# Mott insulator and Hubbard model
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According to the band theory of metals (Bloch theorem), a half-filled band (valence band) leads to a metallic conductivity. A fully filled band (valence band) leads to an insulator. There is an energy gap between the valence band and the conduction band. There is no electrical conduction. In this band theory no interaction between electrons is taken into account. Free electrons move in a periodic potential of the crystal. When there is one electron per unit cell of the system, the valence band is a half filled by electrons. When there are two electrons per unit cell, the valence band is fully occupied by electrons. Depending on the number of electrons, the system becomes metallic for the odd number and insulator for the even number.

In 1937, the situation changed when de Boer and Verwey reported that many transition metal oxides such as NiO are insulator, but not a metal in spite of the fact that the d-band of these systems is partially filled by electrons. Peierls pointed out that such a behavior may be caused by the electron correlation. This problem was deeply considered by Mott. The insulator is a result of the significance of the strong repulsive Coulomb interaction between electrons. Such an insulator is called Mott insulator. The insulating nature of half-filled band (one electron in each lattice site, electron spin either up or down states). When one electron with up spin moves to the nearest neighbor site where one electron with opposite spin state exist. This is allowed by the Pauli's exclusion principle. The probability of this process depends on the magnitude of the repulsive Coulomb interaction U between electrons in the same site. If U is small, this process leads to the metallic conductivity of the system. If U is large, this process is neglected, leading to the half-filled insulator.

In most of Mott insulator, spins in the nearest neighbor site are antiparallel, forming an antiferromagnetic spin order. Slater proposed that Mott insulators are related to the formation of antiferromagnetic order. The periodicity of antiferromagnet is twice larger than that of the crystal lattice.

In 1949, Mott proposed a model for NiO as an insulator, where conduction is based on the formula
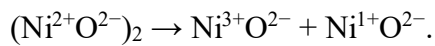
$$(Ni^{2+}O^{2-})_2 \rightarrow Ni^{3+}O^{2-} + Ni^{1+}O^{2-}.$$

In this situation, the formation of an energy gap preventing conduction can be understood as the competition between the Coulomb potential U between $3d$ electrons and the transfer integral t of $3d$ electrons between neighboring atoms (the transfer integral is a part of the tight-binding approximation). The total energy gap is then

$$E_{gap} = U - 2zt,$$

where z is the number of nearest-neighbor atoms. In general, Mott insulators occur when the repulsive Coulomb potential U is large enough to create an energy gap. One of the simplest theories of Mott insulators is the 1963 Hubbard model. The crossover from a metal to a Mott insulator as U is increased can be predicted within the so-called dynamical mean field theory.
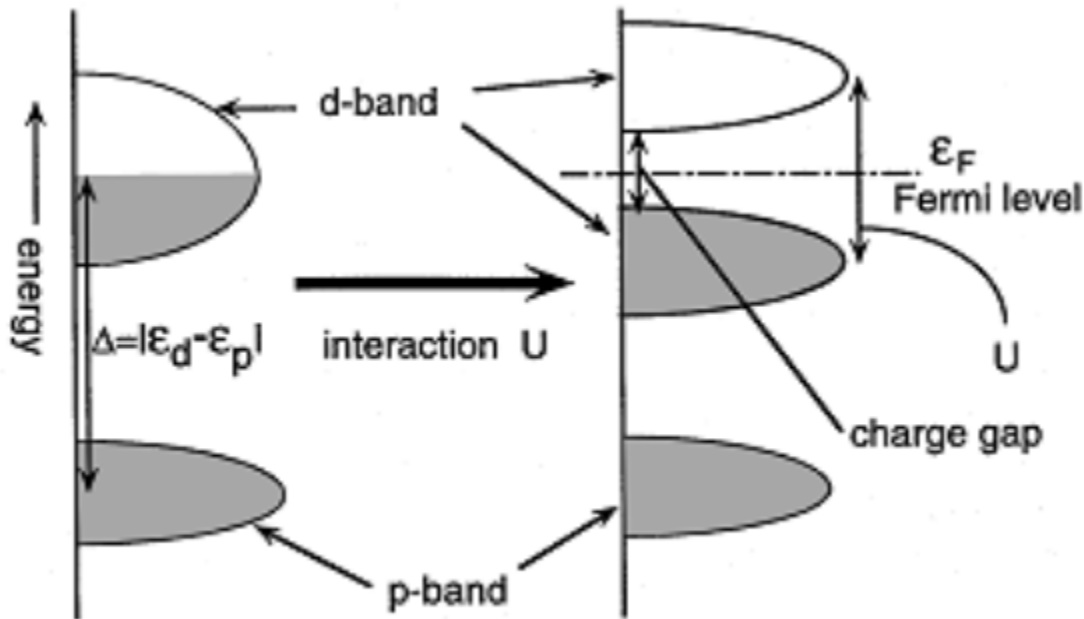https://en.wikipedia.org/wiki/Mott_insulator

Fig. The p band remains unchanged after including the interaction U, while the d band splits into two sub-bands and opens up a charge gap. The corresponding state become an insulator.

