The Energy of Polarons and Bipolarons in Relation to High T_c Superconductivity

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Bachelor thesis

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Abstract

In this thesis we investigate the possibility of the formation of a bipolaron out of two polarons in a polarizable lattice. The formation of a bipolaron in such a lattice is thought to be a possible explanation for high T_c superconductivity. Based on classical electrostatics the energy of two mutually interacting polarizable particles is generalized to N interacting particles. This result has been used to device of a numerical simulation for the energy of a uniform square lattice and a CuO_2 lattice. Through these calculations it is found that only for a highly unlikely set of material parameters (such as the polarizability of the particles) it is possible to assimilate a bipolaron without having an external force to keep it together.

Contents

1 The unfamiliar realm of high T_c superconductivity

Ever since Kamerlingh Onnes discovered superconductivity in 1911 it has been one of the primal areas for physics research worldwide. Simply by lowering the temperature to the vicinity of absolute zero Onnes discovered that some materials lose all their resistivity and become superconductors. The ongoing research to this phenomenon has provided for countless surprises, applications and—how could it not be?—new questions. By 1956 Onnes' observations were explained by Bardeen, Schrieffer and Cooper in their BCS theory featuring Cooper pairs [1]. Whenever one electron passes through a lattice it causes a lattice vibration (or, more pointedly: "an electron-phonon interaction"), the classical explanation goes. In some cases it is advantageous for a second electron to trail the first one, albeit with opposite momentums. These two electrons are said to be a Cooper pair, and BCS theory explains how they facilitate superconductivity.

However, this theory also imposed a ceiling for the value of T_c, the critical temperature above which a material loses its interesting resistive properties and becomes an ordinary conductor. This prediction was violated in 1986 with the discovery of a new class of superconductors: the high T_c superconductors. Bednorz and Müller discovered that a Ba-La-Cu-O system under the right configuration could have a T_c of up to 35 K [2]. This cuprate caused a violation of the theory by only a couple of degrees, so it was not very quarrelsome from that prospect. A bigger threat for BCS theory was the fact that the lattice vibrations in this material did not influence the critical temperature whatsoever, so the explanation BCS theory gave did not apply. Ever since scientists around the world have been searching for an explanation, but to no avail.

The record for the value of T_c has been going up ever since with the ongoing discovery of new classes of superconductors, the most recent being the 2008 discovery of the FeAs (or: Fe-based pnictide) superconductors with a critical temperature of 43 K [3] (this is not the current record[1], by the way).

Up to date a lot of exciting new materials have been discovered; the problem of today is that a satisfying explanation is still lacking. Clearly, for reasons mentioned above, BCS theory cannot facilitate for the newly found superconducting classes. A few proposals have been done, though, one of them being an explanation through polarons in Fe-based pnictides [5, 6]. A polaron is formed when an electron is placed in a polarizable lattice and causes its surrounding particles to polarize. Now, if two of those electrons are present in such a lattice (assuming there is a large enough distance between the two such that the Coulomb interaction is negligible) two polarons are formed, costing twice the work. The question is what would happen to the total energy of the system when the two electrons are brought closer together, in such a manner that their Coulomb interaction grows tremendously but the work required for the polarization of the neighboring particles decreases. If this provides for an energy

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[1] The current record was set in 1995 and is thought to be 138 K [4].

win it means that it would be more favorable for two electrons to stick closely together, contrary to what one might think. The formation of such a bipolaron could be an analogue to Cooper pairs for the high T_c superconductors.

1.1 Goals and approach

The research reported in this thesis aims to apply the model of Sawatzky *et al.* for Fe-based pnictides to cuprates. In [5, 6] a quantum mechanical model is derived for the description of the energy of such a polaron/bipolaron configuration in a pnictide. This is then used to compare the energies of both situations and in such a manner form a model for superconductivity in this very material.

The two different material classes under discussion here (Fe-based pnictides and cuprates) seem somewhat comparable so it would make sense to investigate a possible application of the pnictide model to a cuprate lattice. This thesis focusses on the computation of the energy of such a system through the theories of classical electrostatics. Firstly, a relation for the energy of a dipole in an external field is derived, after which the energy of two polarizable particles interacting with each other is computed. This result will be used for a generalization to a system consisting of an unspecified number of particles. Using this penultimate result, an algorithm will be coded that enables the energy calculation of various types of systems, but most prominently the cuprate lattices.

2 The basics: The link between polarization and energy

Whenever a charged particle (a unipole[2] with charge q, for example) moves through a changing potential field (brought about by an electric field)x, work is required. Since any electric force field is conservative, a potential ϕ can be defined such that $\mathbf{E} = \nabla\phi$. This allows for a simplification to the the way work is calculated, since it consists formally of a path integral. Using the fundamental theorem of vector calculus[3] this integral simply transforms into the difference of the potential at begin- and endpoints. So the potential of a particle at any given moment equals the amount of work it took for it to get there from infinity, where the magnitude of the electric field (and thus the potential) generally equals zero.

So the work that is performed on the particle is stored in the form of the potential energy (V), this is not exactly equal to the potential ϕ mentioned above since the particle's charge has to be taken into account as well. It turns out the particle's potential energy V is related to the field's potential ϕ by

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[2] This is an interesting case of terminology; configurational moments ought to be named according to Latin cardinals (this is not always the case, though, "dipole" is Greek, for instance). In the case of a single charge there is no wide agreement on which term to use (not as wide as with "dipole"). Therefore a single charge will be referred to as a "unipole" here. Another, perhaps more pragmetic, reason to use "unipole" instead of "monopole" is to avoid confusion with the magnetic domain. (p. 44 of [7].)

[3] $W = -\int_P^Q q\mathbf{E}\cdot d\mathbf{s} = -\,q\int_P^Q \nabla\phi ds = -q\{\phi(Q) - \phi(P)\}$

$$V = q\phi. \tag{1}$$

This makes it possible to calculate the electrostatic energy stored in a particle that has found its way into a familiar potential field ϕ. From this result the energies of other types of moments (dipoles, quadrupoles, octupoles, &cetera) can be calculated, too, although this requires some more mathematical work (see pp. 92-93 of [7]). This results in the following expression for the potential energy of every imaginable particle, defined through a linear combination of electric moments,

$$V = q\phi(\mathbf{0}) + \mathbf{m}\cdot\nabla\phi(\mathbf{0}) + \mathbf{Q} : \nabla\nabla\phi(\mathbf{0}) + \cdots . \tag{2}$$

Here $\mathbf{m}$ and $\mathbf{Q}$ denote total dipole and quadrupole moments, respectively, and the double nabla is a tensor[4]. The function ϕ and its gradients are evaluated at the origin, which is defined as the center of mass of the particle. Of course, the series extends indefinitely with higher order multipole moments, and thus allows for a description of every possible particle.

Provided that this form of energy is the only relevant one the relation allows us to compute the total amount of energy stored in configurations of point charges, charged volumes and charged surfaces.

2.1 The total energy of an ideal dipole

Since almost all particles are polarizable to some extent, the electrostatic energy as proposed in eq. (1) is never the only form of (electric) energy present: the polarization of something takes work, too. A suitable example is an atom placed in a uniform field, the field will cause the negatively charged electron cloud and the positively charged nucleus to shift with respect to one another. Since this new formation is not the most favorable one energetically speaking, work has to be performed. The question is, how much?

Let us suppose for now that all concerned particles are linearly polarizable dipoles. This means that the total induced dipole moment[5] $\mathbf{p}$ (defined as the difference between the total dipole moment $\mathbf{m}$ and the permanent dipole moment $\boldsymbol{\mu}$) is linked to the external field $\mathbf{E}_0$ by

$$\mathbf{p} = \alpha\mathbf{E}_0 \tag{3}$$

where α is a scalar called the *polarizability*. This is a reasonable assumption since the displacement of the electron cloud with regards to the atom nucleus is

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[4] There is a subtle difference between $\nabla\nabla$ and $\nabla^2 = \nabla\cdot\nabla$ which is the divergence of the gradient, so it is important not to confuse the two. As is said, the double nabla operator is a tensor, or a covariant, derivative. In this case it is a three-by-three matrix conceived of by vector-multiplying two nablas.

[5] There may seem to be a conflict in the terminology used here, eq. (3) shows what is generally agreed to be the *polarization* instead of the *dipole moment*. In principle these are two different quantities. However, the polarization is defined as the ratio of the dipole moment and the volume it occupies. Throughout this thesis a unit cell of size 1 is considered, so there is virtually no difference. Hence the two terms will be used interchangeably.

linearly dependent on the external field for low values of $\mathbf{E}_0$. It should be noted, though, that an atom practically never behaves like the ideal dipole described here. Generally, the polarization moment of any particle can be described as a linear combination of unipoles, dipoles, quadrupoles, and so on, but this will be considered later on.

Now the total work required to assemble a certain configuration can be said to be built up out of two parts: $W_{tot} = V + W_{pol}$ where W_{pol} denotes the polarization work. When the system reaches equilibrium $dW_{tot} = 0$ and so $dW_{pol} = -dV$. The right-hand side of the last equation can be related to $d\mathbf{p}$ and then integration gives the expression for W_{pol} we have been looking for, namely

$$W_{pol} = \frac{1}{2}\mathbf{p} \cdot \mathbf{E_0} \tag{4}$$

A much more elaborate derivation of eq. (4) is given on pp. 110-111 of [7]. The potential of an ideal dipole moment is given by $V = -\mathbf{m} \cdot \mathbf{E_0}$ (cf. eq. 2); combining this with the fact that the total dipole moment $\mathbf{m}$ is the sum of induced, and permanent moments $\mathbf{p}$ and $\boldsymbol{\mu}$ it is found that

$$W_{tot} = -(\mathbf{p} + \boldsymbol{\mu}) \cdot \mathbf{E_0} + \frac{1}{2}\mathbf{p} \cdot \mathbf{E_0}$$

or, rewriting using eq. (3) gives

$$W_{tot} = -\boldsymbol{\mu}{\cdot}\mathbf{E_0} - \frac{1}{2}\alpha E_0^2. \tag{5}$$

2.2 Interaction energy between non-polarizable particles

One of the assumptions that has been made up to this point is that all particles interact with some kind of (uniform) external field $\mathbf{E_0}$. In reality, however, situations where two particles interact with *each other* are much more common. And therefore it is worthwhile to device of a way to calculate the work required to bring one particle in another's field. For completeness' sake a particle is not *just* a unipole or dipole from this moment on, but rather an unspecified combination of all possible multipole moments.

