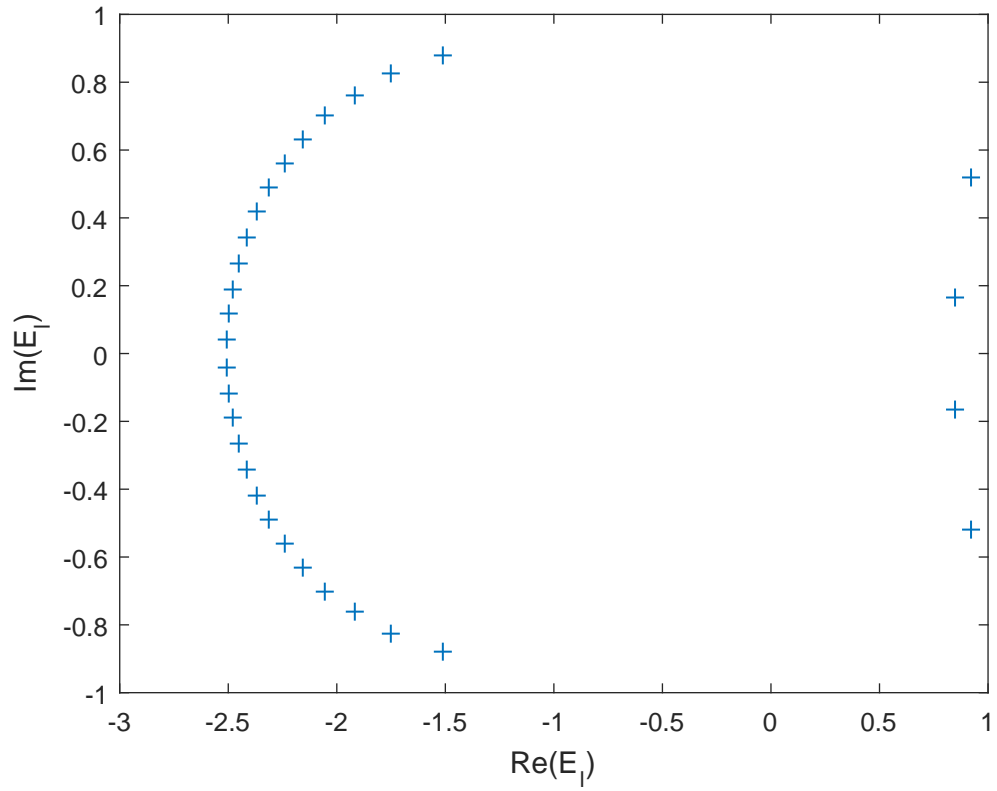
Figure 2. Solutions of Richardson equations for one of the excited states in a two level system with state energies ± 1 and degeneracies $d = 30$ containing $M = 30$ pairs of electrons and having the coupling constant $g = -GM = 1$.
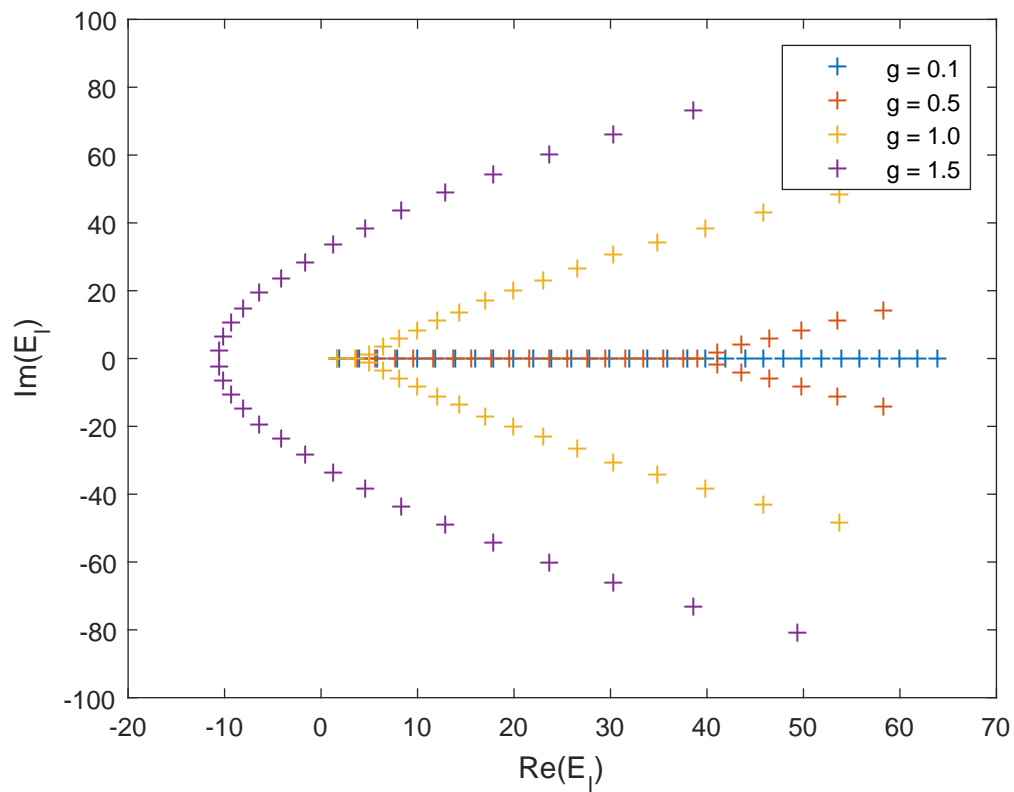
Figure 3. Solutions to the Richardson equations for an equally spaced system with $N = 64$ energy states distributed on the interval $[0, 2\omega]$, $\omega = 32$, having $M = 32$ electron pairs and different coupling constants $g = -GN/(2\omega) = -G$.
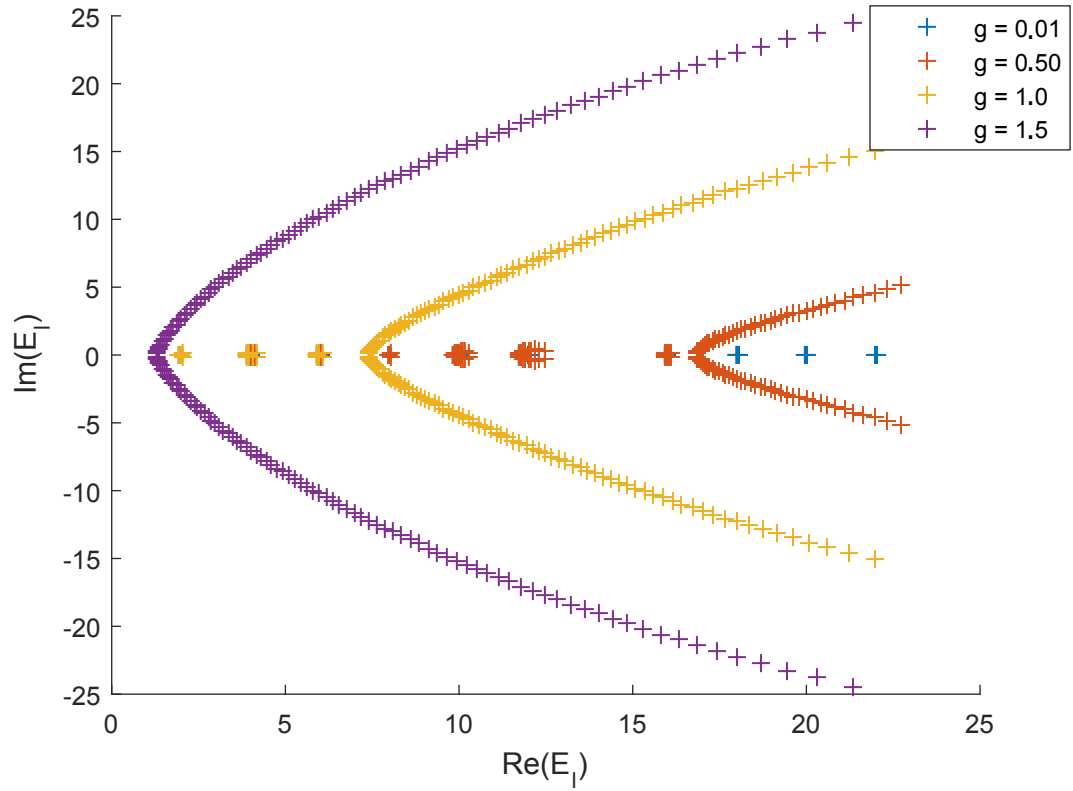
Figure 4. Solutions to the Richardson equations for a three dimensional system with $N = 340$ energy states with dispersion $\epsilon_{\boldsymbol{k}} = \hbar^2 k^2/(2m)$ having $M = 170$ electron pairs and different coupling constants $g = -GN/(V\omega) = -G/V$. Here ω is the Fermi energy and V the normalization volume. The energies are in units of the smallest energy state.

4 Calculating the ground state energies

The question remains, however, in which cases is the Richardson model a better description of the system than the BCS model, and when is the difference relevant. This is a complicated question, and one way to get a guess at it is to calculate the expectation values of the full Hamiltonian (9) with the ground states of these models. We can then compare these energies, and as both of the model ground states try to approximate the ground state of the full Hamiltonian, we can think that the model with a lower ground state energy is a better approximation. Below we calculate the energies of the ground states for this comparison.