1. Mott insulator

In 1937, Jan Hendrik de Boer and Evert Johannes Willem Verwey pointed out that a variety of transition metal oxides (MnO, CoO) predicted to be conductors by band theory (because they have an odd number of electrons per unit cell) are insulators. Nevill Mott and Rudolf Peierls (1937) predicted that this anomaly can be explained by including Coulomb interactions between electrons.

In 1949, in particular, Mott proposed a model for NiO:

Ni^{2+}: $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^8$
O2-: $(1s)^2(2s)^2(2p)^6$
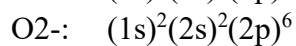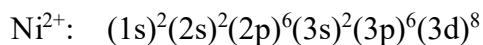
(which has an even number of electrons) are as an insulator, where conduction is based on the formula
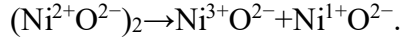
$$(Ni^{2+}O^{2-})_2 \rightarrow Ni^{3+}O^{2-} + Ni^{1+}O^{2-}.$$

In this situation, the formation of an energy gap preventing conduction can be understood as the competition between the Coulomb potential U between electrons and the transfer integral t of electrons between neighboring atoms (the transfer integral is a part of the tight-binding approximation). The total energy gap is then

$$E_{\text{gap}} = U - 2zt,$$

where z is the number of nearest-neighbor atoms. In general, the system becomes insulator when the repulsive Coulomb potential U is large enough to create an energy gap ($E_{gap} > 0$). One of the simplest theories of Mott insulators is the Hubbard model (1963). When $t > U/(2z)$, $E_{gap} < 0$, leading to the conduction as a result of spontaneous generation of Ni^{3+} and Ni^+. We call an insulator with large U as Mott insulator.

Here we discuss the origin of the Mott insulator. We show that for a half-filled band, the repulsive interaction makes the Mott insulator antiferromagnetic: virtual hopping lowers the energy of anti-aligned neighboring spins.

2. Hubbard model

We consider a virtual hydrogen atom has only one electron, in the so-called 1s orbital, which can either be spin up ($|+\rangle$ or spin down ($|\downarrow\rangle$ This orbital can be occupied by at most two electrons, one with spin up and one down (Pauli exclusion principle). There is only one electron per unit cell. According to the band theory, the 1s orbital to form a continuous band, which would be exactly half-full. The 1D chain of hydrogen atoms is thus predicted to be a conductor under conventional band theory. We now consider the case where the spacing between the hydrogen atoms is gradually increased. At some point it is expected that the chain must become an insulator. The Hubbard Hamiltonian is now made up of two components. The first component is the hopping integral. The hopping integral is typically represented by the letter t because it represents the kinetic energy of electrons hopping between atoms. The second term is then the on-site repulsionthat represents the potential energy arising from the charges on the electrons. The Hubbard Hamiltonian then takes the form

$$H = \sum_{\{i,j\}\sigma} (t_{ij}\hat{c}_{i\sigma}^+ \hat{c}_{j\sigma} + h.c.) + U\sum_j \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$$

where $\langle i,j \rangle$ represents summation over nearest-neighbor lattice sites. Note that both t and U are positive quantities. $\hat{n}_{j\sigma} = \hat{c}_{j\sigma}^+ \hat{c}_{j\sigma}$ is the number operator of electron. When the second term is included, however, we end up with a more realistic model that also predicts a transition from conductor to insulator as the inter-atomic spacing is increased. In the limit where the spacing is infinite (or if we ignore the first term), the chain simply resolves into a set of isolated magnetic

moments. Additionally, when there are some contributions from the first term, but the material remains an insulator, the overlap integral provides for exchange interactions between neighboring magnetic moments, which may lead to a variety of interesting magnetic correlations, such as ferromagnetic, antiferromagnetic, etc. depending on the exact solutions of the model. The one-dimensional Hubbard model was solved by Lieb and Wu using the Bethe ansatz.