Analogously to what has been done before the work that is required for a particle (particle 1) to move into the field of another (particle 2) can be calculated by eq. (2), the only difference being that the potential is caused a particle instead of an external field. Calculating the potential of particle 2 by using what has been derived so far causes the origin to shift to the center of mass of this particle, which is not desirable because the potential at the site of particle 1 is what matters. This means a coordinate transformation is necessary, ultimately resulting the following relation for the energy:

$$W_{12} = q_1\phi_2(\mathbf{0}) - \boldsymbol{\mu}_1 \cdot \nabla\phi_2(\mathbf{0}) + \boldsymbol{\Theta}_1 : \nabla\nabla\phi_2(\mathbf{0}) - \cdots , \tag{6}$$

where the $\mathbf{0}$ vector now denotes the origin as defined by the first particle's center of mass. (A much more thorough discussion on the origin of the minus signs is provided on pp. 114-115 of [7].)

An expression for ϕ_2 in terms of the multipole moments can be derived and substituted to eq. (6) in order to derive a formula where the required work W_{12} is solely expressed in terms of the particles' multipole moments. The result is rather bulky and has therefore been omitted here. It *does* show, however, which multipole interactions are of importance. The charge-charge interaction, for example, will always be dominant, whereas the dipole-quadrupole interaction is irrelevant at almost any scale since it falls off with r^{-4}.

Later, the total interaction between two dipoles will turn out to be rather important. The energy belonging to such a configuration is given by

$$W_{12} = \frac{e_1 e_2}{s} + (e_1 \boldsymbol{\mu_1} - e_2 \boldsymbol{\mu_2}) \cdot \nabla \frac{1}{s} - \boldsymbol{\mu_1} \boldsymbol{\mu_2} : \nabla\nabla \frac{1}{s}. \tag{7}$$

Here s equals the distance between both particles.

2.3 Interaction energy between polarizable particles

For a complete description of the interaction energy between particles, polarization should be taken into account as well. This is a very mathematical routine. It starts by noting that the induced polarization at the one particle is linearly dependent on the field of the other, whereafter polarization-work terms can be added to the equation for W_{12} discussed above. For two polarizable dipoles (with total moment $\mathbf{m_i}$ and induced moment $\mathbf{p_i}$) the total energy is equal to

$$W_{12} = \frac{e_1 e_2}{s} + (e_1 \mathbf{m_2} - e_2 \mathbf{m_1}) \cdot \nabla \frac{1}{s} - \mathbf{m_1} \mathbf{m_2} : \nabla\nabla \frac{1}{s} + \frac{1}{2} \mathbf{p_1} \cdot \mathbf{E_2}(\mathbf{0}) + \frac{1}{2} \mathbf{p_2} \cdot \mathbf{E_1}(\mathbf{s}). \tag{8}$$

Note that the permanent dipole moments $\boldsymbol{\mu_i}$ from eq. (7) have simply been replaced with total moments $\mathbf{m_i}$, this is allowed because the character of a dipole moment does not matter for the interaction energy.

This equation might look "finished," but unfortunately an induced dipole moment depends on other (induced) dipole moments. So in order to get an analytic expression for this energy both induced dipole moments ought to be expressed in terms of polarizabilities and distances. This is done on pp. 120-121 of [7] through a fairly complicated but comprehensible substitution process.

The result is an expression for W_{12} covering any possible configuration of two dipoles or unipoles in terms of the particles' respective moments. It has been included underneath, but for brevity reasons the permanent dipole moments have been set to 0.

$$W_{12} = \frac{A_2}{A_4} \frac{e_1 e_2}{s} - \frac{1}{2 A_4 s^4} (\alpha_1 e_2^2 + \alpha_2 e_1^2) \tag{9}$$

Here $A_n = 1 - n \alpha_1 \alpha_2 / s^6$ and s denotes the distance between particles 1 and 2. This relation makes for a rather powerful tool for calculating the energy in a

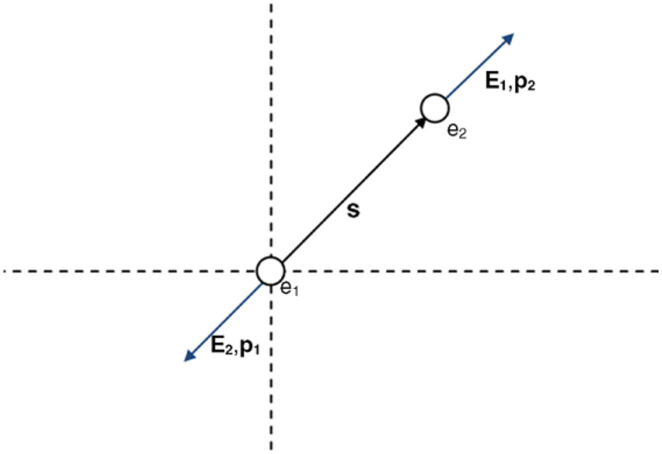

Figure 1: Rough sketch of a configuration of two polarizable particles with charges e_1 and e_2. The (initial) field vectors of both particles have been drawn at the relevant place.

number of configurations; for example two molecules that are brought together (approximated as two dipoles) or an atom and an electron (a dipole and an unipole.)

Eq. (9) is one way of simplifying eq. (8). It is a very neat expression of the energy of two polarizable particles only in terms of their respective charges and polarizabilities. But if one does not really care about ending up with an expression that still includes dipole moments and field strengths that depend on one another, a different approach can be taken. Analytically this is disastrous, for solving it in terms of charegs and polarizabilites will become nearly impossible. Numerical algorithms, however, make it possible to calculate all the relevant variables up to a certain accuracy, so it can be useful in another way.

From here on the permanent dipole $\boldsymbol{\mu_i}$ will be set to zero, doing this simplifies everything tremendously and in later applications it will be considered zero anyway. The field strengths $\mathbf{E_2(0)}$ and $\mathbf{E_1(s)}$ (see fig. 1 for a sketch) are the factors that can be fairly easily expressed in terms of the particles themselves. Knowing that both fields are composed of an individual charge and a dipole moment they can be written as

$$\begin{aligned}\mathbf{E_2}(\mathbf{0}) &= e_2\nabla\frac{1}{s} + \mathbf{p_2}\cdot\nabla\nabla\frac{1}{s} \\ \mathbf{E_1}(\mathbf{s}) &= -e_1\nabla\frac{1}{s} + \mathbf{p_1}\cdot\nabla\nabla\frac{1}{s}.\end{aligned} \tag{10}$$

The minus sign in the second expression serves to get the direction of the field right. Plugging these back into eq. (8) and simplifying gives

$$\begin{aligned} W_{12} &= \frac{e_1 e_2}{s} + (e_1\mathbf{p_2} - e_2\mathbf{p_1})\cdot\nabla\frac{1}{s} - \mathbf{p_1}\mathbf{p_2} : \nabla\nabla\frac{1}{s} + \frac{1}{2}e_2\mathbf{p_1}\cdot\nabla\frac{1}{s} + \\ &\quad + \frac{1}{2}\mathbf{p_1}\mathbf{p_2} : \nabla\nabla\frac{1}{s} - \frac{1}{2}e_1\mathbf{p_2}\nabla\frac{1}{s} + \frac{1}{2}\mathbf{p_1}\mathbf{p_2} : \nabla\nabla\frac{1}{s} \qquad (11) \\ &= \frac{e_1 e_2}{s} + \frac{1}{2}\mathbf{p_2}\nabla\frac{e_1}{s} - \frac{1}{2}\mathbf{p_1}\nabla\frac{e_2}{s} \\ &= \frac{e_1 e_2}{s} - \frac{1}{2}\mathbf{p_2}\cdot\mathbf{E^b_{21}} - \frac{1}{2}\mathbf{p_1}\cdot\mathbf{E^b_{12}}. \qquad (12) \end{aligned}$$

In the last line $\mathbf{E^b_{ij}}$ denotes the so called "bare field" caused by particle j, experienced by i. This is the initial field, caused only by Coulomb contributions from single charges, so it does not include any effects arising from the polarized particles. The last step can perhaps be understood by comparing this to the first terms in eqs. (10) which denote this "bare field." Intuitively the ultimate result might feel a little strange since it only includes Coulomb contributions and product term of the polarization that interacts with the bare field. The explanation is, however, that the dipole interaction terms dropped out when the correct expression for the **E**-field was plugged in. It should be noted that the real field, $\mathbf{E_{ij}}$, still has influence, despite the fact it may have disappeared from the equation. It is stil included in $\mathbf{p_i}$ since the polarization is the polarizability times the real field.

This is a very interesting expression since it expresses the total energy in terms of the initial fields. An important question is, though, whether this same approach can be used for more particles.

3 Deriving an equation for three dipoles

The approach used in [7] works very well for two particles: eq. (9) provides for an easy way to calculate the energy of such a two-particle system if their polarizations, charges and separating distance is known. Unfortunately it is rather hard to extend this expression to describe configurations consisting of more particles. Expression (8), however, looks much more "tweakable," so to speak, and if it would be possible to derive an expression that looks like eq. (12) for more particles from this it would tremendously improve simplicity. In order to this, though, we need to generalize the way eq. (8) was derived so that somewhere along the way more particles can be added. For now the total number will be limited to three, this will - later on - allow for expansion to a number of N particles.