4.1 Ground state energy of the Richardson model

Now we want to calculate the energy of the Richardson model ground state using the full BCS Hamiltonian

$$H = \sum_{\boldsymbol{k},\sigma} \epsilon_{\boldsymbol{k}} n_{\boldsymbol{k},\sigma} + \frac{G}{2V} \sum_{\boldsymbol{k},\boldsymbol{k'}\boldsymbol{q}} \sum_{\sigma\sigma'} c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q},\sigma} c^{\dagger}_{\boldsymbol{k'}-\boldsymbol{q},\sigma'} c_{\boldsymbol{k'}\sigma'} c_{\boldsymbol{k}\sigma} \equiv H_0 + H_I. \tag{38}$$

The energy of the ansatz state is

$$\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \tag{39}$$

where we have to divide by $\langle \Psi | \Psi \rangle$ because the ansatz state $|\Psi\rangle$ is not normalized. Before substituting the ansatz let us write it in a little bit different form.

$$|\Psi\rangle = \prod_{i=1}^{M} S_i^{\dagger} |0\rangle = \prod_{i=1}^{M} \sum_{\boldsymbol{k}} \frac{b_{\boldsymbol{k}}^{\dagger}}{2\epsilon_{\boldsymbol{k}} - E_i} |0\rangle$$

$$= \sum_{\boldsymbol{k}_1} \frac{b_{\boldsymbol{k}_1}^{\dagger}}{2\epsilon_{\boldsymbol{k}_1} - E_1} \sum_{\boldsymbol{k}_2} \frac{b_{\boldsymbol{k}_2}^{\dagger}}{2\epsilon_{\boldsymbol{k}_2} - E_2} \cdots \sum_{\boldsymbol{k}_M} \frac{b_{\boldsymbol{k}_M}^{\dagger}}{2\epsilon_{\boldsymbol{k}_M} - E_M}$$

$$= \sum_{\boldsymbol{k}_1 \ldots \boldsymbol{k}_M} \prod_{i=1}^{M} \frac{b_{\boldsymbol{k}_i}^{\dagger}}{2\epsilon_{\boldsymbol{k}_i} - E_i} |0\rangle = \sum_{\{\boldsymbol{k}_i\}} \left(\sum_{P} \prod_{i=1}^{M} \frac{1}{2\epsilon_{\boldsymbol{k}_{P(i)}} - E_i} \right) \prod_{i=1}^{M} b_{\boldsymbol{k}_i}^{\dagger} |0\rangle. \tag{40}$$

Here now the sum over $\{\boldsymbol{k}_i\}$ means that we sum through all sets containing M distinct values of $\boldsymbol{k}$, which are ordered in an arbitrary order and labelled $\boldsymbol{k}_i$ accordingly. Note that the ordering does not matter here, as we speak only of the set of the

values of $\boldsymbol{k}$. The different permutations are taken into account in the next sum, which is over P, a permutation on the set $\{1, \dots, M\}$, meaning that it is a bijection $P : \{1, \dots, M\} \to \{1, \dots, M\}$. For the last equality of equation (40) to hold the operators $b_{\boldsymbol{k}}^{\dagger}$ have to commute, because then they are not affected by the permuting of the indices. This is the case with electrons, as the electron operators anti-commute, so the electron pair operators corresponding to different $\boldsymbol{k}$ commute.

Now we can write the ansatz again in a rather compact form

$$|\Psi\rangle = \sum_{\{\boldsymbol{k}_i\}} C_{\{\boldsymbol{k}_i\}} \prod_{i=1}^{M} b_{\boldsymbol{k}_i}^{\dagger} |0\rangle, \tag{41}$$

where we define a coefficient

$$C_{\{\boldsymbol{k}_i\}} = \sum_P \prod_{i=1}^{M} \frac{1}{2\epsilon_{\boldsymbol{k}_{P(i)}} - E_i}. \tag{42}$$

The latter depends on the set $\{\boldsymbol{k}_i\}$.

Now we can first calculate $\langle \Psi | \Psi \rangle$ using the new form for the ansatz.

$$\langle \Psi | \Psi \rangle = \langle 0 | \sum_{\{\boldsymbol{k}_i^1\}} C_{\{\boldsymbol{k}_i^1\}}^{*} \prod_{i=1}^{M} b_{\boldsymbol{k}_i^1} \sum_{\{\boldsymbol{k}_i^2\}} C_{\{\boldsymbol{k}_i^2\}} \prod_{i=1}^{M} b_{\boldsymbol{k}_i^2}^{\dagger} |0\rangle$$

$$= \sum_{\{\boldsymbol{k}_i^1\}\{\boldsymbol{k}_i^2\}} C_{\{\boldsymbol{k}_i^1\}}^{*} C_{\{\boldsymbol{k}_i^2\}} \langle 0 | \prod_{i=1}^{M} \left(c_{-\boldsymbol{k}_i^1 \downarrow} c_{\boldsymbol{k}_i^1 \uparrow} \right) \prod_{i=1}^{M} \left(c_{\boldsymbol{k}_i^2 \uparrow}^{\dagger} c_{-\boldsymbol{k}_i^2 \downarrow}^{\dagger} \right) |0\rangle. \tag{43}$$

Here we use the superscripts on $\boldsymbol{k}_i^1$ and $\boldsymbol{k}_i^2$ in order to differentiate between the two sets. It is clear from the context that the superscript does not indicate an exponent. On the last equality we have now reverted the pair creation and annihilation operators $b_{\boldsymbol{k}}^{\dagger}$ and $b_{\boldsymbol{k}}$ back to pairs of fermion creation and annihilation operators $c_{\boldsymbol{k}\uparrow}^{\dagger} c_{-\boldsymbol{k}\downarrow}^{\dagger}$ and $c_{-\boldsymbol{k}\downarrow} c_{\boldsymbol{k}\uparrow}$.

The vacuum expectation value in (43) is now essentially of the form

$$\langle 0 | c_1 c_2 c_3 c_4 \dots c_{n-1} c_n c_2^{\dagger} c_1^{\dagger} c_4^{\dagger} c_3^{\dagger} \dots c_n^{\dagger} c_{n-1}^{\dagger} |0\rangle, \tag{44}$$

with even n. Assuming that $c_i \neq c_j$ for all $i \neq j$ this expectation value evaluates to

$$\langle 0 | c_1 c_2 c_3 c_4 \dots c_{n-1} c_n c_2^{\dagger} c_1^{\dagger} c_4^{\dagger} c_3^{\dagger} \dots c_n^{\dagger} c_{n-1}^{\dagger} |0\rangle = 1, \tag{45}$$

because every state considered is created once and then destroyed once, so in the end we are left with only $\langle 0 | 0 \rangle$. Note however that for this to hold, all the indices of annihilation operators have to have a counterpart creation operator and vice versa. If this is not the case, the vacuum expectation value is equal to zero. This property is used in the calculations below.

Let us now apply this to our calculation of $\langle\Psi|\Psi\rangle$.

$$\sum_{\{\boldsymbol{k}_i^1\}\{\boldsymbol{k}_i^2\}} C^*_{\{\boldsymbol{k}_i^1\}} C_{\{\boldsymbol{k}_i^2\}} \langle 0| \prod_{i=1}^{M} \left(c_{-\boldsymbol{k}_i^1\downarrow} c_{\boldsymbol{k}_i^1\uparrow} \right) \prod_{i=1}^{M} \left(c^\dagger_{\boldsymbol{k}_i^2\uparrow} c^\dagger_{-\boldsymbol{k}_i^2\downarrow} \right) |0\rangle$$

$$= \sum_{\{\boldsymbol{k}_i^1\}\{\boldsymbol{k}_i^2\}} C^*_{\{\boldsymbol{k}_i^1\}} C_{\{\boldsymbol{k}_i^2\}} \delta^{\{\boldsymbol{k}_i^2\}}_{\{\boldsymbol{k}_i^1\}}, \tag{46}$$

where we defined

$$\delta^{\{\boldsymbol{k}_i^2\}}_{\{\boldsymbol{k}_i^1\}} = \begin{cases} 1 & \{\boldsymbol{k}_i^1\} = \{\boldsymbol{k}_i^2\} \\ 0 & \{\boldsymbol{k}_i^1\} \neq \{\boldsymbol{k}_i^2\} \end{cases}. \tag{47}$$

It results from the fact that the same indices have to be found on both creation and annihilation operators in order for the result to be non-zero. This delta function has a similar effect on the sum as ordinary Kronecker delta (indeed it is actually a Kronecker delta on space of all subsets of the wave vector space). Note that as the operator pairs in (46) commute, we can reorder them so that the situation is the same as in equation (45). Now

$$\sum_{\{\boldsymbol{k}_i^1\}\{\boldsymbol{k}_i^2\}} C^*_{\{\boldsymbol{k}_i^1\}} C_{\{\boldsymbol{k}_i^2\}} \delta^{\{\boldsymbol{k}_i^2\}}_{\{\boldsymbol{k}_i^1\}} = \sum_{\{\boldsymbol{k}_i\}} C^*_{\{\boldsymbol{k}_i\}} C_{\{\boldsymbol{k}_i\}} = \sum_{\{\boldsymbol{k}_i\}} \left| C_{\{\boldsymbol{k}_i\}} \right|^2. \tag{48}$$

So we found

$$\langle\Psi|\Psi\rangle = \sum_{\{\boldsymbol{k}_i\}} \left| C_{\{\boldsymbol{k}_i\}} \right|^2. \tag{49}$$

This result is expected, because the state $|\Psi\rangle$ is just a linear combination of orthogonal states with coefficients $C_{\{\boldsymbol{k}_i\}}$.