3.   Eigenvalue problem
((Han problem 28-4))
F. Han; Problems in Solid State Physics with Solutions (World Scientific, 2012).

Consider the Hubbard Hamiltonian for two lattice sites

$$H = -t\sum_{\sigma}(\hat{c}_{1\sigma}^{+}\hat{c}_{2\sigma} + \hat{c}_{2\sigma}^{+}\hat{c}_{1\sigma}) + U(\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + \hat{n}_{2\uparrow}\hat{n}_{2\downarrow})$$

where $\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^{+}\hat{c}_{i\sigma}$ is the electron number operator of spin σ on the site i, t the hopping matrix element, and $U > 0$ the on-site Coulomb interaction energy. Assume that there are two electrons in the system. For this problem, we use the basis set:
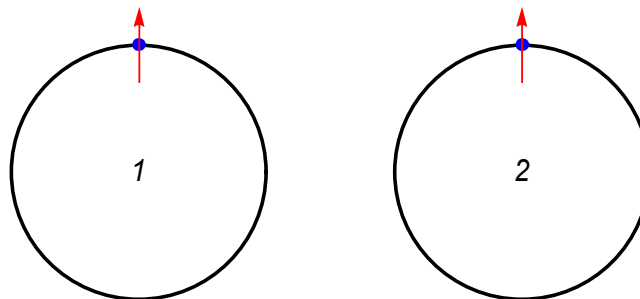
$$|\psi_1\rangle = |++\rangle, \quad |\psi_2\rangle = |--\rangle, \quad |\psi_3\rangle = |+-\rangle,$$
$$|\psi_4\rangle = |-+\rangle, \quad |\psi_5\rangle = |0 \updownarrow\rangle, \quad |\psi_6\rangle = |\updownarrow 0\rangle.$$

where the symbols in the first and second positions in a ket denote the occupations of the first and second sites, respectively, with 0 for not being occupied and ↑, ↓, ↕ for being occupied by one up-sign electron, one down-spin electron and two electrons of opposite spins.
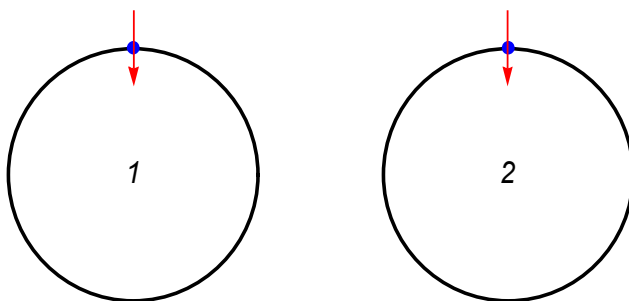
(1)   Find the eigenvalues and eigenvectors of the Hamiltonian. Plot the eigenvalues.
(2)   Guess the band structure if the two sites are replaced with an infinite lattice with one electron per site for $U/t \gg 1$.
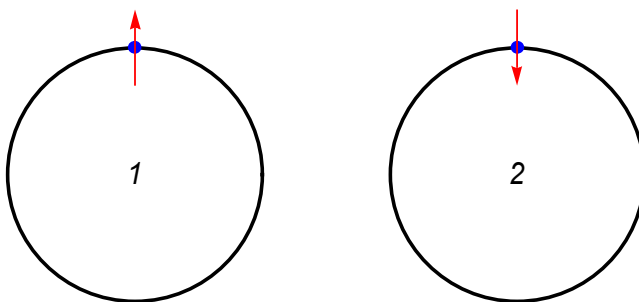
((Solution))
We first define the following six states.

$$\left|\psi_1\right\rangle = \left|\uparrow\uparrow\right\rangle$$
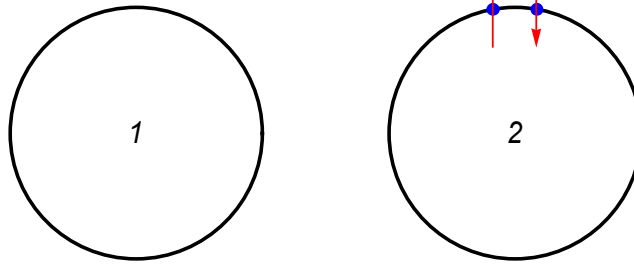