The first thing that has to be changed is the coordinate system. The approach that is used in [7] chooses the center of mass of either of the two particles as the origin. This will not work anymore when expanding to more particles since there are multiple interactions. Therefore an arbitrary origin has to be chosen, such that the vector $\mathbf{r_i}$ gives the position of particle i with respect to that origin. As can be observed from eq. (8) distances between particles are important, there they are denoted by the letter s, from now on $\mathbf{r_{ij}}$ defined as

$$\mathbf{r_{ij}} \equiv \mathbf{r_j} - \mathbf{r_i}$$

will give us inter-particle distances. Note that this vector points from spot i to j. (And on a side note: whenever the non-bold r_{ij} is used this will describe the scalar length of this very vector, and $\mathbf{\hat{r}_{ij}}$ denotes the unit vector in the direction of $\mathbf{r_{ij}}$.)

Having defined a coordinate system we can go on and start calculating the energy. First the "potential" contribution will be derived (due to Coulomb interactions and the like) after which the polarization part (see eq. (4)) will be added.

In order to calculate the amount of potential energy that is present the amount of work required for the assembly of the system will be summed, giving the total amount of energy that went into it. So at first there is just one particle, then a second one is added; this costs work (given by eq. (7)) since it interacts with the first particle and is a contribution to the total potential energy. Then the third particle is brought in which - interacting with the first two particles - will give the last contribution.

The work required to get the third particle in place is given by

$$W_3 = e_3\phi_{12}(\mathbf{r_3}) + \mathbf{p_3}\cdot\nabla\phi_{12}(\mathbf{r_3}), \tag{13}$$

which is largely analogous to eq. (6). The potential $\phi_{12}(\mathbf{r})$ caused by the first two particles is somewhat more complicated since it is the sum of both Coulomb and dipole contributions. Evaluated at $\mathbf{r_3}$, it equals

$$\begin{aligned} \phi_{12}(\mathbf{r_3}) &= \frac{e_1}{r_{13}} + \frac{e_2}{r_{23}} + \frac{\mathbf{p_1}\cdot\mathbf{\hat{r}_{13}}}{r_{13}^2} + \frac{\mathbf{p_2}\cdot\mathbf{\hat{r}_{23}}}{r_{23}^2} \\ &= \frac{e_1}{r_{13}} + \frac{e_2}{r_{23}} - \mathbf{p_1}\cdot\nabla\frac{1}{r_{13}} - \mathbf{p_2}\cdot\nabla\frac{1}{r_{23}}. \end{aligned}$$

Substituting this back into eq. (13) gives

$$\begin{aligned} W_3 &= \frac{e_1e_3}{r_{13}} + \frac{e_2e_3}{r_{23}} - e_3\mathbf{p_1}\cdot\nabla\frac{1}{r_{13}} - e_3\mathbf{p_2}\cdot\nabla\frac{1}{r_{23}} + e_1\mathbf{p_3}\cdot\nabla\frac{1}{r_{13}} + e_2\mathbf{p_3}\cdot\nabla\frac{1}{r_{23}} - \\ &\quad -\mathbf{p_1p_3} : \nabla\nabla\frac{1}{r_{13}} - \mathbf{p_2p_3} : \nabla\nabla\frac{1}{r_{23}} \\ &= \frac{e_1e_3}{r_{13}} + \frac{e_2e_3}{r_{23}} + (e_1\mathbf{p_3} - e_3\mathbf{p_1})\cdot\nabla\frac{1}{r_{13}} + (e_2\mathbf{p_3} - e_3\mathbf{p_2})\cdot\nabla\frac{1}{r_{23}} - \\ &\quad -\mathbf{p_1p_3} : \nabla\nabla\frac{1}{r_{13}} - \mathbf{p_2p_3} : \nabla\nabla\frac{1}{r_{23}}. \end{aligned}$$

This expression for the potential energy of particle three looks a remarkable lot like eq. (7) which is not very strange since they describe very comparable situations. In order to get the *total* energy the two of them have to be added together along with some polarization terms, so $W_{tot} = W_{12} + W_3 + W_{pol,1} + W_{pol,2} + W_{pol,3}$, resulting in

$$\begin{aligned}
W_{tot} &= \frac{e_1e_2}{r_{12}} + \frac{e_1e_3}{r_{13}} + \frac{e_2e_3}{r_{23}} + (e_1\mathbf{p_2} - e_2\mathbf{p_1}) \cdot \nabla\frac{1}{r_{12}} + (e_1\mathbf{p_3} - e_3\mathbf{p_1}) \cdot \nabla\frac{1}{r_{13}} + \\
&\quad +(e_2\mathbf{p_3} - e_3\mathbf{p_2}) \cdot \nabla\frac{1}{r_{23}} - \mathbf{p_1}\mathbf{p_2} : \nabla\nabla\frac{1}{r_{12}} - \mathbf{p_1}\mathbf{p_3} : \nabla\nabla\frac{1}{r_{13}} - \\
&\quad -\mathbf{p_2}\mathbf{p_3} : \nabla\nabla\frac{1}{r_{23}} + \frac{1}{2}\mathbf{p_1} \cdot \mathbf{E_1}(\mathbf{r_1}) + \frac{1}{2}\mathbf{p_2} \cdot \mathbf{E_2}(\mathbf{r_2}) + \frac{1}{2}\mathbf{p_3} \cdot \mathbf{E_3}(\mathbf{r_3}).
\end{aligned}$$

Fortunately some simplifications can be made by plugging in the appropriate expressions for the electric fields on the last line. They look a lot like eqs. (10), the only difference being the fact that there are now three equations[6] that each account for two particles. Plugging them in and rearranging everything allows for simplification again:

$$\begin{aligned}
W_{tot} &= \frac{e_1e_2}{r_{12}} + \frac{e_1e_3}{r_{13}} + \frac{e_2e_3}{r_{23}} + \frac{1}{2}(e_1\mathbf{p_2} - e_2\mathbf{p_1}) \cdot \nabla\frac{1}{r_{12}} + \\
&\quad +\frac{1}{2}(e_1\mathbf{p_3} - e_3\mathbf{p_1}) \cdot \nabla\frac{1}{r_{13}} + \frac{1}{2}(e_2\mathbf{p_3} - e_3\mathbf{p_2}) \cdot \nabla\frac{1}{r_{23}} \\
&= \frac{e_1e_2}{r_{12}} + \frac{e_1e_3}{r_{13}} + \frac{e_2e_3}{r_{23}} - \frac{1}{2}\mathbf{p_2} \cdot \mathbf{E^b_{21}} - \frac{1}{2}\mathbf{p_1} \cdot \mathbf{E^b_{12}} - \\
&\quad -\frac{1}{2}\mathbf{p_3} \cdot \mathbf{E^b_{31}} - \frac{1}{2}\mathbf{p_1} \cdot \mathbf{E^b_{13}} - \frac{1}{2}\mathbf{p_3} \cdot \mathbf{E_{32}} - \frac{1}{2}\mathbf{p_2} \cdot \mathbf{E^b_{23}}. \qquad (14)
\end{aligned}$$

Surprisingly, the bare electric fields allow for a simplification again. There seems to be a very predictable pattern in this: all possible combinations of bare fields are present. The challenge now, is to generalize this even further to an unspecified number of particles.

4 Calculating the energy of a configuration of N dipoles

Since every particle interacts with every other particle the "$N = 3$ model" as shown in eq. (14) would not be of much use. Fortunately a very similar approach can be taken to arrive at an expression for N particles.

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[6] For completeness's sake they have been included here

$$\begin{aligned}
\mathbf{E_1}(\mathbf{r_1}) &= e_2\nabla\frac{1}{r_{12}} + \mathbf{p_2} \cdot \nabla\nabla\frac{1}{r_{12}} + e_3\nabla\frac{1}{r_{13}} + \mathbf{p_3} \cdot \nabla\nabla\frac{1}{r_{13}} \\
\mathbf{E_2}(\mathbf{r_2}) &= -e_1\nabla\frac{1}{r_{12}} + \mathbf{p_1} \cdot \nabla\nabla\frac{1}{r_{12}} + e_3\nabla\frac{1}{r_{23}} + \mathbf{p_3} \cdot \nabla\nabla\frac{1}{r_{23}} \\
\mathbf{E_3}(\mathbf{r_3}) &= -e_1\nabla\frac{1}{r_{13}} + \mathbf{p_1} \cdot \nabla\nabla\frac{1}{r_{13}} - e_2\nabla\frac{1}{r_{23}} + \mathbf{p_2} \cdot \nabla\nabla\frac{1}{r_{23}}.
\end{aligned}$$

Let us start by observing that the total energy of this system equals $W_{tot} = \sum_{i=1}^{N} W_{pot,i} + W_{pol,i}$ where $W_{pot,i}$ is the work it took to bring particle i in to the configuration of all the $i-1$ particles that were present before him. Then by the conventional definition (cf. eqs. (2), (6) and (13))

$$W_{pot,i} = e_i\phi_i(\mathbf{r_i}) + \mathbf{p_i}\cdot\nabla\phi_i(\mathbf{r_i}),$$

where $\phi_i(\mathbf{r_i})$ equals the potential caused by all the particles $1,\cdots,i-1$, of course. This potential can be written as the following sum

$$\phi_i = \sum_{j=1}^{i-1}(\frac{e_j}{r_{ij}} + \frac{\mathbf{p_j}\cdot\hat{\mathbf{r_{ij}}}}{r_{ij}^2}).$$

Contrary to the potential energy of the i-th particle, the polarization work depends on *all* other particles. (This is because the **E**-field[7] in the expression depends on all the other particles.) The **E**-field experienced by particle i is derived to be

$$\mathbf{E_i}(\mathbf{r_i}) = \sum_{j=1}^{i-1}(-e_j\nabla\frac{1}{r_{ij}} + \mathbf{p_j}\cdot\nabla\nabla\frac{1}{r_{ij}}) + \sum_{j=i+1}^{N}(e_j\nabla\frac{1}{r_{ij}} + \mathbf{p_j}\cdot\nabla\nabla\frac{1}{r_{ij}}). \tag{15}$$

The polarization work still equals $W_{pol,i} = \frac{1}{2}\mathbf{p_i}\cdot\mathbf{E_i}(\mathbf{r_i})$ so an expression for W_{tot} is almost there. Like before terms cancel against one another (for example the dipole-dipole interaction term), and because this happens in the very same manner as it did for three particles this part has been omitted here.

