Real space BCS like states in a linear chain

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We use a quantum harmonic cyclic linear chain, define a pseudo potential for the particles and add two electrons. An ansatz for the multi particle wave function is chosen and the energy of the quantum mechanic system is calculated. Compared to "free" electrons the energy is lower, which often is interpreted as gap.

I. QUANTUM LINEAR HARMONIC CHAIN IN REAL SPACE

We follow [1] for the linear harmonic chain. The Hamiltonian of the classical system is:

$$H = \sum_{n=1}^{N} \left(\frac{p_n^2}{2m} + \frac{1}{2}\kappa q_n^2 + \frac{1}{2}\gamma (q_n - q_{n+1})^2 \right).$$

We diagonalize the Hamiltonian using

$$f_n^{(k)} = \frac{1}{\sqrt{N}} e^{-\frac{2\pi i}{N} kn} \quad \text{for} \quad k = 0, \ldots, N-1.$$

The new coordinates are

$$q_n = \sum_k Q_k f_n^{(k)} = \frac{1}{\sqrt{N}} \sum_k Q_k e^{-\frac{2\pi i}{N} kn},$$

with the reverse transformation

$$Q_k = \sum_n q_n f_n^{(-k)} = \frac{1}{\sqrt{N}} \sum_n q_n e^{\frac{2\pi i}{N} kn},$$

and the Hamiltonian

$$H = \sum_k \left(\frac{|P_k|^2}{2m} + \frac{1}{2}\omega_k |Q_k|^2 \right). \tag{1}$$

The Hamiltonian of uncoupled harmonic oscillators with the ω_k fulfilling the textbook results $\omega_k = \sqrt{2\omega^2(1-\cos(ka))}$ [2]. We will use ω_k as parameters $\overrightarrow{\omega}$ later, as it will be influenced by electron-phonon coupling. The Schrödinger equation of the harmonic oscillator has the ground state

$$\phi_{k,ground}(Q_k;\omega_k) = e^{-\omega_k (|Q_k|)^2},$$

and the first excited state

$$\phi_{k,excited}(Q_k;\omega_k) = \sqrt{\omega_k} Q_k e^{-\omega_k |Q_k|^2}.$$

The wave function ϕ_{phonon} using the real space variable $\vec{q} = (q_1, ..., q_n)$ is

$$\phi_{ph}(\vec{q};\overrightarrow{\omega}) = \prod_k \phi_k(Q_k;\omega_k) = \prod_k \phi_k(Q_k(\vec{q});\omega_k) \ ,$$

with the ϕ_k being $\phi_{k,ground}$ or $\phi_{k,excited}$.

II. MULTI-PARTICLE "TWO ELECTRON IN HARMONIC CHAIN" WAVE FUNCTION

A Cooper pair consists of two electrons within a solid. As a model we construct a multi particle state with two electrons and a harmonic chain. The electron wave functions will depend on the position of the nuclei. To get a finite

number of parameters for the electron wave function we express it in plane waves. The coefficients will depend on the Fourier coefficients Q_k of the linear harmonic chain, therefore we choose the ansatz

$$\phi_{el}(x;k,\overrightarrow{a},\overrightarrow{Q}) = \left(\sum_{m=0}^{\infty} a_m Q_{m \bmod N} e^{i\cdot\frac{2\pi}{l}\cdot m\cdot x}\right)\cdot e^{i\cdot\frac{2\pi}{l}\cdot k\cdot x}\ , \tag{2}$$

with l being the length of the linear harmonic chain and k the wave number of the electron. The electron wave function is expressed as an infinite series (which will be cut off for our calculations), but the $\overrightarrow{Q}$ has only N elements, as the chain has N nuclei. Therefore if a k belongs to a multiple of a Q_k, the corresponding Q_k is used by the modulus function.