Let us then calculate the energy of the ansatz $|\Psi\rangle$. First we calculate the contribution of H_I defined in (38)

$$\langle\Psi|H_I|\Psi\rangle = \sum_{\{\boldsymbol{k}_i^1\}\{\boldsymbol{k}_i^2\}} C^*_{\{\boldsymbol{k}_i^1\}} C_{\{\boldsymbol{k}_i^2\}} \langle 0| \prod_{i=1}^{M} \left(c_{-\boldsymbol{k}_i^1\downarrow} c_{\boldsymbol{k}_i^1\uparrow} \right)$$

$$\times \left(\frac{G}{2V} \sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q},\sigma,\sigma'} c^\dagger_{\boldsymbol{k}+\boldsymbol{q},\sigma} c^\dagger_{\boldsymbol{k}'-\boldsymbol{q},\sigma'} c_{\boldsymbol{k}',\sigma'} c_{\boldsymbol{k},\sigma} \right) \prod_{i=1}^{M} \left(c^\dagger_{\boldsymbol{k}_i^2\uparrow} c^\dagger_{-\boldsymbol{k}_i^2\downarrow} \right) |0\rangle$$

$$= \frac{G}{2V} \sum_{\{\boldsymbol{k}_i^1\}\{\boldsymbol{k}_i^2\}} \sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q},\sigma,\sigma'} C^*_{\{\boldsymbol{k}_i^1\}} C_{\{\boldsymbol{k}_i^2\}}$$

$$\times \langle 0| \prod_{i=1}^{M} \left(c_{-\boldsymbol{k}_i^1\downarrow} c_{\boldsymbol{k}_i^1\uparrow} \right) c^\dagger_{\boldsymbol{k}+\boldsymbol{q},\sigma} c^\dagger_{\boldsymbol{k}'-\boldsymbol{q},\sigma'} c_{\boldsymbol{k}',\sigma'} c_{\boldsymbol{k},\sigma} \prod_{i=1}^{M} \left(c^\dagger_{\boldsymbol{k}_i^2\uparrow} c^\dagger_{-\boldsymbol{k}_i^2\downarrow} \right) |0\rangle. \tag{50}$$

Now we can use the Wick's theorem to calculate the expectation value. Hence we get

$$
\frac{G}{2V} \sum_{\{k_i^1\}\{k_i^2\}} \sum_{k,k',q,\sigma,\sigma'} C^*_{\{k_i^1\}} C_{\{k_i^2\}}
$$

$$
\times \Bigg[\sum_{k_1 \in \{k_i^1\}} \sum_{k_2 \in \{k_i^2\}} \delta^{\{k_i^2\}\backslash k_2}_{\{k_i^1\}\backslash k_1} \Big(\delta_{k_1(k+q)} \delta_{-k_1(k'-q)} \delta_{k_2 k} \delta_{-k_2 k'} \delta_{\uparrow\sigma} \delta_{\downarrow\sigma'}
$$

$$
+ \delta_{k_1(k'-q)} \delta_{-k_1(k+q)} \delta_{k_2 k'} \delta_{-k_2 k} \delta_{\uparrow\sigma'} \delta_{\downarrow\sigma} \Big)
$$

$$
+ \delta^{\{k_i^2\}}_{\{k_i^1\}} \sum_{\substack{k_1,k_1' \in \{k_i^1\} \\ k_1 \neq k_1'}} \sum_{\substack{k_2,k_2' \in \{k_i^2\} \\ k_2 \neq k_2'}} \Big(\delta_{(k+q)k_1} \delta_{(k'-q)k_1'} \delta_{k'k_2} \delta_{kk_2'} \delta_{\sigma\sigma'} \big(\delta_{k_1 k_2'} \delta_{k_1' k2} - \delta_{k_1 k_2} \delta_{k_1' k_2'} \big)
$$

$$
+ \delta_{(k+q)k_1} \delta_{(k'-q)(-k_1')} \delta_{k'(-k_2)} \delta_{kk_2'} \delta_{\sigma\uparrow} \delta_{\sigma'\downarrow} \delta_{k_1 k_2'} \delta_{k_1' k_2}
$$

$$
+ \delta_{(k+q)(-k_1)} \delta_{(k'-q)k_1'} \delta_{k'k_2} \delta_{k(-k_2')} \delta_{\sigma\downarrow} \delta_{\sigma'\uparrow} \delta_{k_1 k_2'} \delta_{k_1' k_2} \Big) \Bigg].
\tag{51}
$$

By calculating the sums we get

$$
\frac{G}{V} \Bigg[\sum_{\{k_i\}'} \sum_{\substack{k_1,k_2 \notin \{k_i\}' \\ k_1 \neq k_2}} C^*_{\{k_i\}' \cup \{k_1\}} C_{\{k_i\}' \cup \{k_2\}} + \sum_{\{k_i\}} |C_{\{k_i\}}|^2 M + \sum_{\{k_i\}} |C_{\{k_i\}}|^2 \left(M^2 - M \right) \Bigg]
\tag{52}
$$

$$
= \frac{G}{V} \Bigg[\sum_{\{k_i\}'} \sum_{\substack{k_1,k_2 \notin \{k_i\}' \\ k_1 \neq k_2}} C^*_{\{k_i\}' \cup \{k_1\}} C_{\{k_i\}' \cup \{k_2\}} + \sum_{\{k_i\}} \langle \Psi | \Psi \rangle M^2 \Bigg].
\tag{53}
$$

Here we denote a set of $M-1$ $\boldsymbol{k}$-vectors by $\{\boldsymbol{k}_i\}'$, and the prime separates it from a set with M elements.

What remains to be done is to calculate the contribution of H_0 to the energy.

$$
\langle \Psi | H_0 | \Psi \rangle
$$

$$
= \sum_{\{k_i^1\}\{k_i^2\}} \sum_{k,\sigma} C^*_{\{k_i^1\}} C_{\{k_i^2\}} \langle 0 | \prod_{i=1}^{M} \left(c_{-k_i^1 \downarrow} c_{k_i^1 \uparrow} \right) \epsilon_k c^\dagger_{k,\sigma} c_{k,\sigma} \prod_{i=1}^{M} \left(c^\dagger_{k_i^2 \uparrow} c^\dagger_{-k_i^2 \downarrow} \right) | 0 \rangle
$$

$$
= \sum_{\{k_i\}} \left| C_{\{k_i\}} \right|^2 \sum_{i=1}^{M} \left(\epsilon_{k_i} + \epsilon_{-k_i} \right).
\tag{54}
$$

Now we can finally write down the total energy of the ansatz state

$$\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{1}{\langle\Psi|\Psi\rangle}\sum_{\{\boldsymbol{k}_i\}}\left|C_{\{\boldsymbol{k}_i\}}\right|^2\sum_{i=1}^{M}\left(\epsilon_{\boldsymbol{k}_i}+\epsilon_{-\boldsymbol{k}_i}\right)+\frac{G}{V}M^2$$
$$+\frac{G}{V\langle\Psi|\Psi\rangle}\sum_{\substack{\{\boldsymbol{k}_i\}'\\ \boldsymbol{k}_1\neq\boldsymbol{k}_i\neq\boldsymbol{k}_2\\ \boldsymbol{k}_1\neq\boldsymbol{k}_2}}C^*_{\{\boldsymbol{k}_i\}'\cup\{\boldsymbol{k}_1\}}C_{\{\boldsymbol{k}_i\}'\cup\{\boldsymbol{k}_2\}}. \tag{55}$$

This equation is already calculable, but for further calculations we would like to get rid of the constants $C_{\{\boldsymbol{k}_i\}}$. This can be achieved by using the fact that the Richardson ansatz is an eigenstate of the reduced BCS Hamiltonian H_R with an energy of sum of the pair energies E_i which determine the ansatz state.

So let us next calculate
$$\frac{\langle\Psi|H_R|\Psi\rangle}{\langle\Psi|\Psi\rangle}, \tag{56}$$

where
$$H_R = \sum_{\boldsymbol{k},\sigma}\epsilon_{\boldsymbol{k}}n_{\boldsymbol{k},\sigma}+\frac{G}{V}\sum_{\boldsymbol{k},\boldsymbol{k}'}c^\dagger_{\boldsymbol{k}\uparrow}c^\dagger_{-\boldsymbol{k}\downarrow}c_{-\boldsymbol{k}'\downarrow}c_{\boldsymbol{k}'\uparrow} \tag{57}$$

is the reduced BCS Hamiltonian. We can easily see that the difference to the full BCS Hamiltonian is the lack of some of the interaction terms, so the calculation is very similar to the one above. We can get the reduced BCS Hamiltonian from the full BCS Hamiltonian by restricting the second sum in (38) by requiring that $\boldsymbol{k}=-\boldsymbol{k}'$ and σ is the opposite spin to σ'

If we now consider equation (51), we notice that the latter sum vanishes. Thus we get from the sums

$$\frac{G}{V}\left[\sum_{\{\boldsymbol{k}_i\}'}\sum_{\substack{\boldsymbol{k}_1,\boldsymbol{k}_2\notin\{\boldsymbol{k}_i\}'\\ \boldsymbol{k}_1\neq\boldsymbol{k}_2}}C^*_{\{\boldsymbol{k}_i\}'\cup\{\boldsymbol{k}_1\}}C_{\{\boldsymbol{k}_i\}'\cup\{\boldsymbol{k}_2\}}+\sum_{\{\boldsymbol{k}_i\}}\langle\Psi|\Psi\rangle M\right]. \tag{58}$$

This leads to the total energy of

$$\frac{\langle\Psi|H_R|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{1}{\langle\Psi|\Psi\rangle}\sum_{\{\boldsymbol{k}_i\}}\left|C_{\{\boldsymbol{k}_i\}}\right|^2\sum_{i=1}^{M}\left(\epsilon_{\boldsymbol{k}_i}+\epsilon_{-\boldsymbol{k}_i}\right)+\frac{G}{V}M$$
$$+\frac{G}{V\langle\Psi|\Psi\rangle}\sum_{\substack{\{\boldsymbol{k}_i\}'\\ \boldsymbol{k}_1\neq\boldsymbol{k}_i\neq\boldsymbol{k}_2\\ \boldsymbol{k}_1\neq\boldsymbol{k}_2}}C^*_{\{\boldsymbol{k}_i\}'\cup\{\boldsymbol{k}_1\}}C_{\{\boldsymbol{k}_i\}'\cup\{\boldsymbol{k}_2\}}. \tag{59}$$

But on the other hand we know that

$$\frac{\langle\Psi|H_R|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \sum_{i=1}^{M}E_i, \tag{60}$$

where E_i are the pair energies defining the ansatz state, which can be solved from the Richardson equation. Thus for the full BCS Hamiltonian energy we now get

$$\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \sum_{i=1}^{M} E_i + \frac{G}{V}\left(M^2 - M\right). \tag{61}$$

Whenever we can solve the pair energies E_l we can use equation (61) to calculate the full Hamiltonian energy of the system.