Ultimately - and how elegant is this expression? - W_{tot} is given by

$$W_{tot} = \sum_{i=1}^{N}\sum_{j=1}^{i-1}(\frac{e_ie_j}{r_{ij}} + \frac{1}{2}e_j\mathbf{p_i}\cdot\nabla\frac{1}{r_{ij}} - \frac{1}{2}e_i\mathbf{p_j}\cdot\nabla\frac{1}{r_{ij}}).$$

Observing that the “bare field approach[8]” can be taken again this equation can be simplified even more into

$$W_{tot} = \sum_{i=1}^{N}\sum_{j=1}^{i-1}(\frac{e_ie_j}{r_{ij}} - \frac{1}{2}\mathbf{p_i}\cdot\mathbf{E^b_{ij}} - \frac{1}{2}\mathbf{p_j}\cdot\mathbf{E^b_{ji}}). \tag{16}$$

It might seem a little strange that j runs from 1 to $n-1$. Conceptually this can be explained by not willing to count terms twice, the last two terms, however,

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[7] Watch out, here the *final* field is meant again. The bare field will make its comeback later.

[8] If unsure about the sign change this simplification brings to the second term, then cf. eq. (15). Here it says that the bare field caused by particle j at site i gets a negative sign for $j < i$, which is the case here.

are counted twice within the summation. Therefore it can be simplified further,

$$\begin{aligned} W_{tot} &= \sum_{i=1}^{N}\sum_{j=1}^{i-1}\frac{e_i e_j}{r_{ij}} - \\ &-\frac{1}{2}\sum_{i=1}^{N}\mathbf{p_i}\cdot(\mathbf{E^b_{i,1}}+\mathbf{E^b_{i,2}}+\cdots+\mathbf{E^b_{i,i-1}}+\mathbf{E^b_{i,i+1}}+\cdots+\mathbf{E^b_{i,N}}), \end{aligned} \tag{17}$$

providing

$$\boxed{W_{tot} = \sum_{i=1}^{N}\sum_{j=1}^{i-1}\frac{e_i e_j}{r_{ij}} - \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}\mathbf{p_i}\cdot\mathbf{E^b_{ij}}.} \tag{18}$$

Eq. (18) relates the total work to all the degrees of freedom that are allowed in a polarizable lattice, therefore it is the main analytical result of this thesis. It might be a somewhat more logical expression than eq. (17), since the field that is multiplied with $\mathbf{p_i}$ is now the sum over all “bare” contributions. The Coulomb sum is still the same, for charge-charge interactions ought not be counted twice. To show that this result is still somewhat dependant of the actual field $\mathbf{E_{ij}}$ instead of just the bare field $\mathbf{E^b_{ij}}$ the polarization $\mathbf{p_i}$ could be rewritten using $\mathbf{p_i} = \alpha\mathbf{E_{ij}}$, but it will be left to the reader to do this.

5 The road to dimensionless quantities

The structure of eq. (18) suggests that the energy of a certain system satisfying all the conditions can be calculated numerically. Later an algorithm will be written to calculate all one could possibly want to know about the type of system described above. But before actually doing so, it is important to carefully consider the relationship between the physical quantities that were dealt with earlier on, and their dimensionless counterparts that will be used in the code. That is what will be taken into consideration during this section.

In order to calculate all the dimensionless expressions for all the relevant variables need to be derived. Since this is not completely trivial this process will be described here.

Let us start with the expression for the Coulomb interaction energy between two electrons. The physical value of this energy is given by

$$W_{cou} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}, \tag{19}$$

where r represents the distance between respective electrons and all the other values in play are constants. This expression can be translated into a dimensionless number relatively easy, for r can be written in terms of a dimensionless[9]

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[9] Dimensionless quantities are denoted by placing a tilde ($\tilde{}$) above the physical quantity.

distance $\widetilde{r}$ using the lattice constant a such that $r = a\widetilde{r}$. Substituting this into expression (19) leaves us with

$$W_{cou} = \frac{e^2}{4\pi\epsilon_0 a}\frac{1}{\widetilde{r}}.$$

Since all the factors before the dimensionless $1/\widetilde{r}$ are constants, the dimensionless counterpart of W_{cou} equals

$$\widetilde{W}_{cou} = \frac{1}{\widetilde{r}}, \tag{20}$$

where W_{cou} and $\widetilde{W}_{cou}$ are related by

$$W_{cou} = \frac{e^2}{4\pi\epsilon_0 a}\widetilde{W}_{cou}. \tag{21}$$

This is the first quantity of interest to the algorithm; the others are the polarization $\mathbf{p}$, the polarization energy W_{pol}, the electric field $\mathbf{E}$ and the polarizability α. They are all related through expressions (3) and (4), which will make the "undimensionalization" easy.

The relation between $\mathbf{E}$ and $\widetilde{\mathbf{E}}$ is fairly straightforward and analogous to what was just done for the Coulomb interaction energy. The physical electric field of an electron is given by

$$\mathbf{E} = \frac{e}{4\pi\epsilon_0}\frac{\hat{\mathbf{r}}}{r^2} = \frac{e}{4\pi\epsilon_0}\frac{\mathbf{r}}{r^3},$$

and thus making the various occurrences of r dimensionless again this transforms into

$$\mathbf{E} = \frac{e}{4\pi\epsilon_0 a^2}\frac{\widetilde{\mathbf{r}}}{\widetilde{r}^2}.$$

And so the dimensionless $\widetilde{\mathbf{E}}$ will be given by

$$\widetilde{\mathbf{E}} = \frac{\widetilde{\mathbf{r}}}{\widetilde{r}^2}.$$

Substituting this into the dimensionless flavor of eq. (3) ($\widetilde{\mathbf{p}} = \widetilde{\alpha}\widetilde{\mathbf{E}}$) the relations between the physical polarizability and polarization and their dimensionless counterparts can be found. This goes as follows:

$$\begin{aligned}
\widetilde{\mathbf{p}} &= \widetilde{\alpha}\widetilde{\mathbf{E}} \\
\widetilde{\mathbf{p}} &= \widetilde{\alpha}\frac{\mathbf{E}}{\frac{e}{4\pi\epsilon_0 a^2}} \\
\widetilde{\mathbf{p}} &= \frac{4\pi\epsilon_0 a^3}{ea}\widetilde{\alpha}\mathbf{E} \\
ea\widetilde{\mathbf{p}} &= 4\pi\epsilon_0 a^3\widetilde{\alpha}\mathbf{E}.
\end{aligned}$$

This last line should be equivalent to the original, physical eq. (3), which is only possible if

$$\mathbf{p} = ea\widetilde{\mathbf{p}} \tag{22}$$

and if

$$\alpha = 4\pi\epsilon_0 a^3 \widetilde{\alpha}. \tag{23}$$

Therefore, these are the relations between the physical polarizability and polarization, and their dimensionless counterparts.

The only physical quantity left is the polarization energy W_{pol}. Using the dimensionless alternative to relation (4) this goes as follows,

$$\begin{aligned}
\widetilde{W}_{pol} &= \frac{1}{2}\widetilde{\mathbf{p}} \cdot \widetilde{\mathbf{E}} \\
\widetilde{W}_{pol} &= \frac{1}{2}\frac{\mathbf{p}}{ea} \cdot \frac{\mathbf{E}}{\frac{e}{4\pi\epsilon_0 a^2}} = \frac{1}{2}\frac{4\pi\epsilon_0 a}{e^2}\mathbf{p} \cdot \mathbf{E} \\
\frac{e^2}{4\pi\epsilon_0 a}\widetilde{W}_{pol} &= \frac{1}{2}\mathbf{p} \cdot \mathbf{E}.
\end{aligned}$$

Using the same argument as before this leads to the conclusion that

$$W_{pol} = \frac{e^2}{4\pi\epsilon_0 a}\widetilde{W}_{pol} \tag{24}$$

which carries the same factor as the conversion relation of $\widetilde{W}_{cou}$ (eq. (21)) which is very fortunate since this means they can be freely subtracted and added to one another in the numerical code[10].

6 Putting theory into practice: Modeling a 2D layer

Now that all the ingredients for a correctly functioning algorithm have been derived we can actually start thinking about writing the code. For a start, the algorithm's function will be to calculate the energy of a two dimensional atomic lattice with uniform polarization α (since we are now headed off into the numerical world all quantities will be dimensionless unless stated otherwise). The atoms themselves are assumed to have no permanent polarization μ so all the above will apply. In order to induce some polarization two free electrons will be programmed into the lattice as well.

The script itself has been omitted here for it will not add a lot of value, however, for those interested copy of the code used for the calculation described

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[10] In the code something like $\widetilde{W}_{cou} - \widetilde{W}_{pol}$ will be done. In order to interpret those values they should be converted to physical entities, meaning a multiplication with a certain conversion factor. In this case this factor is the same for both terms, meaning they are fully comparable, both in the numerical and in the physical regime.

in §6.2 has been included in the appendix. The workings of the code in general will briefly be explained here.