$$\left|\psi_2\right\rangle = \left|\downarrow\downarrow\right\rangle$$

$$\left|\psi_3\right\rangle = \left|\uparrow\downarrow\right\rangle$$
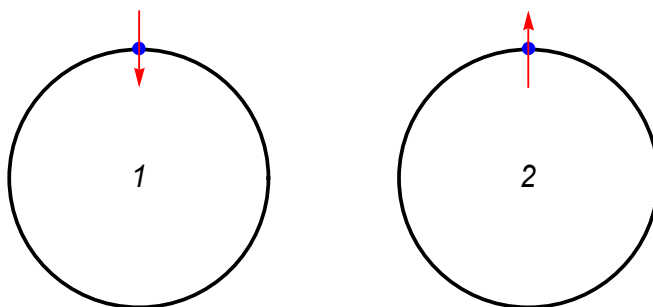
$$\left|\psi_4\right\rangle = \left|\downarrow\uparrow\right\rangle$$

$$|\psi_5\rangle = |0 \updownarrow\rangle$$
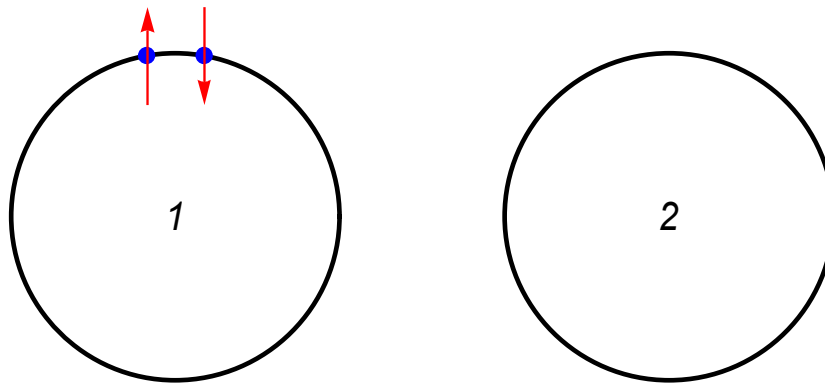
$$|\psi_6\rangle = |\updownarrow 0\rangle$$

We solve the eigenvalue problem

$$\hat{H} \begin{pmatrix} |\psi_1\rangle \\ |\psi_2\rangle \\ |\psi_3\rangle \\ |\psi_4\rangle \\ |\psi_5\rangle \\ |\psi_6\rangle \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -t & -t \\ 0 & 0 & 0 & 0 & -t & -t \\ 0 & 0 & -t & -t & U & 0 \\ 0 & 0 & -t & t & 0 & U \end{pmatrix} \begin{pmatrix} |\psi_1\rangle \\ |\psi_2\rangle \\ |\psi_3\rangle \\ |\psi_4\rangle \\ |\psi_5\rangle \\ |\psi_6\rangle \end{pmatrix} = \varepsilon \begin{pmatrix} |\psi_1\rangle \\ |\psi_2\rangle \\ |\psi_3\rangle \\ |\psi_4\rangle \\ |\psi_5\rangle \\ |\psi_6\rangle \end{pmatrix}$$

We note that

$$\hat{H}|\psi_1\rangle = 0, \quad \hat{H}|\psi_2\rangle = 0$$

which means that $|\psi_1\rangle$ and $|\psi_2\rangle$ are the eigenkets of $\hat{H}$ with eigenvalue 0. The Hamiltonian based on the sub-basis of $\{|\psi_3\rangle, |\psi_4\rangle, |\psi_5\rangle, |\psi_6\rangle\}$ and $|\psi_2\rangle$ is given by

$$\begin{pmatrix} 0 & 0 & -t & -t \\ 0 & 0 & -t & -t \\ -t & -t & U & 0 \\ -t & -t & 0 & U \end{pmatrix}$$

where

$$H|\uparrow\downarrow\rangle = -t|0\updownarrow\rangle - t|\updownarrow 0\rangle, \qquad\qquad H|\downarrow\uparrow\rangle = -t|0\updownarrow\rangle - t|\updownarrow 0\rangle$$

$$H|0\updownarrow\rangle = -t|\uparrow\downarrow\rangle - t|\downarrow\uparrow\rangle + U|0\updownarrow\rangle, \quad H|\updownarrow 0\rangle = -t|\uparrow\downarrow\rangle - t|\downarrow\uparrow\rangle + U|\updownarrow 0\rangle$$

leading to the matrix elements

$$\langle 0\updownarrow|H|\uparrow\downarrow\rangle = \langle \updownarrow 0|H|\uparrow\downarrow\rangle = -t$$

$$\langle 0\updownarrow|H|0\updownarrow\rangle = \langle \updownarrow 0|H|\updownarrow 0\rangle = U$$

We use the Mathematica to solve this eigenvalue problem.