4.2 Energy of a general paired state containing fixed number of electrons

It turns out we can extend our treatment to apply to any system containing only a fixed number of paired electrons. If we now take a closer look on the form

$$|\Psi\rangle = \sum_{\{\boldsymbol{k}_i\}} C_{\{\boldsymbol{k}_i\}} \prod_{i=1}^{M} b_{\boldsymbol{k}_i}^\dagger |0\rangle \tag{62}$$

we notice that with a suitable choice of constants $C_{\{\boldsymbol{k}_i\}}$ it can describe any given state with a fixed number of electrons occupying only time-reversed state pairs. Furthermore the calculations above do not depend on the Richardson ansatz state definition of the constants (42). So the total energy of any paired state with fixed number of electrons is given by equation (55). In general this equation is not very useful in calculations, because the number of terms to calculate can increase exponentially with the number of one-particle states.

From equation (61) we can now deduce that the difference between the reduced Hamiltonian and the full Hamiltonian energies of any normalised state containing M pairs of electrons is

$$\langle\Psi|H - H_R|\Psi\rangle = \frac{G}{V}(M^2 - M). \tag{63}$$

If we now find the ground state of the reduced BCS Hamiltonian with Richardson ansatz with M electron pairs we have also found the ground state of the full BCS Hamiltonian under the restriction that all the electrons are paired. If some of the electrons are allowed not to be paired then there might be states with lower energies.

We can get the result (63) with a less mathematical method as well. Let us consider an arbitrary state $|\Psi\rangle$ having exactly M paired electrons. For this state we now want to evaluate

$$\langle\Psi|H - H_R|\Psi\rangle =$$

$$\langle\Psi|\frac{G}{2V}\left(\sum_{\substack{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}\\\boldsymbol{k}\neq-\boldsymbol{k}'}}\sum_{\sigma\sigma'} c_{\boldsymbol{k}+\boldsymbol{q},\sigma}^\dagger c_{\boldsymbol{k}'-\boldsymbol{q},\sigma'}^\dagger c_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}\sigma} + \sum_{\boldsymbol{k},\boldsymbol{q}}\sum_{\sigma} c_{\boldsymbol{k}+\boldsymbol{q},\sigma}^\dagger c_{-\boldsymbol{k}-\boldsymbol{q},\sigma}^\dagger c_{-\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma}\right)|\Psi\rangle. \tag{64}$$

First we notice that any interactions between electrons having the same spin disappear, since for any given $\boldsymbol{k}$, $\boldsymbol{k}'$ and $\boldsymbol{q}$ we have a term $c^\dagger_{\boldsymbol{k}+\boldsymbol{q},\sigma}c^\dagger_{\boldsymbol{k}'-\boldsymbol{q},\sigma}c_{\boldsymbol{k}'\sigma}c_{\boldsymbol{k}\sigma}$ in the sum, but we also have summation indices $\boldsymbol{k}$, $\boldsymbol{k}'$ and $\boldsymbol{q}' = \boldsymbol{k}' - \boldsymbol{k} - \boldsymbol{q}$ resulting in a term $c^\dagger_{\boldsymbol{k}'-\boldsymbol{q},\sigma}c^\dagger_{\boldsymbol{k}+\boldsymbol{q},\sigma}c_{\boldsymbol{k}'\sigma}c_{\boldsymbol{k}\sigma}$. This term is otherwise identical, but the two creation operators have switched places. As they anti-commute it means that the two terms cancel each other. Thus there are no interactions between electrons having the same spin. Physically this is due to the contact interaction requiring the electrons occupy the same point in space to interact and Pauli exclusion principle forbids that if the electrons have the same spin.

So we are left with

$$\langle\Psi|H - H_R|\Psi\rangle = \frac{G}{2V}\langle\Psi|\sum_{\substack{\boldsymbol{k},\boldsymbol{k}'\boldsymbol{q}\\\boldsymbol{k}\neq-\boldsymbol{k}'}}\sum_{\sigma\neq\sigma'}c^\dagger_{\boldsymbol{k}+\boldsymbol{q},\sigma}c^\dagger_{\boldsymbol{k}'-\boldsymbol{q},\sigma'}c_{\boldsymbol{k}'\sigma'}c_{\boldsymbol{k}\sigma}|\Psi\rangle. \tag{65}$$

Next we note that the state $|\Psi\rangle$ contains only paired electrons. This means that the interaction terms considered cannot scatter any of the electrons, as this would result in breaking one of the electron pairs. So in the end we have

$$\langle\Psi|H - H_R|\Psi\rangle = \frac{G}{V}\langle\Psi|\sum_{\substack{\boldsymbol{k},\boldsymbol{k}'\\\boldsymbol{k}\neq-\boldsymbol{k}'}}c^\dagger_{\boldsymbol{k},\uparrow}c^\dagger_{\boldsymbol{k}',\downarrow}c_{\boldsymbol{k}'\downarrow}c_{\boldsymbol{k}\uparrow}|\Psi\rangle. \tag{66}$$

Now even if the state $|\Psi\rangle$ was a superposition of several different states they all have M electron pairs and do not interact with each other via the terms considered here. Now for all of them we effectively have interactions between all electron pairs, so there are $M^2 - M$ interactions, and thus for a normalised state we have

$$\langle\Psi|H - H_R|\Psi\rangle = \frac{G}{V}\left(M^2 - M\right), \tag{67}$$

just as we conclude above.

4.3   Energy of the BCS ground state

Let us next calculate the energy of the BCS ground state. Because we want to compare the energy to that of the Richardson ground state, we use the same Hamiltonian, i.e. the canonical one without the chemical potential. However we use the chemical potential in the definition of the ground state in order to set the average number of electrons.

We define the BCS ground state now as the normalized state $|\Psi_G\rangle$ for which

$$\gamma_{\boldsymbol{k}\uparrow}|\Psi_G\rangle = \gamma_{\boldsymbol{k}\downarrow}|\Psi_G\rangle = 0, \tag{68}$$

for all $\gamma_{\boldsymbol{k}\sigma}$, where $\gamma_{\boldsymbol{k}\sigma}$ are the bogoliubon operators. They are defined by equations (26). Then we want to calculate the expectation value of the full Hamiltonian (38).

Here I go through the calculation in parts. Let us start with the single-particle Hamiltonian H_0.

The expectation value of H_0 is now

$$\langle\Psi_G|H_0|\Psi_G\rangle = \langle\Psi_G|\sum_{k,\sigma}\epsilon_k n_{k\sigma}|\Psi_G\rangle = \sum_{k,\sigma}\langle\Psi_G|\epsilon_k c_{k\sigma}^\dagger c_{k\sigma}|\Psi_G\rangle$$

$$= \sum_k\langle\Psi_G|\epsilon_k(u_k\gamma_{k\downarrow}^\dagger + v_k^*\gamma_{k\uparrow})(u_k^*\gamma_{k\downarrow} + v_k\gamma_{k\uparrow}^\dagger)$$
$$+(-v_{-k}^*\gamma_{-k\downarrow} + u_{-k}\gamma_{-k\uparrow}^\dagger)(-v_{-k}\gamma_{-k\downarrow}^\dagger + u_{-k}^*\gamma_{-k\uparrow})|\Psi_G\rangle. \tag{69}$$

When we open the brackets in this expression we get different terms with two γ operators. Only terms with $\gamma_{k\sigma}\gamma_{k\sigma}^\dagger$ give a non-zero contribution to the sum, since the Bogoliubov operators are fermionic operators with the BCS ground state as their vacuum. So in the end we get

$$\langle\Psi_G|H_0|\Psi_G\rangle = 2\sum_k \epsilon_k |v_k|^2, \tag{70}$$

which was to be expected, as $|v_k|^2$ is the probability that state k is occupied.

Next let us tackle the interaction Hamiltonian. Its expectation value is

$$\langle\Psi_G|H_I|\Psi_G\rangle = \langle\Psi_G|\frac{G}{2V}\sum_{k,k',q}\sum_{\sigma,\sigma'} c_{k+q,\sigma}^\dagger c_{k'-q,\sigma'}^\dagger c_{k'\sigma'} c_{k\sigma}|\Psi_G\rangle. \tag{71}$$

We now divide the sums over the spins into separate cases in order to use the Bogoliubov transformation. First we examine the contribution of the case $\sigma = \sigma' = \uparrow$.

$$\frac{G}{2V}\sum_{k,k',q}\langle\Psi_G|c_{k+q,\uparrow}^\dagger c_{k'-q,\uparrow}^\dagger c_{k'\uparrow} c_{k\uparrow}|\Psi_G\rangle$$

$$= \frac{G}{2V}\sum_{k,k',q}\langle\Psi_G|(u_{k+q}\gamma_{(k+q)\downarrow}^\dagger + v_{k+q}^*\gamma_{(k+q)\uparrow})(u_{k'-q}\gamma_{(k'-q)\downarrow}^\dagger + v_{k'-q}^*\gamma_{(k'-q)\uparrow})$$
$$\times(u_{k'}^*\gamma_{k'\downarrow} + v_{k'}\gamma_{k'\uparrow}^\dagger)(u_k^*\gamma_{k\downarrow} + v_k\gamma_{k\uparrow}^\dagger)|\Psi_G\rangle. \tag{72}$$

Multiplying open all the parenthesis gives us now 16 terms, but luckily we can again remove all those which have $\gamma^\dagger$ as the leftmost operator, γ as the rightmost operator or do not have the same number of γ and $\gamma^\dagger$ operators. As a result we get

$$\frac{G}{2V}\sum_{k,k',q}\langle\Psi_G|v_{k+q}^*\gamma_{(k+q)\uparrow}\left(u_{k'-q}\gamma_{(k'-q)\downarrow}^\dagger u_{k'}^*\gamma_{k'\downarrow} + v_{k'-q}^*\gamma_{(k'-q)\uparrow}v_{k'}\gamma_{k'\uparrow}^\dagger\right)v_k\gamma_{k\uparrow}^\dagger|\Psi_G\rangle$$

$$= \frac{G}{2V}\sum_{k,k',q}\langle\Psi_G|v_{k+q}^*u_{k'-q}u_{k'}^*v_k\gamma_{(k+q)\uparrow}\gamma_{(k'-q)\downarrow}^\dagger\gamma_{k'\downarrow}\gamma_{k\uparrow}^\dagger$$
$$+v_{k+q}^*v_{k'-q}^*v_{k'}v_k\gamma_{(k+q)\uparrow}\gamma_{(k'-q)\uparrow}\gamma_{k'\uparrow}^\dagger\gamma_{k\uparrow}^\dagger|\Psi_G\rangle. \tag{73}$$