Immediately after the moment the system comes into being there is no polarization whatsoever and the only energy present is given by the interaction between the electrons. This starting energy (which equals the first few terms of eq. (18)) will stay the same all the time; the contribution of the polarization terms will be subtracted at a later time. After having calculated the energy the algorithm moves on to calculate the initial field strengths and induced polarizations due to the electrons at all the sites. The now polarized atoms will start to interact with each other, cause each other to polarize even further. This is, of course, an effect that iterates infinitely and can only be approached using numerical methods. This is done by comparing the change in the polarization of one particle after each run for a number of times until the system has converged enough.

Then the “final” polarization of each particle is known and eq. (18) can be used to calculate the total energy of the system. $\mathbf{E}^{\mathbf{b}}_{\mathbf{ij}}$ is, of course, the bare field which is caused only by the electrons. This has been taken into account.

6.1 A uniform system

The model sketched here enables us to draw some conclusions about whether it is favorable for electrons to stick closer together in a lattice like this or to stay further apart. In the model system described above it has been found that a bigger distance between electrons is energetically more favorable. So apparently the Coulomb interaction term dominates over the polarization contributions every time. But what is the influence of the polarizability α? Because the higher the value of this constant, the more the system will polarize, and the higher the polarization energy will be. The algorithm has been run for a range of values of α, varying between 0 and 0.16. For values above the latter the system becomes unstable; this is caused by the dipoles that influence one another, for high values of α this interaction does not converge so the algorithm never stops. Actually this is a result of the ferro-electric mean field explanation, meaning that under certain conditions a material’s polarization can be maintained by itself, and no external field is necessary. This is something different from permanent polarization, since it has to be induced.

In this case two systems of 25-by-25 sites on a square latice have been simulated. The value of the total energy of the system a function of α is shown in fig. 2. In the left plot the two electrons are separated from one another, and in the figure in the middle they are closer together.

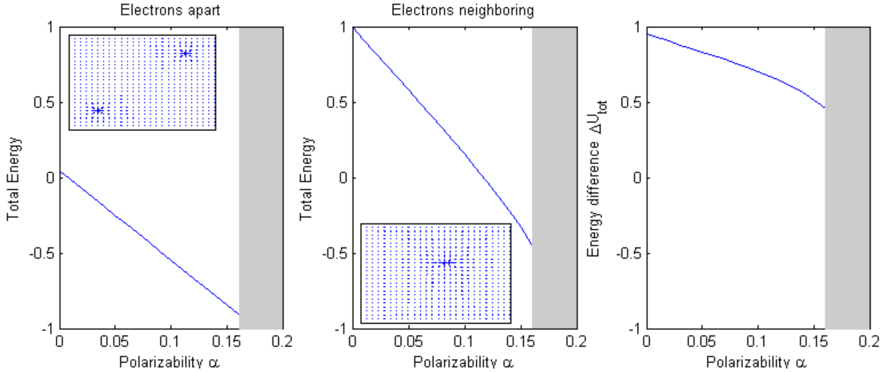


Figure 2: Total energy as a function of the polarizability (blue line) for the two systems (inset). The system where the electrons are far apart and do not interact with one another is on the left, and the system where the electrons are neighboring is in the middle. The regime where α causes an instability is depicted as well (shaded gray). On the right the energy difference (defined as the energy of the neighboring configuration minus the separated configuration) between the two configurations has been plotted.

This leads to the interesting conclusion that for a select range of polarizability, a system with two neighboring electrons exhibits a negative total energy; basically meaning it is energetically possible to have bipolarons in the system. Although the plot of the energy difference on the right shows it is at no time more favorable for electrons to be neighboring, but further elaboration on this conclusion will be postponed until later on, after the same approach has been applied to a more realistic lattice of CuO_2.

6.2 A copper oxide lattice

The approach laid out above can be extended to model more realistic lattices, such as ionic lattices or cuprates. In this case the latter has been chosen for its relevance to high T_c superconductivity. This lattice contains some minor structural differences compared to the “plain” one described above: when considering a two dimensional layer each copper atom is surrounded by four oxygen atoms, but not each row contains copper atoms. The ones that do not alternatingly feature a oxygen atom and a gap at their sites (see fig. 3 for a schematic representation and a CuO_2 unit cell.) Three-dimensionally this leads to two tetraeders with oxygen atoms at their points, sticked back-to-back, around every copper atom. But for now the two dimensional case will be considered.

Another difference with the square lattice is that the polarization is not uniform anymore. Therefore different values of α are ascribed to the different kinds of atoms, namely α_{Cu} for the copper atoms, and α_O for their oxygen neighbors. In order to get an idea of the energy of such a two dimensional lattice two different cases with varying α_O will be considered: i) when $\alpha_{Cu} = 0$

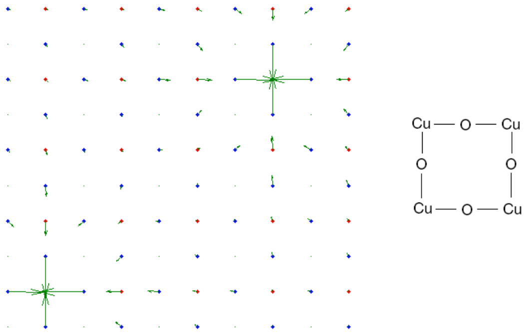


Figure 3: Two dimensional CuO lattice, plotted with polarization (left). The blue sites represent oxygen atoms and the red sites copper atoms. On the right the structure of a CuO_2 unit cell is shown.

and ii) when $\alpha_{Cu} = \alpha_O$. These are the extreme cases, and practically any physical system will lie between them. In the system with neighboring electrons they were chosen to neighbor one another diagonally (see fig. 4a), on oxygen sites, so that the distance between them equals $\sqrt{2}$ lattice units, if the algorithm functions correctly $\frac{1}{\sqrt{2}}$ should be the value of the Coulomb interaction energy since this should equal the reciprocal value of the distance between the electrons (cf. eq. (21)). The results of the different cases are shown in fig. 5.

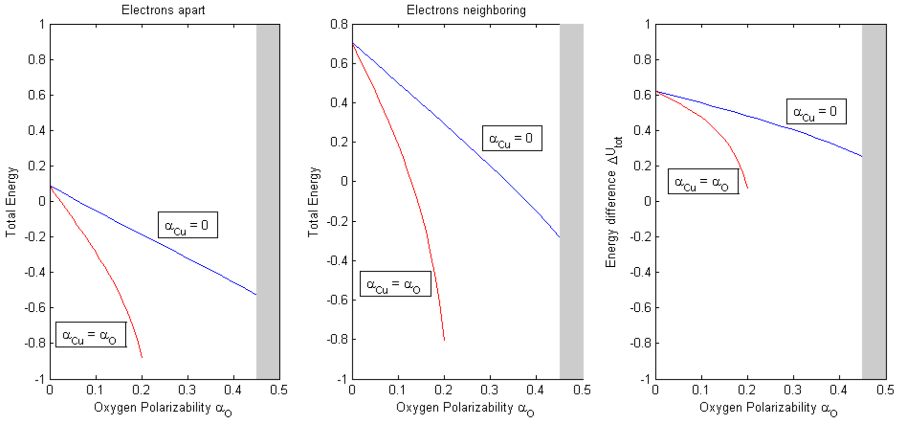


Figure 5: Total energy (left, middle) and energy difference (right) of the two systems for two cases: $\alpha_{Cu} = 0$ (red line) and $\alpha_{Cu} = \alpha_O$ (blue line). The gray area marks the unstable region for the $\alpha_{Cu} = 0$ case.

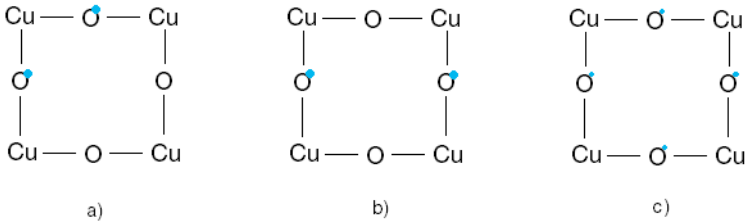
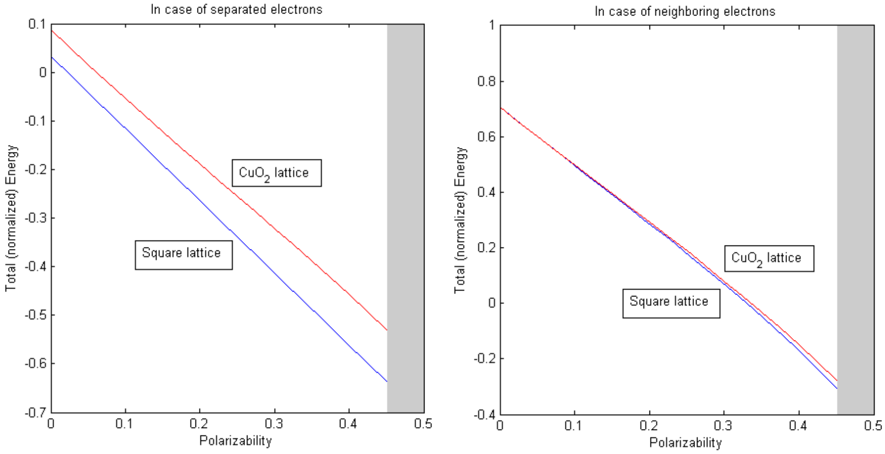


Figure 4: Positions of the electrons (blue dots) in various systems: the CuO_2 lattice, diagonally neighboring (a) and horizontally neighboring (b), and the Zhang-Rice singlet (c) where one electron is spread out over four sites. (Note that in case of the latter there are actually two of those clouds.)