Eigenvalue   Eigenket

(i)   Triplet state;

$\varepsilon = 0$ $|\psi_1\rangle = |++\rangle$

$\varepsilon = 0$ $|\psi_2\rangle = |--\rangle$

$\varepsilon = 0$ $\dfrac{|\psi_3\rangle - |\psi_4\rangle}{\sqrt{2}} = \dfrac{|+-\rangle - |-+\rangle}{\sqrt{2}}$

(ii)   Singlet state

$\varepsilon = U$ $\dfrac{|\psi_5\rangle - |\psi_6\rangle}{\sqrt{2}} = \dfrac{|0\updownarrow\rangle - |\updownarrow 0\rangle}{\sqrt{2}}$

(iii)

$$\varepsilon_G = \frac{U + \sqrt{U^2 + 16t^2}}{2}$$

$$|\psi_1\rangle + |\psi_6\rangle - \frac{U}{2t}(|\psi_3\rangle - |\psi_4\rangle)$$

(iv)   The ground state

$$\varepsilon_G = \frac{U - \sqrt{U^2 + 16t^2}}{2} \qquad \text{(ground state)}$$

$$\frac{U + \sqrt{U^2 + 16t^2}}{4t}(|\psi_1\rangle + |\psi_2\rangle) + |\psi_5\rangle + |\psi_6\rangle$$

This eigenket is not normalized. For $U \gg 4t$ the ground state energy is approximated by

$$\varepsilon_G = -\frac{4t^2}{U}.$$

(f)

$$\varepsilon_G = \frac{U + \sqrt{U^2 + 16t^2}}{2}$$

$$\frac{U - \sqrt{U^2 + 16t^2}}{4t}(|\psi_1\rangle + |\psi_2\rangle) + |\psi_5\rangle + |\psi_6\rangle$$
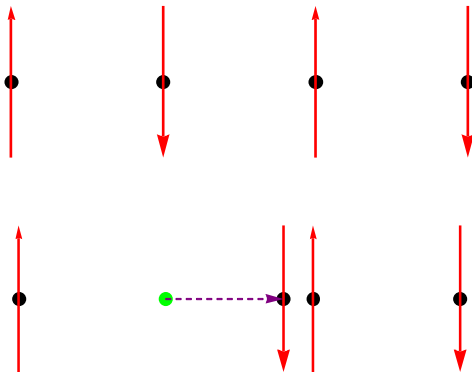
This eigenket is not normalized.

((Mathematica))

```
Clear["Global`*"]; A1 = ( 0   0   -t  -t )
                        ( 0   0   -t  -t )  ;
                        ( -t  -t   U   0 )
                        ( -t  -t   0   U )
```
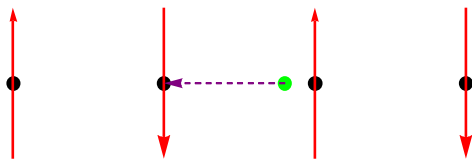
Eigensystem[A1] // FullSimplify

$$\left\{\left\{0,\ U,\ \frac{1}{2}\left(U-\sqrt{16\,t^2+U^2}\right),\ \frac{1}{2}\left(U+\sqrt{16\,t^2+U^2}\right)\right\},\right.$$

$$\{\{-1,\ 1,\ 0,\ 0\},\ \{0,\ 0,\ -1,\ 1\},$$

$$\left\{\frac{U+\sqrt{16\,t^2+U^2}}{4\,t},\ \frac{U+\sqrt{16\,t^2+U^2}}{4\,t},\ 1,\ 1\right\},$$

$$\left.\left\{-\frac{4\,t}{U+\sqrt{16\,t^2+U^2}},\ -\frac{4\,t}{U+\sqrt{16\,t^2+U^2}},\ 1,\ 1\right\}\right\}\right\}$$

4.   Effective Hamiltonian for Mott insulator ((Shiba))

The intermediate state.