Now the terms with four Bogoliubon operators can be calculated by using the Wick's theorem. Thus

$$\langle \Psi_G | \gamma_{(k+q)\uparrow} \gamma^\dagger_{(k'-q)\downarrow} \gamma_{k'\downarrow} \gamma^\dagger_{k\uparrow} | \Psi_G \rangle = \delta_{(k+q)(k'-q)} \delta_{k'k} \delta_{\uparrow\downarrow} = 0 \tag{74}$$

$$\langle \Psi_G | \gamma_{(k+q)\uparrow} \gamma_{(k'-q)\uparrow} \gamma^\dagger_{k'\uparrow} \gamma^\dagger_{k\uparrow} | \Psi_G \rangle = \delta_{(k+q)k} \delta_{(k'-q)k'} \delta_{\uparrow\uparrow} - \delta_{(k+q)k'} \delta_{(k'-q)k} \delta_{\uparrow\uparrow}. \tag{75}$$

Using these in equation (73) yields

$$\frac{G}{2V} \sum_{k,k',q} v^*_{k+q} v^*_{k'-q} v_{k'} v_k \left(\delta_{(k+q)k} \delta_{(k'-q)k'} \delta_{\uparrow\uparrow} - \delta_{(k+q)k'} \delta_{(k'-q)k} \delta_{\uparrow\uparrow} \right)$$

$$= \frac{G}{2V} \sum_{k,k'} (v^*_k v^*_{k'} v_{k'} v_k - v^*_{k'} v^*_k v_{k'} v_k) = 0. \tag{76}$$

Very similarly now returning to the Hamiltonian (71) the term $\sigma = \sigma' = \downarrow$ gives a zero contribution. Let us then next calculate the case $\sigma = \uparrow, \sigma' = \downarrow$. By similar reasoning as above we get

$$\frac{G}{2V} \sum_{k,k',q} \langle \Psi_G | c^\dagger_{k+q,\uparrow} c^\dagger_{k'-q,\downarrow} c_{k'\downarrow} c_{k\uparrow} | \Psi_G \rangle$$

$$= \frac{G}{2V} \sum_{k,k',q} \langle \Psi_G | (u_{k+q} \gamma^\dagger_{(k+q)\downarrow} + v^*_{k+q} \gamma_{(k+q)\uparrow})(-v^*_{-k'+q} \gamma_{(-k'+q)\downarrow} + u_{-k'+q} \gamma^\dagger_{(-k+q)\uparrow})$$

$$\times (-v_{-k'} \gamma^\dagger_{-k'\downarrow} + u^*_{-k'} \gamma_{-k'\uparrow})(u^*_k \gamma_{k\downarrow} + v_k \gamma^\dagger_{k\uparrow}) | \Psi_G \rangle$$

$$= \frac{G}{2V} \sum_{k,k',q} \langle \Psi_G | v^*_{k+q} \gamma_{(k+q)\uparrow}$$

$$\times \left(v^*_{-k'+q} \gamma_{(-k'+q)\downarrow} v_{-k'} \gamma^\dagger_{-k'\downarrow} + u_{-k'+q} \gamma^\dagger_{(-k+q)\uparrow} u^*_{-k'} \gamma_{-k'\uparrow} \right) v_k \gamma^\dagger_{k\uparrow} | \Psi_G \rangle$$

$$= \frac{G}{2V} \sum_{k,k',q} \left(v^*_{k+q} v^*_{-k'+q} v_{-k'} v_k \left(\delta_{(k+q)k} \delta_{(-k'+q)(-k')} \delta_{\uparrow\uparrow} \delta_{\downarrow\downarrow} - \delta_{(k+q)(-k')} \delta_{(-k'+q)k} \delta_{\uparrow\downarrow} \right) \right.$$

$$\left. + v^*_{k+q} u_{-k'+q} u^*_{-k'} v_k \delta_{(k+q)(-k'+q)} \delta_{-k'k} \delta_{\uparrow\uparrow} \right)$$

$$= \frac{G}{2V} \sum_{k,k'} v^*_k v^*_{-k'} v_{-k'} v_k + \frac{G}{2V} \sum_{k,q} v^*_{k+q} u_{k+q} u^*_k v_k$$

$$= \frac{G}{2V} \sum_{k,k'} |v_k v_{k'}|^2 + \frac{G}{2V} \sum_{k,k'} v^*_{k'} u_{k'} u^*_k v_k \tag{77}$$

where we changed some indexing on the last line.

With some indexing renaming also the case $\sigma = \downarrow, \sigma' = \uparrow$ gives the same result, so in the end we get

$$\langle \Psi_G | H | \Psi_G \rangle = 2 \sum_{\boldsymbol{k}} \epsilon_{\boldsymbol{k}} |v_{\boldsymbol{k}}|^2 + \frac{G}{V} \sum_{\boldsymbol{k}, \boldsymbol{k}'} |v_{\boldsymbol{k}} v_{\boldsymbol{k}'}|^2 + \frac{G}{V} \sum_{\boldsymbol{k}, \boldsymbol{k}'} v_{\boldsymbol{k}'}^* u_{\boldsymbol{k}'} u_{\boldsymbol{k}}^* v_{\boldsymbol{k}}. \tag{78}$$

For further processing we want to calculate Δ as a function of $u_{\boldsymbol{k}}$ and $v_{\boldsymbol{k}}$. Let us start from the definition (24) and use the Bogoliubov transformation

$$\begin{aligned} \Delta &= -\sum_{\boldsymbol{k}} \frac{G}{V} d_{\boldsymbol{k}} = -\frac{G}{V} \sum_{\boldsymbol{k}} \langle \Psi_G | c_{-\boldsymbol{k}\downarrow} c_{\boldsymbol{k}\uparrow} | \Psi_G \rangle \\ &= -\frac{G}{V} \sum_{\boldsymbol{k}} \langle \Psi_G | \left(-v_{\boldsymbol{k}} \gamma_{\boldsymbol{k}\downarrow}^\dagger + u_{\boldsymbol{k}}^* \gamma_{\boldsymbol{k}\uparrow} \right) \left(u_{\boldsymbol{k}}^* \gamma_{\boldsymbol{k}\downarrow} + v_{\boldsymbol{k}} \gamma_{\boldsymbol{k}\uparrow}^\dagger \right) | \Psi_G \rangle. \end{aligned} \tag{79}$$

Now we can use the property of the BCS ground state that it is the vacuum for the bogoliubon operators, hence only expectation values of operator pairs $\gamma_{\boldsymbol{k}\sigma} \gamma_{\boldsymbol{k}\sigma}^\dagger$ will give a non-zero contribution. Thus we get

$$\Delta = -\frac{G}{V} \sum_{\boldsymbol{k}} \langle \Psi_G | u_{\boldsymbol{k}}^* \gamma_{\boldsymbol{k}\uparrow} v_{\boldsymbol{k}} \gamma_{\boldsymbol{k}\uparrow}^\dagger | \Psi_G \rangle = -\frac{G}{V} \sum_{\boldsymbol{k}} u_{\boldsymbol{k}}^* v_{\boldsymbol{k}} \tag{80}$$

By using equation (80) and $\bar{M} = \sum_{\boldsymbol{k}} |v_{\boldsymbol{k}}|^2$ equation (78) can be reformulated into

$$\langle \Psi_G | H | \Psi_G \rangle = 2 \sum_{\boldsymbol{k}} \epsilon_{\boldsymbol{k}} |v_{\boldsymbol{k}}|^2 + \frac{G}{V} \bar{M}^2 + \frac{V}{G} |\Delta|^2, \tag{81}$$

where now $\bar{M}$ is the expectation value for the number of electron pairs.

Next we would like to know how this energy relates to the expectation value of the reduced BCS Hamiltonian. In order to easily see it from this result, we write the reduced BCS Hamiltonian H_R in the form

$$H_R = \sum_{\boldsymbol{k}, \sigma} \epsilon_{\boldsymbol{k}} n_{\boldsymbol{k}, \sigma} + \frac{G}{2V} \sum_{\boldsymbol{k}, \boldsymbol{k}', \boldsymbol{q}} \sum_{\sigma, \sigma'} c_{\boldsymbol{k}+\boldsymbol{q}, \sigma}^\dagger c_{\boldsymbol{k}'-\boldsymbol{q}, \sigma'}^\dagger c_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}\sigma} \delta_{-\boldsymbol{k}'\boldsymbol{k}} \delta_{\sigma'\bar{\sigma}}, \tag{82}$$

where $\bar{\sigma}$ is the spin opposite to σ. By following the above calculation with this change we get

$$\langle \Psi_G | H_R | \Psi_G \rangle = 2 \sum_{\boldsymbol{k}} \epsilon_{\boldsymbol{k}} |v_{\boldsymbol{k}}|^2 + \frac{G}{V} \sum_{\boldsymbol{k}} |v_{\boldsymbol{k}}|^4 + \frac{G}{V} \sum_{\boldsymbol{k}, \boldsymbol{k}'} v_{\boldsymbol{k}'}^* u_{\boldsymbol{k}'} u_{\boldsymbol{k}}^* v_{\boldsymbol{k}}. \tag{83}$$