As expected, the energy in the case of neighboring electrons for $\alpha_O = \alpha_{Cu} = 0$ equals $\frac{1}{\sqrt{2}}$, but this should hardly come as a surprise. A better check for the code would be to compare the $\alpha_{Cu} = 0$ case to the outcome of the algorithm for a homogenous material that was produced earlier on. Because the $\alpha_{Cu} = 0$ case (with lattice constant a) should be equivalent to the homogenous material (with lattice constant $a' = a\sqrt{2}$), because its participating particles (the oxygen atoms) effectively form a square lattice of particles at a distance $a\sqrt{2}$ apart. In order to do this the total energies for both situations will be calculated, after which they will be converted to their physical values using eqs. (23) and (24) using the appropriate lattice constant, which will make them comparable. The respective plots of the total energies as function of the polarizability are shown in fig. 6.


In case of separated electrons

In case of neighboring electrons

Figure 6: Total energies of the two systems as function of their polarizabilities. On the left the energies for separated electrons are compared, while on the right the energies for neighboring electrons are compared. The square lattice has been assigned the lattice constant $a = \sqrt{2}$, so the CuO_2 lattice gets $a = 1$, accordingly. Since the copper polarizability α_{Cu} has been set zero it is thus effectively a square lattice with constant $a_{eff} = \sqrt{2}$.

Fig. 6 compares the energies for both cases (separated electrons and neighboring electrons). In the case of neighboring electrons the results are almost the same for any polarizability. This is very good news since it tells us that the code is in agreement with what we knew for the square lattice. The case of separated electrons, on the other hand, shows a bigger difference between the energy values. This can be explained by a difference in the Coulomb interaction. Obviously the distance between the two electrons in the two systems is not the same, thus causing another value for the Coulomb repulsion. But since the energy difference stays approximately the same for almost all polarizabilities this also confirms the code. It is to be expected that this energy difference grows smaller when larger lattices are used, for then boundary effects do not come into play and both initial energies will equal zero. On top of all this the critical polarizabilities are the same as well. This has been explicitly verified by converting the critical polarizability of the uniform system (approximately 0.16 with unspecified lattice constant) to the critical polarizability of a system with lattice constant $a = \sqrt{2}$ using eq. (23). Ignoring all the constants (i.e. $4\pi\epsilon_0$) it was found that the value translated to be about 0.45, which is in agreement with what was found in the CuO_2 case. This is a very nice conclusion, since it confirms that the algorithms that were used function correctly, and are consistent.

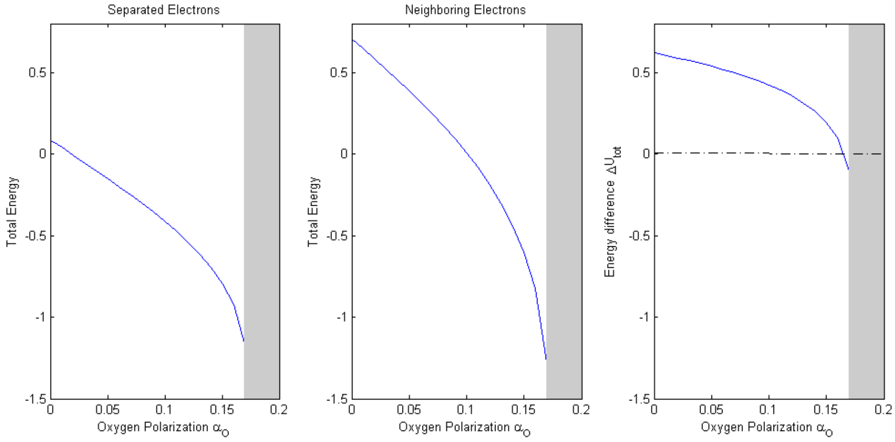


Figure 7: Total energy (left, middle) and energy difference (right, for clarity $\Delta U_{tot} = 0$ has been drawn) of the two configurations as a function of α_O in case $\alpha_{Cu} = 1.5 \cdot \alpha_O$. As always, the gray area marks the unstable region.

6.3 Extreme values

Now that the workings of the algorithm have been thoroughly verified it is interesting to calculate some other possible configurations. Especially in relation to high T_c superconductivity it is of interest to deliberately look for situations where it is energetically favorable (i.e. $\Delta U_{tot} < 0$) for two electrons to stick together. So what if the cases represented in fig. 5 are not the extremes, what would happen if α_{Cu} were not to equal α_O but were to exceed it by a certain factor? At this point it does not really matter whether this is physically allowed, it probably is not. This hypothetical situation has been computed in the case $\alpha_{Cu} = 1.5 \cdot \alpha_O$. As one would expect the critical polarizability is lower than 0.2; the highest calculable oxygen polarizability was found to equal 0.17. The results are depicted in fig. 7.

This is very interesting, as can be seen from the energy difference plot there are possible polarizability values for which the sign of the energy difference flips. This means that the configuration of neighboring electrons is energetically favorable above separated electrons. This is a familiar process that makes materials superconductive. And even though this hypothetical CuO_2 lattice might not be physically correct, it does prove a point: a layer with the right polarizabilities may facilitate superconductivity.

6.4 Moving the electrons around

Up to and until here we assumed that the electrons would neighbor one another diagonally on oxygen-sites. But perhaps a more realistic case to analyze would be the one where the electrons neighbor one another horizontally instead of

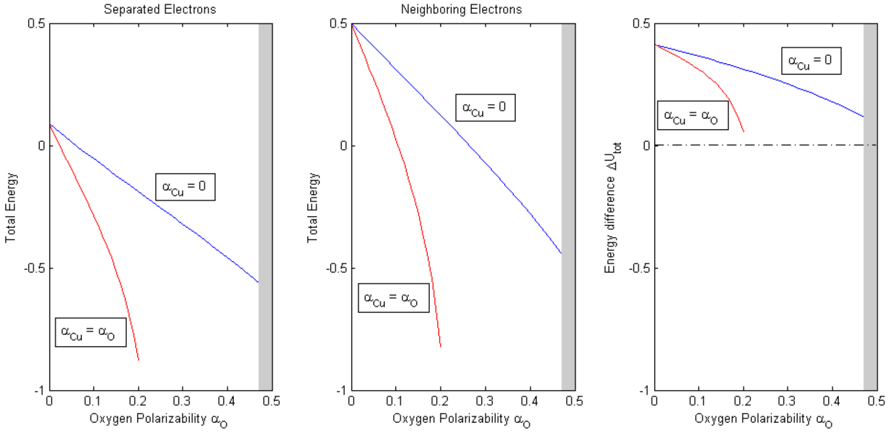


Figure 8: Total energy (left, middle) and energy difference (right) of the two systems for two cases: $\alpha_{Cu} = 0$ (red line) and $\alpha_{Cu} = \alpha_O$ (blue line) in case the electrons neighbor horizontally. The gray area marks the unstable region for the $\alpha_{Cu} = 0$ case.

diagonally (see fig. 4b). This would mean the distance between the two would grow so intuitively one would be inclined to say this would not be advantageous whatsoever; because it would lower both the Coulomb interaction energy and the polarization energy. But why assume when you have a highly configurable code at your disposal? After all, the lattice under discussion has a lot of holes and is therefore atypical. Basically the same approach has been taken as for the diagonally neighboring electrons; except one electron has been moved to another site. The critical polarizability was found to increase a little bit (to 0.475 for $\alpha_{Cu} = 0$, it stayed the same for $\alpha_{Cu} = \alpha_O$), which is not very remarkable since the bare field intensity does decrease. The results for this particular system are shown in fig. 8.

Apparently this system does not depict any behavior that might be associated with superconductivity for any choice of polarizability. However, its energy difference in the case $\alpha_{Cu} = \alpha_O$ does get closer to zero than it does in case of diagonally neighboring electrons. This is no surprise because the Coulomb interaction energy of neighboring electrons is quite a bit smaller (cf. fig. 5). Following the approach taken here there is another (hypothetical) configuration that could be of interest as well: what would happen if the electrons were placed on a copper instead of an oxygen site? After all it means the structure of field with respect to the lattice is different so interesting things might occur. As it turns out, however, not much happens. The total energies lie somewhere in between the results for diagonally neighboring electrons and horizontally neighboring pairs. Therefore the graphs for this particular configuration have been omitted.

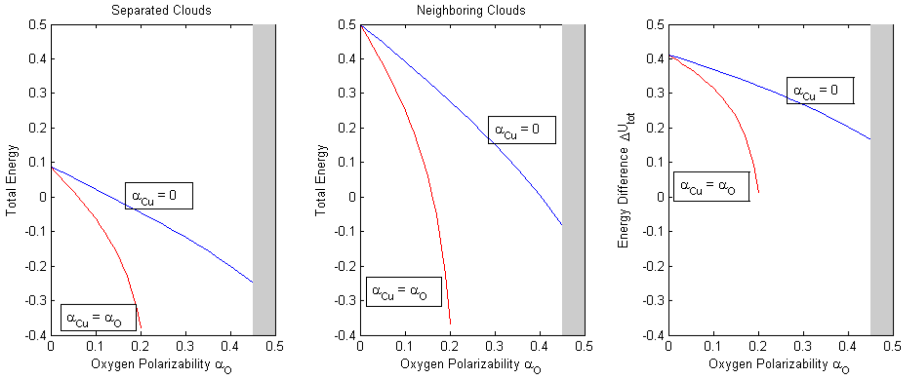


Figure 9: Total energies (left, center) and energy difference (right) for two Zhang-Rice singlets in a CuO_2 layer. Two different configurations were calculated: one where they are separated (left) and one where they are touching at one point (center) under two different assumptions for the polarizabilities: $\alpha_{Cu} = 0$ (blue line) and $\alpha_{Cu} = \alpha_O$ (red line).