We use the second order perturbation for the 1D Hubbard model. In the presence of the perturbation, the ground state energy can be evaluated as

$$\Delta E = E_0 + \langle \Phi_0 | H' | \Phi_0 \rangle + \sum_n \frac{\left| \langle n | H' | \Phi_0 \rangle \right|^2}{E_0 - E_n}$$

$$= E_0 - \frac{zt^2}{U}$$

where z is the number of nearest neighbors. In this case $z = 2$. t is the hopping or transfer matrix element between nearest neighbors. U is called the Hubbard-U weighs the strength of the correlation in case of two electrons at the same site. Thus the ground state energy is lowered when the perturbation is added to the original system. In other word, the antiferromagnetic spin alignment is favorable energetically.

Here we introduce the Dirac exchange operator $\hat{P}_{12}$ for two spins with spin ½, where

$$\hat{P}_{12} |++\rangle = |++\rangle, \qquad \hat{P}_{12} |--\rangle = |--\rangle$$

$$\hat{P}_{12} |+-\rangle = |-+\rangle, \qquad \hat{P}_{12} |-+\rangle = |+-\rangle$$

So $|++\rangle$ and $|--\rangle$ are the eigenkets of the Dirac exchange operator $\hat{P}_{12}$ with the eigenvalue 1. However the kets $|+-\rangle$ and $|-+\rangle$ are not the eigenkets of $\hat{P}_{12}$. But the combinations of these states are eigenkets of $\hat{P}_{12}$,

$$\hat{P}_{12} \left(\frac{|+-\rangle + |-+\rangle}{\sqrt{2}} \right) = \frac{|+-\rangle + |-+\rangle}{\sqrt{2}} \qquad \text{(eigenvalue: 1)}$$

$$\hat{P}_{12} \left(\frac{|+-\rangle - |-+\rangle}{\sqrt{2}} \right) = -\left(\frac{|+-\rangle - |-+\rangle}{\sqrt{2}} \right) \qquad \text{(eigenvalue: -1)}$$

We note that the Dirac exchange operator is given by

$$\hat{P}_{12} = \frac{1}{2}(\hat{1} + \hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2) = \frac{1}{2}(\hat{1} + 4\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2)$$

where $\hat{\boldsymbol{\sigma}}$ is the Pauli spin operator, and $\boldsymbol{S} = \frac{1}{2}\boldsymbol{\sigma}$

Note that

$$\hat{P}_{12}\left|\psi_{AF}\right\rangle = -\left|\psi_{AF}\right\rangle,, \qquad \hat{P}_{12}\left|\psi_{F}\right\rangle = \left|\psi_{F}\right\rangle,$$

with

$$\hat{H}_{eff}\left|\psi_{AF}\right\rangle = -\frac{2t^2}{U}\left|\psi_{AF}\right\rangle$$

$$\hat{H}_{eff}\left|\psi_{F}\right\rangle = 0\left|\psi_{F}\right\rangle$$

The effective Hamiltonian can be expressed by

$$\begin{aligned}
H_{eff} &= \frac{t^2}{U}(\hat{P}_{12} - \hat{1}) \\
&= \frac{t^2}{2U}(\hat{\sigma}_1 \cdot \hat{\sigma}_2 - \hat{1}) \\
&= \frac{2t^2}{U}\hat{S}_1 \cdot \hat{S}_2 - \frac{t^2}{2U}\hat{1} \\
&= 2J(\hat{S}_1 \cdot \hat{S}_2 - \frac{1}{4}\hat{1})
\end{aligned}$$

with

$$J = \frac{t^2}{U}$$

Since $J > 0$, the effective Hamiltonian is described by an antiferromagnetic Heisenberg model. The physical meaning of the interaction is as follows. The antiferromagnetic exchange interaction between adjacent spins leads to the lowering of energy in the system. When the neighboring spins are coupled ferromagnetically, the transfer of electrons is prohibited because of the Pauli's exclusion principle. So the energy of the system remains unchanged. In Mott insulators, the system is an antiferromagnet.

((**Note**))
For $U \gg 4t$ the ground state energy is approximated by

$$\varepsilon_G = -\frac{4t^2}{U}.$$

If we use this,

$$
\begin{aligned}
H_{eff} &= \frac{2t^2}{U}(\hat{P}_{12} - \hat{1}) \\
&= \frac{t^2}{U}(\hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2 - \hat{1}) \\
&= \frac{4t^2}{U}\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2 - \frac{t^2}{U}\hat{1} \\
&= 2J(\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2 - \frac{1}{4}\hat{1})
\end{aligned}
$$

with

$$J = \frac{2t^2}{U}$$

So the system is well described by an antiferromagnetic Heisenberg model. The ground state is an antiferromagnetic state.

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