Two electron wave functions must be anti-symmetrized, as electrons are fermions. In the following we assume the electrons having different spins, therefore we have to symmetrize the real space part of the wave function

$$\phi_{2-el}(x_1,x_2;k_1,k_2,\overrightarrow{a},\overrightarrow{Q}) = \\ \phi_{el}(x_1;k_1,\overrightarrow{a},\overrightarrow{Q})\cdot\phi_{el}(x_2;k_2,\overrightarrow{a},\overrightarrow{Q}) + \phi_{el}(x_2;k_1,\overrightarrow{a},\overrightarrow{Q})\cdot\phi_{el}(x_1;k_2,\overrightarrow{a},\overrightarrow{Q})\ . \tag{3}$$

Our complete (not normalized) wave function is

$$\Phi(x_1,x_2,\overrightarrow{q};k_1,k_2,\overrightarrow{\omega},\overrightarrow{a}) = \phi_{ph}(\vec{q};\overrightarrow{\omega})\cdot\phi_{2-el}(x_1,x_2;k_1,k_2,\overrightarrow{a},\overrightarrow{Q}(\overrightarrow{q}))\ .$$

III. CONSTRUCTION THE HAMILTONIAN

The potential of the harmonic chain using a constant C_{ph} is

$$V_{ph}(\overrightarrow{q}) = C_{ph}\sum_{l=1}^{N}(q_l - q_{l+1})^2\,,$$

assuming cyclic boundary conditions $q_{N+1} = q_1$. As within a solid we construct a potential form the positions of the nuclei of the harmonic chain. We use a model potential with a constant C_{el}

$$V_{el}(x;\overrightarrow{q}) = C_{el}\cdot\sum_{i\in nuclei}(q_{0,i} + q_i - x)^4\ .$$

For a real solid one would take some quasi-potential. We tried to over estimate the electron-phonon coupling, as this increases the bounding energy of the Cooper pairs and reduces the required accuracy of the calculation (number of Monte-Carlo evaluations). With this potentials and the electron mass m_e and the mass of the nuclei m_{nucl} (in atomic units) the Hamiltonian is

$$H = \frac{1}{2m_e}\left(\frac{\partial^2}{\partial(x_1)^2} + \frac{\partial^2}{\partial(x_2)^2}\right) + \frac{1}{2m_{nucl}}\cdot\left(\sum_{l=1}^{N}\frac{\partial^2}{\partial(q_l)^2}\right) + V_{el}(x_1;\overrightarrow{q}) + V_{el}(x_2;\overrightarrow{q}) + V_{ph}(\overrightarrow{q})\ .$$

IV. SOLVING THE SCHRÖDINGER EQUATION WITH MONTE-CARLO INTEGRATION

With the Hamiltonian we can calculate the energy using the stationary Schrödinger equation

$$E(\overrightarrow{\omega},\overrightarrow{a};k_1,k_2) = \frac{\int_{\overrightarrow{q},x_1,x_2}\Phi^* H\Phi}{\int_{\overrightarrow{q},x_1,x_2}\Phi^*\Phi}, \tag{4}$$

which depends on the two momentums of the electrons chosen, and the parameters of our multi particle wave function $\overrightarrow{\omega}$ and $\overrightarrow{a}$. The integrals have to been evaluated over the positions of the two electrons and and the displacements of the nuclei. As we assume a cyclic linear chain, the electron positions are finite, and the displacements decay rapidly. We can use a small volume for the Monte-Carlo integration. To find the ground state we optimize $E(\overrightarrow{\omega},\overrightarrow{a};k_1,k_2)$ with respect to $\overrightarrow{\omega}$ and $\overrightarrow{a}$. The python source code is available on GitHub [3].