6.5 The Zhang-Rice singlet

Another way to describe electrons in lattices such as the CuO_2 lattice might be by using the so called Zhang-Rice singlet as proposed in [9]. This is a result that follow from a quantum mechanical approach where one electron is not located at a single oxygen site, but rather at four, in such a manner that the charge is distributed equally (effectively that will mean a charge of $\frac{e}{4}$ at each site, see fig. 4c). A few small adaptions to the existing algorithm will make the computation of such a system possible. Initially, as an approximation, each electron is replaced with four "quarter electrons," so when the bare fields are calculated there are now eight contributions instead of two. The Coulomb interaction energy will be approximated by assuming each cloud of "quarter electrons" has its center of mass at the center of each cloud, so that only a single term has to be calculated. This approximation is necessary because two neighboring clouds could cause conflicts otherwise, since there is at least one site where their electrons would overlap and interfere, meaning an infinite interaction energy.

From here on the calculation is pretty straightforward and corresponds to what has been done before. It remains disputable though whether analyzing this configuration in this manner makes sense. Clearly the Zhang-Rice singlet is a quantum mechanical phenomenon and it would not make a lot of sense to calculate the accompanying system energy using classical tools. However, its an interesting case to analyze and that is why it has been done. The graphs featuring the total energies and energy difference have been included in fig. 9.

The results look a lot like what we have seen thus far for electrons that were located at a single site. There are no surprised whatsoever, neither of the energy differences sneaks beneath zero, although it is reasonable to think there is a combination of polarizabilities for which it will (cf. fig. 7), but that is not the point. This should not be seen as a definitive proof for the Zhang-Rice bipolaron not causing high T_c superconductivity at all; it is clearly a quantum mechanical construct, and those effects have not been taken into account here.

7 Modeling a slab of La_2CuO_4

Now that the case for a two dimensional system has been analyzed it is of interest to ask what happens when we use the same approach to analyze a three dimensional system. After all, the vast majority of lattices is three dimensional and only in very few cases two-dimensionality plays a role. It was chosen to analyze three layers of the La_2CuO_4 lattice, which is known for its high T_c superconductivity properties. In case neighboring electrons prove to be energetically favorable above separated electrons this could turn out to be an explanation for its superconductive properties.

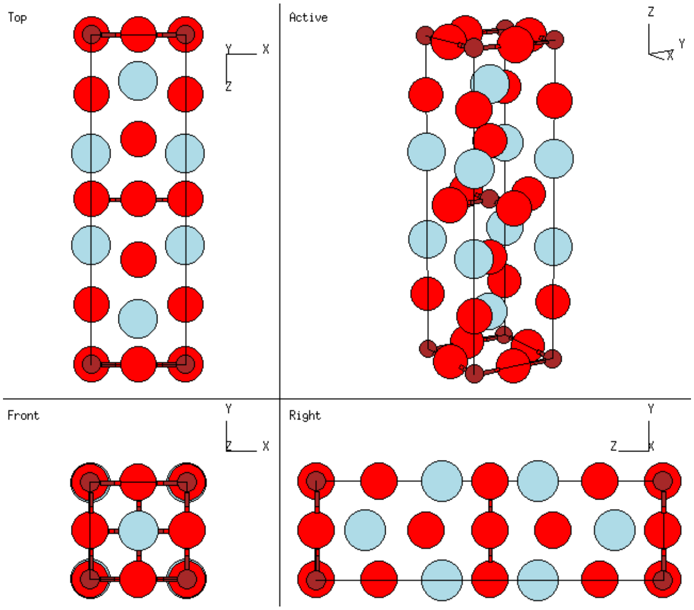


Figure 10: Structure of La_2CuO_4. The blue, red and maroon particles represent lanthanum, oxygen and copper atoms, respectively. (Courtesy of [8]).

So, what does this structure look like? Basically it is a CuO_2 layer sandwiched between two La_2O_2 layers (see fig. 10 for a graphical representation). When analyzing entire materials instead of just a few layers it is of importance to realize that La_2CuO_4 almost never occurs as a lattice by itself, rather, it is part of another lattice (such as, for example, $(La, Ba)_2CuO_4$ where there

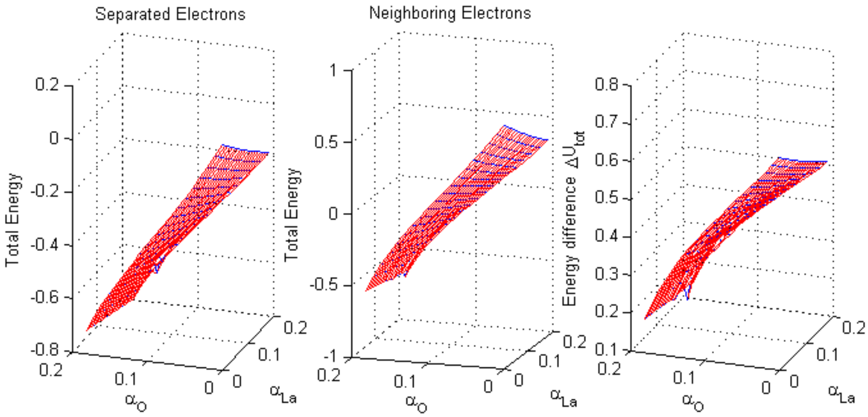


Figure 11: Total energy for different values of α_{La} (constant along red lines) and α_O (constant along blue lines). α_{Cu} was chosen to equal α_O at all times. As usual, the figure on the left represents the system with separated electrons, whereas the figure in the middle represents the system with neighboring electrons. The graph on the right shows the energy difference between the two situations.

are layers containing barium as well.) But for now we will restrict ourselves to La_2CuO_4 because this is believed to be the part causing superconductivity. In order to get an idea of what happens in this structure its three layers will be simulated.

The same approach as above has been followed, the only difference being that all the vectors (fields, polarizations, &cetera) have three instead of two components. This has been accounted for in the algorithm. Such as was done for the CuO_2 layer, the polarizabilities were chosen to vary, only here three values are of importance, α_{La}, α_O and α_{Cu}, respectively the polarizability of lanthanum, oxygen and copper. It was chosen that $\alpha_{Cu} = \alpha_O$ since that case has a better prospect of finding $\Delta U_{tot} < 0$ compared to $\alpha_{Cu} = 0$. α_O and α_{La} vary between 0 and 0.18 since for higher values the system proves to be unstable. A three-dimensional plot of the energy for various values of both parameters has been made, it is included in fig. 10.

This figure confirms some of our suspicions; for a fixed α_{La} and α_O the energy of the system with the larger distance between the two electrons will be the lowest. This should hardly come as a surprise since the Coulomb interaction energy provides for a considerable contribution. However, there is a significant range of polarizations for which the energy of the second system (the one with neighboring electrons) is less than zero. This means that it is definitely possible for the system to arrange itself in this manner for there is no external energy input needed (this would be the case if the energy were to be larger than zero.) But since the energy of a system with separated electrons is still lower, this is the one energetically more favorable.

8 Discussion and Summary

During the past twenty pages or so we constructed a model for two electrons in a polarizable lattice of arbitrary size. This was done after conceiving a thorough mathematical framework derived from the principles of electrostatics. The results of this derivation (especially eq. (18)) depict a certain beauty in their simplicity. They were mainly used for the coding of an algorithm that calculates the total energies (a sum of the Coulomb repulsion and the total induced polarization work) of numerous systems.

The energies of two different configurations were computed and compared: the configuration where the electrons were separated and interacted in a negligible manner and the configuration where the electrons were on neighboring lattice sites. It was found that most of the time the latter situation was not as favorable as the prior. The only parameters for which the data explicably show a preference for neighboring electrons is in the case of an CuO_2 lattice when $\alpha_{Cu} = 1.5 \cdot \alpha_O$ for $\alpha_O \geq 0.16$ (fig. 7). This might not be a physically sensible system in the sense that there will never be copper or oxygen ions with those parameters; however, the mere fact that it is possible is interesting since there might be other materials that *do* have these properties.

The question remains, however, how much sense this approach makes. Especially in cases such as the Zhang-Rice singlet we are clearly dealing with a quantum mechanical phenomenon and what would be the use of one describing that using classical tools? Quantitatively it would not make sense at all, for the results probably do not agree with experiment. It might sketch the contours of a qualitative picture, though, but in order to do that well one probably has to be more thorough than we were here.

The theory analyzed, discussed and elaborated in this thesis is very interesting. It would require some more work—especially on the quantum mechanical portion of the whole—to prove for an explanation for high T_c superconductivity. Also, three dimensional effects have hardly been taken into account, while these could be the crucial part causing superconductivity. It is too early to say bipolarons do or do not cause materials to become superconductive. It can be hoped, though, that the results acquired here will make for a very minor contribution in the worldwide quest looking to explain this intriguing phenomenon.