Now we know that $|v_{\boldsymbol{k}}|^4 = |v_{\boldsymbol{k}}|^2 - |v_{\boldsymbol{k}} u_{\boldsymbol{k}}|^2$ and $2 v_{\boldsymbol{k}} u_{\boldsymbol{k}}^* = \Delta / E_{\boldsymbol{k}}$. To get the latter equation we solve Δ from equation (31) to get

$$\Delta = \frac{u_{\boldsymbol{k}}^*}{v_{\boldsymbol{k}}^*} \left(E_{\boldsymbol{k}} - \epsilon_{\boldsymbol{k}} \right). \tag{84}$$

Then we substitute this into $\Delta/E_{\boldsymbol{k}}$ to get

$$\frac{\Delta}{E_{\boldsymbol{k}}} = \frac{u_{\boldsymbol{k}}^*}{v_{\boldsymbol{k}}^*} \left(1 - \frac{\epsilon_{\boldsymbol{k}}}{E_{\boldsymbol{k}}}\right) \tag{85}$$

and then using equation (32) we get the desired result

$$\frac{\Delta}{E_{\boldsymbol{k}}} = 2 v_{\boldsymbol{k}} u_{\boldsymbol{k}}^* \tag{86}$$

Now we can reformulate equation (83) as

$$\langle \Psi_G | H_R | \Psi_G \rangle = 2 \sum_{\boldsymbol{k}} \epsilon_{\boldsymbol{k}} |v_{\boldsymbol{k}}|^2 + \frac{G}{V}\left(\bar{M} - \frac{1}{4}\sum_{\boldsymbol{k}} \frac{|\Delta|^2}{E_{\boldsymbol{k}}^2}\right) + \frac{V}{G}|\Delta|^2. \tag{87}$$

Thus

$$\langle \Psi_G | H - H_R | \Psi_G \rangle = \frac{G}{V}\sum_{\boldsymbol{k}\neq\boldsymbol{k}'}|v_{\boldsymbol{k}}v_{\boldsymbol{k}'}|^2 = \frac{G}{V}\left(\bar{M}^2 - \bar{M} + \frac{1}{4}\sum_{\boldsymbol{k}}\frac{|\Delta|^2}{E_{\boldsymbol{k}}^2}\right). \tag{88}$$

We can get this equation also by using the result from section 4.2 stating that for any fixed electron number state the difference between the energies is proportional to $M^2 - M$. In the BCS ground state we now have an ensemble of such fixed electron number states $|\Psi_M\rangle$ with exactly M electron pairs, and we calculate the expectation value

$$\langle \Psi_G | H - H_R | \Psi_G \rangle \tag{89}$$

over those states. For each of those states we know that

$$\langle \Psi_M | H - H_R | \Psi_M \rangle = \frac{G}{V}\left(M^2 - M\right). \tag{90}$$

Therefore

$$\langle \Psi_G | H - H_R | \Psi_G \rangle = \frac{G}{V}\left(\langle \Psi_G | M^2 - M | \Psi_G\rangle\right) = \frac{G}{V}\left(\langle \Psi_G | M^2 | \Psi_G\rangle - \langle \Psi_G | M | \Psi_G\rangle\right). \tag{91}$$

We know also that the variance of the BCS ground state is [11]

$$\langle \Psi_G | M^2 | \Psi_G \rangle - \langle \Psi_G | M | \Psi_G \rangle^2 = \sum_{\boldsymbol{k}}|u_{\boldsymbol{k}}v_{\boldsymbol{k}}|^2 = \frac{1}{4}\sum_{\boldsymbol{k}}\frac{|\Delta|^2}{E_{\boldsymbol{k}}^2}. \tag{92}$$

By substituting equation (92) into (91) we get the result (88).

4.4 Self-consistency equations

In order to calculate the BCS ground state energy we need to be able to calculate a value for Δ and μ. This can be done by formulating self-consistency equations for them. We can obtain one equation by substituting $u_{\boldsymbol{k}}^* v_{\boldsymbol{k}}$ solved from equation (86) into (80) to get

$$\Delta = -\frac{G}{2V} \sum_{\boldsymbol{k}} \frac{\Delta}{E_{\boldsymbol{k}}} = -\frac{G}{2V} \sum_{\boldsymbol{k}} \frac{\Delta}{\sqrt{\xi_{\boldsymbol{k}}^2 + |\Delta|^2}}. \tag{93}$$

Now as Δ does not depend on $\boldsymbol{k}$ we can divide both sides of the equation with it and substitute the definition of $\xi_{\boldsymbol{k}}$ into the equation to get the first self-consistency equation

$$1 = -\frac{G}{2V} \sum_{\boldsymbol{k}} \frac{1}{\sqrt{(\epsilon_{\boldsymbol{k}} - \mu)^2 + |\Delta|^2}}. \tag{94}$$

To get the second equation we start from

$$\bar{M} = \sum_{\boldsymbol{k}} |v_{\boldsymbol{k}}|^2. \tag{95}$$

Next we substitute (32) to get

$$\bar{M} = \frac{1}{2} \sum_{\boldsymbol{k}} \left(1 - \frac{\epsilon_{\boldsymbol{k}} - \mu}{\sqrt{(\epsilon_{\boldsymbol{k}} - \mu)^2 + |\Delta|^2}} \right). \tag{96}$$

This is our second self-consistency equation. From equations (94) and (96) Δ and μ can now be solved numerically.

5 Comparison of the ground state energies

Now we would like to compare the ground state energies of the two models in order to determine which of them approximates the true ground state better. This poses a problem, however, as the Richardson ansatz is a canonical ensemble, whereas the BCS ground state is a grand canonical ensemble, and so it is not meaningful to compare their energies.

The BCS ground state should be projected to a fixed number state whenever possible, as was done in the original treatment [3], so we try to change the BCS ground state into a canonical ensemble. The projected state $|\Psi_M\rangle$ with M electron pairs can be formulated as a superposition of BCS ground states (14) with a help of an extra phase factor ϕ. This is done using the equation

$$|\Psi_M\rangle = \frac{1}{2\pi} \int_0^{2\pi} \mathrm{d}\phi e^{-iM\phi} \prod_{\boldsymbol{k}} \left(u_{\boldsymbol{k}} + e^{i\phi} v_{\boldsymbol{k}} c_{\boldsymbol{k}\uparrow}^{\dagger} c_{-\boldsymbol{k}\downarrow}^{\dagger} \right) |0\rangle. \tag{97}$$

Note how the exponentials make sure that only states with M electron pairs do not vanish. Each of the states inside the integral are valid BCS ground states, as the equation (14) gives the BCS ground state for suitable coefficient $v_{\boldsymbol{k}}$ with any phase.

Calculations are usually much more complicated using the fixed electron number ground state (97) instead of the grand canonical ground state (14), and thus the grand canonical ground state is more often used. In principle we can calculate the ground state energy for the fixed electron number ground state using the equation for general fixed particle number state energy (55) as deduced in section 4.2. However the formula is too inefficient for calculations with particle numbers we compare, and so is not used here.

Instead we make an approximation so that we can make use of the grand canonical BCS ground state $|\Psi_G\rangle$. We assume that the BCS ground state $|\Psi_G\rangle$ is close to an eigenstate of the reduced BCS Hamiltonian H_R. This is supported by the assumption that the BCS ground state is a valid approximation of the true ground state of the reduced BCS Hamiltonian. Thus we can approximate that

$$H_R|\Psi_G\rangle \approx E|\Psi_G\rangle, \tag{98}$$

where E is the energy of the state $|\Psi_G\rangle$. As $|\Psi_M\rangle$ is as superposition of BCS ground states, as can be seen from definition (97) it follows that

$$H_R|\Psi_M\rangle \approx E|\Psi_M\rangle. \tag{99}$$

Using these we get

$$\langle \Psi_G | H_R | \Psi_G \rangle \approx \langle \Psi_M | H_R | \Psi_M \rangle. \tag{100}$$

So the energies of the grand canonical and fixed electron number ground states are approximately the same, and so we can just use the energy of the BCS ground state given by (87). Furthermore, because of equation (63) we can calculate the full Hamiltonian energy for the fixed electron number ground state. However, as the difference between the full Hamiltonian and reduced Hamiltonian energies is the same for all fixed particle number states, we can simply compare the reduced Hamiltonian energies to determine the energy difference of two different states.

Now we have the means to compare the BCS ground state and Richardson model ground state energies. We know that the Richardson model ground state has a lower energy since it is the true ground state of the reduced Hamiltonian. In systems with a strong coupling G we expect to see differences in the ground state energies of the BCS and Richardson models, as we have linearised the fluctuations in the BCS model, which should then in general be a better approximation for weaker couplings. Furthermore we also expect a higher energy difference in systems with a small number of particles, as the BCS ground state does not conserve the particle number, and the violation is supposedly more relevant in a small system.

The comparisons presented below are in general calculated in the following way. We first solve the Richardson equations with the methods briefly discussed in section 3 in order to get the parameters E_l. The reduced Hamiltonian energy for the Richardson ansatz state is then calculated by summing these parameters E_l. To calculate the energy of the BCS ground state we first solve numerically the superconducting gap Δ and chemical potential μ from equations (94) and (96). With these values we can then calculate the BCS ground state energies for the reduced Hamiltonian (87).

We first consider the equally spaced system introduced in section 3. We start with a small system containing $N = 8$ spin-degenerate energy states and half-filling, i.e. $M = 4$ electron pairs. The energies of the ground states are shown in figure 5. We notice that the BCS model and Richardson model full energies stay relatively close to each other even with such a small number of electrons. However, the Richardson model energy is slightly lower with all values of g considered.