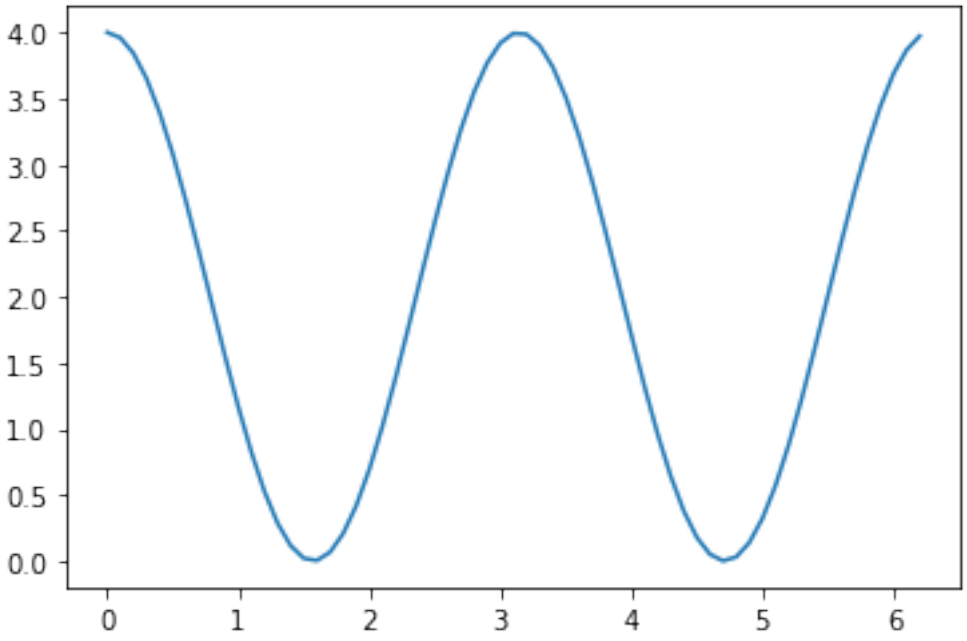

Figure 1. $k_1 = 1$, $k_2 = -1$,$x_2 = 0$ plot of probability $\phi^*(x1) \cdot \phi(x_1)$
with the symmetrized wave function $\phi(x_1, x_2; k_1, k_2) = e^{i \cdot k_1 \cdot x_1} \cdot e^{i \cdot k_2 \cdot x_2} + e^{i \cdot k_1 \cdot x_2} \cdot e^{i \cdot k_1 \cdot x_2}$(jupyter notebook on GitHub)

V. SOME RESULTS

The symmetrized wave function of two free electrons shows correlation between the two electrons, depending on $k_2 - k_1$ (figure 1). As we express the single electron wave function in plane wave, the location probability oscillation for the component with wave vector $k_2 - k_1$is amplified due to correlation, without increasing the kinetic energy with respect to two free electrons. We compare the energy with two free electrons to the one with the symmetrized wave function now. If the function is not symmetrized

$$\phi_{2-el\ (not\ symmetrized)}(x_1, x_2; k_1, k_2, \overrightarrow{a}, \overrightarrow{Q}) \quad = \quad \phi_{el}(x_1; k_1, \overrightarrow{a}, \overrightarrow{Q}) \quad \cdot \quad \phi_{el}(x_2; k_2, \overrightarrow{a}, \overrightarrow{Q}) \quad , \quad (5)$$

the correlation vanishes, and not coupling to the phonons takes place. Calculating equation (4) with a not symmetrized wave function gives the energy for free electrons (with the additional energy of the harmonic chain). Optimizing the energy (4) for the not symmetrized wave function results in the ground state energy with free electrons E_{free}. The number of the parameters $\overrightarrow{a}$ in the one electron wave function (2) is limited to 5 in this calculations ($C_{el} = 2$, $C_{ph} = 0.2$, $m_e = 0.5$, $m_{nucl} = 500$).

If one turns on the symmetrization by replacing equation (5) with equation (3), without changing the parameters of the single electron wave function, the energy E_{BCS} (4) is lower [3] (We only want to demonstrate, that the energy is lowered, in fact the parameters have to be optimized for E_{BCS}, resulting in an even bigger reduction). The energy reduction is present even without phonon excitations (zero point vibrations are enough), the reduction increases, if the corresponding phonon with $k_1 - k_2$ is excited. Usually the difference between the energy of free electrons and the energy with electron-phonon coupling is called the gap

$$\Delta = E_{free} - E_{BCS} \ .$$

VI. OUTLOOK

Extending the multi particle states to an infinite 3D crystal would make it possible to ab initio calculate the gap for BCS superconductors. One might discuss the effect of thermally excited phonons on the gap.

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[1] https://arxiv.org/abs/1907.11311.
[2] https://en.wikipedia.org/wiki/Quantum_harmonic_oscillator.
[3] https://github.com/dsmic/BCS-like-electron-states-in-a-linear-chain.