References

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[8] *The 0201 [(La,Ba)2CuO4] High-Tc Structure*, Naval Research Laboratory, Accessed through `http://cst-www.nrl.navy.mil/lattice/struk/hightc/x0201.html` on 10-10-2011

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9 Appendix

Below the code for the simulation of a CuO_2 lattice has been included. Detailed comments explaining it have been omitted, for a brief explanation please see §6.

```
%polarizationvariesCuO.m
% CuO_lattice_2D.m
% classical_energy.m
% computes the classical energy of a polarizable lattice with two electrons
clear all; clc;
% system conditions
n = 19; %system dimensions
n = n+1; %add 1 for counter to run well
re1 = [5,6]; %position of first electron
re2 = [14,13]; %position of second electron
re3 = [10,11]; %position of thrid electron
re4 = [12,11]; %position of fourth electron
conp = [8,9]; %define point where convergence is measured
% make some space
[x,y] = meshgrid(1:1:n,1:1:n);
l = 0;

for alphaO = 0:0.01:0.2
 disp(alphaO);
 l = l + 1;
 px = zeros(n,n); %polarization storage
 py = zeros(n,n);
 E0x = zeros(n,n); %field storage
 E0y = zeros(n,n);
 qx = zeros(n,n); %running polarization
 qy = zeros(n,n);
 acc1 = zeros(1,30); %convergence of algorhithm
 acc2 = zeros(1,30);

 % some other definitions
 r = 1; %length scale
 eps = 1; %initial convergence rate, 0 means completely converged, 1 means not so
 PP = 0; %the polarization of an arbitrary point
 alphaCu = alphaO;

 % initial energies, supposing it's just the charge-charge interaction that
 % counts
 U1 = 1/(sqrt((re1(1)-re2(1))^2+(re1(2)-re2(2))^2));
 U2 = 1/(sqrt((re3(1)-re4(1))^2+(re3(2)-re4(2))^2));
 Ucou1 = U1;
 Ucou2 = U2;

 for nx = 1:n
 for ny = 1:n
 if ( nx == re1(1) && ny == re1(2) )
 E0x(nx,ny) = 0;
 E0y(nx,ny) = 0;
 px(nx,ny) = 0;
 py(nx,ny) = 0;
 else
 rr = sqrt((nx-re1(1))^2+(ny-re1(2))^2);
 E0x(nx,ny) = -(nx-re1(1))/rr^3;
 E0y(nx,ny) = -(ny-re1(2))/rr^3;
 if ( mod(nx,2) == 0 && mod(ny,2) == 0)
 px(nx,ny) = alphaCu*E0x(nx,ny);
 py(nx,ny) = alphaCu*E0y(nx,ny);
 elseif ( mod(nx,2) == 1 && mod(ny,2) == 1 )
 px(nx,ny) = 0;
 py(nx,ny) = 0;
 else
 px(nx,ny) = alphaO*E0x(nx,ny);
 py(nx,ny) = alphaO*E0y(nx,ny);
 end
```

```
end
end
end

for nx = 1:n
for ny = 1:n
if ( nx == re2(1) && ny == re2(2) )
E0x(nx,ny) = 0;
E0y(nx,ny) = 0;
px(nx,ny) = 0;
py(nx,ny) = 0;
else
rr = sqrt((nx-re2(1))^2+(ny-re2(2))^2);
E0x(nx,ny) = E0x(nx,ny) - (nx-re2(1))/rr^3;
E0y(nx,ny) = E0y(nx,ny) - (ny-re2(2))/rr^3;
if ( mod(nx,2) == 0 && mod(ny,2) == 0)
px(nx,ny) = alphaCu*E0x(nx,ny);
py(nx,ny) = alphaCu*E0y(nx,ny);
elseif ( mod(nx,2) == 1 && mod(ny,2) == 1 )
px(nx,ny) = 0;
py(nx,ny) = 0;
else
px(nx,ny) = alphaO*E0x(nx,ny);
py(nx,ny) = alphaO*E0y(nx,ny);
end
end
end
end

Ebx = E0x; %define bare fields from initial contributions
Eby = E0y;

while ( eps > 0.0001)
for nx = 1:n
for ny = 1:n
sumx = 0;
sumy = 0;
for kx = 1:n
for ky = 1:n
if ( kx == nx && ky == ny)
sumx = sumx + 0;
sumy = sumy + 0;
else
rr = sqrt((nx-kx)^2+(ny-ky)^2);
pr = px(kx,ky)*(nx-kx) + py(kx,ky)*(ny-ky);
sumx = sumx - (px(kx,ky)/rr^3 - 3*pr*(nx-kx)/rr^5);
sumy = sumy - (py(kx,ky)/rr^3 - 3*pr*(ny-ky)/rr^5);
end
end
end
if ( mod(nx,2) == 0 && mod(ny,2) == 0)
qx(nx,ny) = alphaCu*(E0x(nx,ny)+sumx);
qy(nx,ny) = alphaCu*(E0y(nx,ny)+sumy);
elseif ( mod(nx,2) == 1 && mod(ny,2) == 1 )
qx(nx,ny) = 0;
qy(nx,ny) = 0;
else
qx(nx,ny) = alphaO*(E0x(nx,ny)+sumx);
qy(nx,ny) = alphaO*(E0y(nx,ny)+sumy);
end
end
end

for nx = 1:n;
for ny = 1:n;
px(nx,ny) = qx(nx,ny);
py(nx,ny) = qy(nx,ny);
end
```

```
end

eps = abs((px(conp(1),conp(2))-PP)/px(conp(1),conp(2)));
PP = px(conp(1),conp(2));
end
PP = 0;
eps = 1;

for nx = 1:n
for ny = 1:n
U1 = U1 - 0.5*(Ebx(nx,ny)*px(nx,ny)+Eby(nx,ny)*py(nx,ny));
end
end
px1 = px;
py1 = py;
V1(l) = U1;
px = zeros(n,n); %polarization storage
py = zeros(n,n);
E0x = zeros(n,n); %field storage
E0y = zeros(n,n);
qx = zeros(n,n); %running polarization
qy = zeros(n,n);

for nx = 1:n
for ny = 1:n
if ( nx == re3(1) && ny == re3(2) )
E0x(nx,ny) = 0;
E0y(nx,ny) = 0;
px(nx,ny) = 0;
py(nx,ny) = 0;
else
rr = sqrt((nx-re3(1))^2+(ny-re3(2))^2);
E0x(nx,ny) = -(nx-re3(1))/rr^3;
E0y(nx,ny) = -(ny-re3(2))/rr^3;
if ( mod(nx,2) == 0 && mod(ny,2) == 0)
px(nx,ny) = alphaCu*E0x(nx,ny);
py(nx,ny) = alphaCu*E0y(nx,ny);
elseif ( mod(nx,2) == 1 && mod(ny,2) == 1 )
px(nx,ny) = 0;
py(nx,ny) = 0;
else
px(nx,ny) = alpha0*E0x(nx,ny);
py(nx,ny) = alpha0*E0y(nx,ny);
end
end
end
end


for nx = 1:n
for ny = 1:n
if ( nx == re4(1) && ny == re4(2) )
E0x(nx,ny) = 0;
E0y(nx,ny) = 0;
px(nx,ny) = 0;
py(nx,ny) = 0;
else
rr = sqrt((nx-re4(1))^2+(ny-re4(2))^2);
E0x(nx,ny) = E0x(nx,ny) - (nx-re4(1))/rr^3;
E0y(nx,ny) = E0y(nx,ny) - (ny-re4(2))/rr^3;
if ( mod(nx,2) == 0 && mod(ny,2) == 0)
px(nx,ny) = alphaCu*E0x(nx,ny);
py(nx,ny) = alphaCu*E0y(nx,ny);
elseif ( mod(nx,2) == 1 && mod(ny,2) == 1 )
px(nx,ny) = 0;
py(nx,ny) = 0;
else
px(nx,ny) = alpha0*E0x(nx,ny);
```

```
 py(nx,ny) = alpha0*E0y(nx,ny);
 end
 end
 end
 end

 Ebx = E0x; %redefine bare fields from initial contributions
 Eby = E0y;

 while ( eps > 0.0001)
 for nx = 1:n
 for ny = 1:n
 sumx = 0;
 sumy = 0;
 for kx = 1:n
 for ky = 1:n
 if ( kx == nx && ky == ny)
 sumx = sumx + 0;
 sumy = sumy + 0;
 else
 rr = sqrt((nx-kx)^2+(ny-ky)^2);
 pr = px(kx,ky)*(nx-kx) + py(kx,ky)*(ny-ky);
 sumx = sumx - (px(kx,ky)/rr^3 - 3*pr*(nx-kx)/rr^5);
 sumy = sumy - (py(kx,ky)/rr^3 - 3*pr*(ny-ky)/rr^5);
 end
 end
 end
 if ( mod(nx,2) == 0 && mod(ny,2) == 0)
 qx(nx,ny) = alphaCu*(E0x(nx,ny)+sumx);
 qy(nx,ny) = alphaCu*(E0y(nx,ny)+sumy);
 elseif ( mod(nx,2) == 1 && mod(ny,2) == 1 )
 qx(nx,ny) = 0;
 qy(nx,ny) = 0;
 else
 qx(nx,ny) = alpha0*(E0x(nx,ny)+sumx);
 qy(nx,ny) = alpha0*(E0y(nx,ny)+sumy);
 end
 end
 end

 for nx = 1:n
 for ny = 1:n
 px(nx,ny) = qx(nx,ny);
 py(nx,ny) = qy(nx,ny);
 end
 end

 eps = abs((px(conp(1),conp(2))-PP)/px(conp(1),conp(2)));
 PP = px(conp(1),conp(2));
 end

 for nx = 1:n
 for ny = 1:n
 U2 = U2 - 0.5*(Ebx(nx,ny)*px(nx,ny)+Eby(nx,ny)*py(nx,ny));
 end
 end
 V2(l) = U2;
end
alpha = 0:0.01:0.20;
beep; beep; beep;
% close all
% alpha = 0:0.01:0.20;
% subplot(1,2,1);
% plot(alpha,V1);
% hold;
% area([0.20 0.5],[2 2]);
% area([0.20 .5],[-2 -2]);
% axis([0 0.25 -1.5 1.5]);
```

```
% subplot(1,2,2);
% axis([0 0.25 -1.5 1.5]);
% plot(alpha,V2);
% hold;
% area([0.20 0.5],[2 2]);
% area([0.20 0.5],[-2 -2]);

% axis([0 0.25 -1.5 1.5]);
```