The energies of the ground states are shown in figure 6 for an otherwise similar system, but with $N = 200$ and $M = 100$. We notice that the Richardson model and BCS ground state energies are practically indistinguishable. In figure 7 the energy difference between the Richardson and BCS ground states is plotted as a function of the number of the electron pairs. The energy difference is given in the units of the condensation energy E_c, i.e. the energy difference between the non-interacting ground state and the BCS ground state, because this defines an energy scale for the system. From the figure we see, that the energy difference seems to approach zero at higher electron numbers.
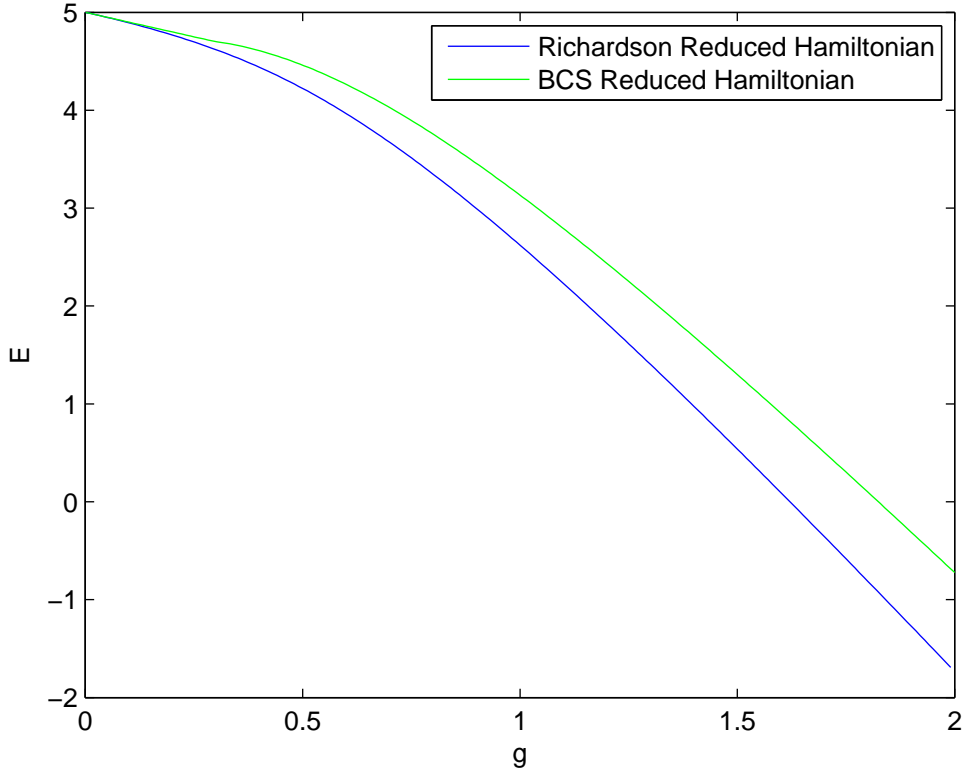
Figure 5. Energies of the BCS and Richardson model ground states obtained from the reduced BCS Hamiltonian as a function of the coupling $g = -GN/(2\omega)$. The system considered has $N = 8$ equally spaced spin-degenerate energy levels divided on interval $[0, 2\omega]$ and $M = 4$ electron pairs. The energies are in units of the Fermi energy, which is now equal to ω.

Let us next consider a three-dimensional box system with dispersion

$$\epsilon_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2m}. \tag{101}$$

We consider a system with $M = 16$ electron pairs and $N = 32$ energy states. The results are shown in figure 8. They are very similar to those of the equally spaced system. Again the energies are close to each other with all couplings. Increasing the number of particles and states results again quickly in indistinguishable energies between the models.

In a two level system with energies $-\epsilon$ and ϵ we can see a larger difference between the two ground states. The results for a system with $M = 32$ electron pairs and $N = 64$ states are shown in figure 9. The results are very similar even for $M = 100$ electron pairs. The energy difference between the two ground states as a function of number of electron pairs is plotted in figure 10. The difference between the energies seems to approach a non-zero constant with increasing particle number with the
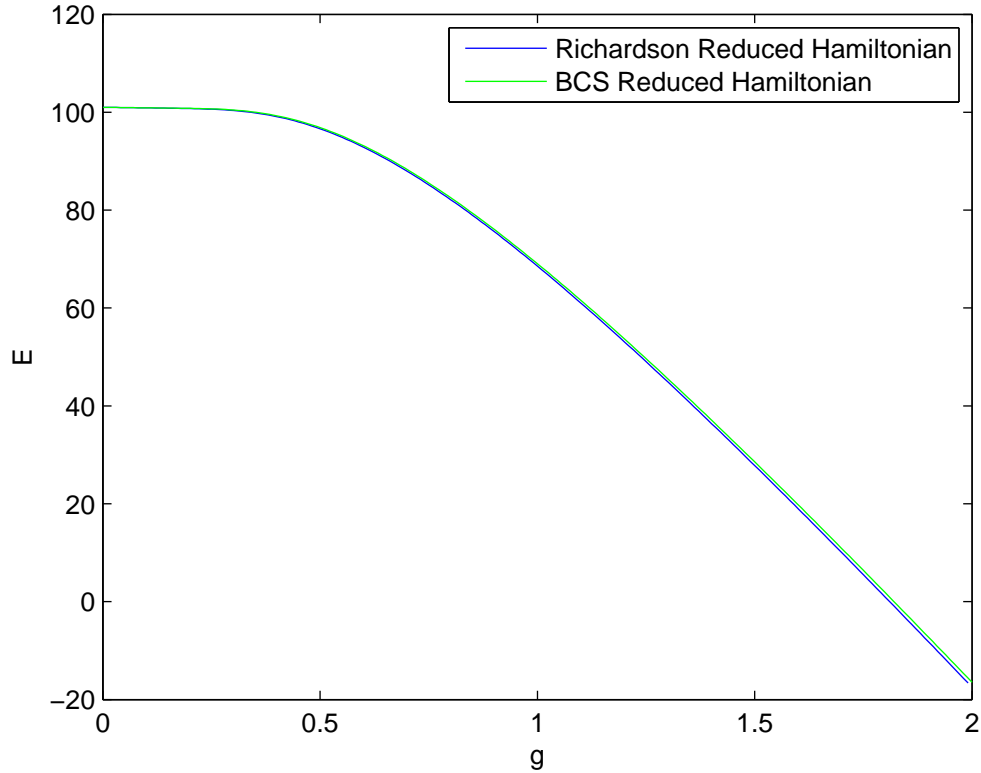
Figure 6. Energies of the BCS and Richardson model ground states obtained from the reduced BCS Hamiltonian as a function of the coupling $g = -GN/(2\omega)$. The system considered has $N = 200$ equally spaced spin-degenerate energy levels divided on interval $[0, 2\omega]$ and $M = 100$ electron pairs. The energies are in units of the Fermi energy, which is now equal to ω.

Richardson model yielding a lower ground state energy, as it should. Because of the difference in ground state energies it seems that in this case using the BCS model can result in a significant error.
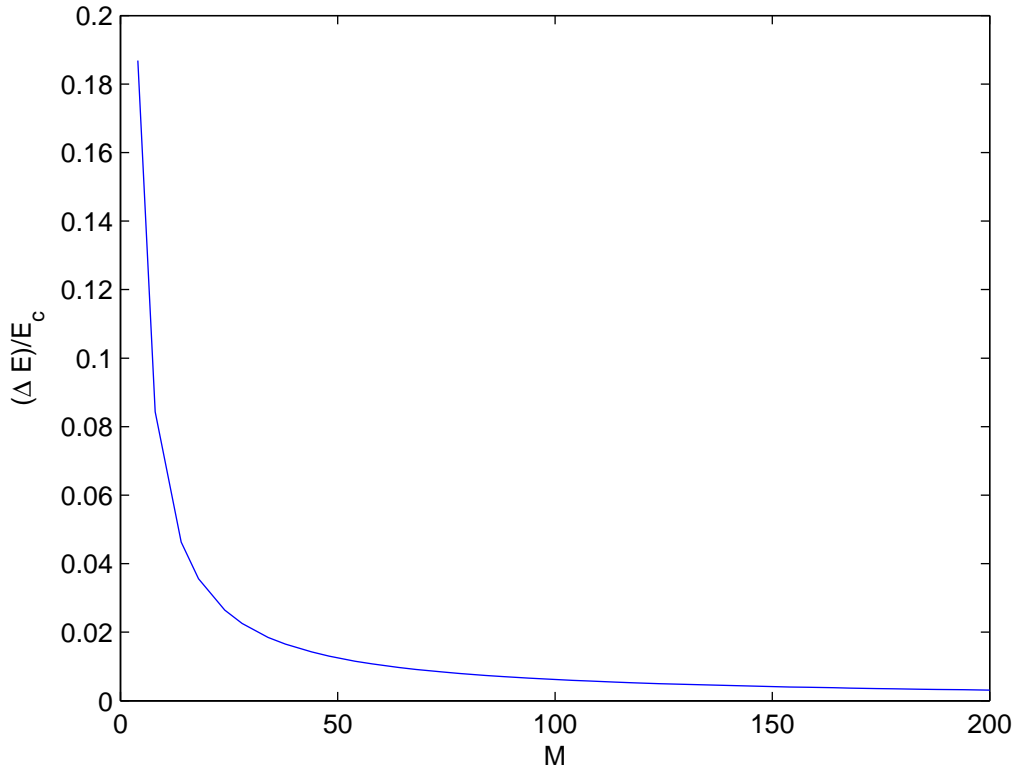
Figure 7. The energy difference ΔE between the Richardson and BCS ground states for the reduced Hamiltonian as a function of number of electron pairs M. The energies are in units of the condensation energy E_c and the system considered has $2M$ spin degenerate energy states equally distributed on interval $[0, 2\omega]$. The system has a coupling constant $g = -G/\omega = 1$.
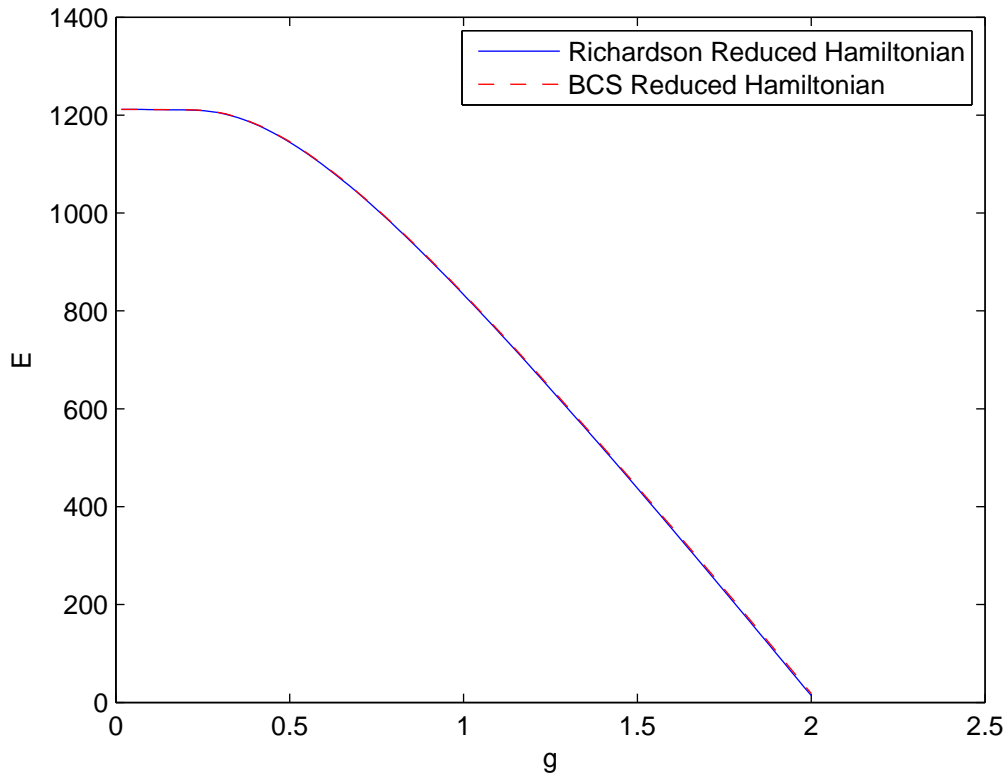
Figure 8. Energies of the BCS and Richardson model ground states with respect to the full and reduced BCS Hamiltonians as functions of the coupling $g = -GN/(V\omega)$, where ω is the Fermi energy and V the normalization volume. The system considered is a box-normalized three-dimensional system with $M = 16$ electron pairs, $N = 32$ spin-degenerate energy states. The energies are in units of ω.
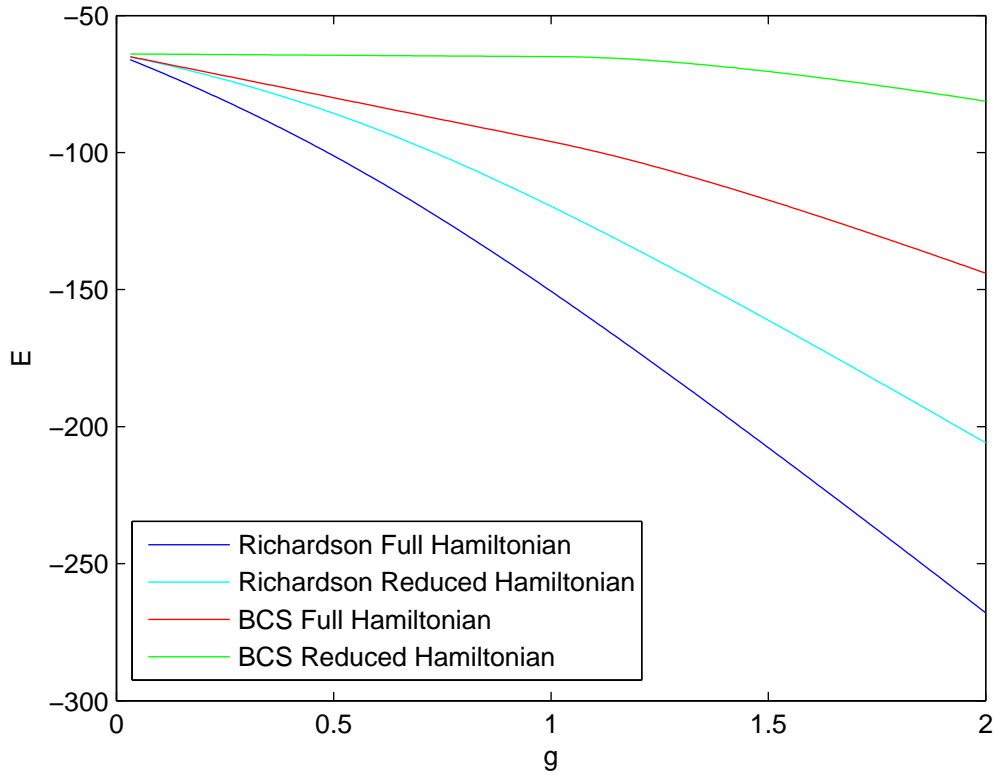
Figure 9. Energies of the BCS and Richardson model ground state with respect to the reduced BCS Hamiltonian as a function of the coupling $g = -GM/\epsilon$. The system considered is a two level system with $M = 32$ electron pairs, $N = 64$ spin-degenerate energy states, half with energy $-\epsilon$ and the rest with energy ϵ. The energies are expressed in units of ϵ.
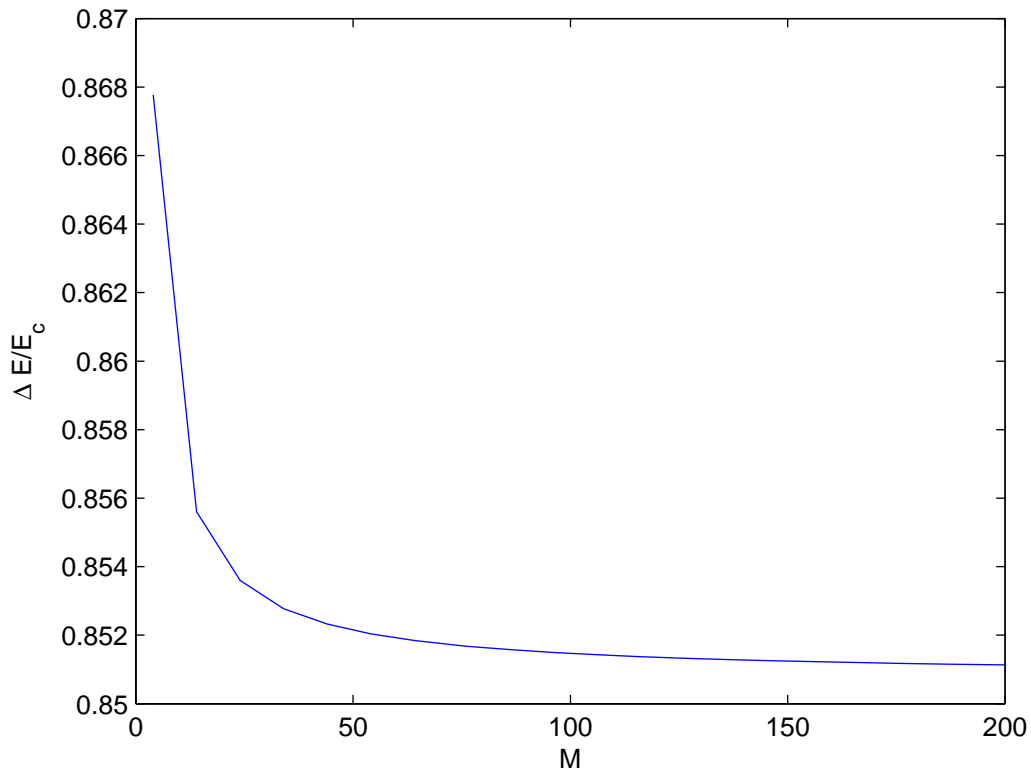
Figure 10. The energy difference ΔE between the Richardson and BCS ground states for the reduced Hamiltonian as a function of number of electron pairs M. The energies are in units of the condensation energy E_c and the system considered is a two level system where the states have energies $-\epsilon$ and ϵ and have degeneracy M. The system has a coupling constant $g = -GM/\epsilon = 1$.

6 Conclusions

I have calculated the expressions for the energies of the BCS model and Richardson model ground states with respect to both the full BCS Hamiltonian and the reduced BCS Hamiltonian. We also introduced a formula for the energy of any state with fixed number of electron pairs. We found that the difference between the two Hamiltonians is proportional to $M^2 - M$ for all paired states with fixed number of electrons. In the BCS model ground state there is in addition a term proportional to $\Delta^2/E_{\boldsymbol{k}}^2$.

Analytical comparison of the energies of the two model ground states is very difficult, as for most systems there are no known analytical solutions for the Richardson equations. For the Richardson model both energy expressions have the sum $\sum_l E_l$ as an important part, and as we have no analytical expression for the E_l, the analytical treatment can usually be done only on some limits, e.g. thermodynamic limit[20].

However, numerical comparison can be done for systems for which we can solve the Richardson equations numerically. From the numerical results we see that in the equally spaced systems and box normalized free electron systems the difference between the energies of the Richardson model ground state and the BCS model ground state are small or negligible, depending on the system size. In small systems there is a small difference, but with already $M = 100$ electron pairs the energies of the two models are practically indistinguishable. So based on this evidence we argue that the BCS model works well in the equally spaced system and the box normalized free electron system.

It is surprising that the BCS model seems to be nearly as good of a description as the Richardson model almost independent of the strength of the coupling and for very small number of particles already. With respect to the particle number we can see the expected trend that BCS model works better with a larger number of particles. However, we are missing the trend that BCS model would work better with small coupling strengths, which would have been possible because the BCS model is based on a mean-field approach.

The two-level system exhibits a clear difference between the two models, suggesting that Richardson model would be more accurate description of this system. This can be due to the two-level system being a very non-linear system, and so we would expect that linearising the fluctuations in the BCS model may give rise to a significant error.

Next it would be interesting to solve the Richardson equations for a flat-band system introduced in 1.2 and compare the ground state energies of the Richardson and BCS

ground states using the methods presented in this thesis. This comparison could possibly validate the expectation that the Richardson model describes the flat-band systems significantly better than the BCS model.

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