

Band Theory III :

The tight binding approximation

Q: What if we had a Bravais lattice of sodium atoms with a lattice constant of 1cm ; would it be a metal?

(Band theory says yes.)

Corollary: Can we understand how energy bands arise, starting from isolated atoms, and increasing the interatomic coupling by bringing the atoms closer together?

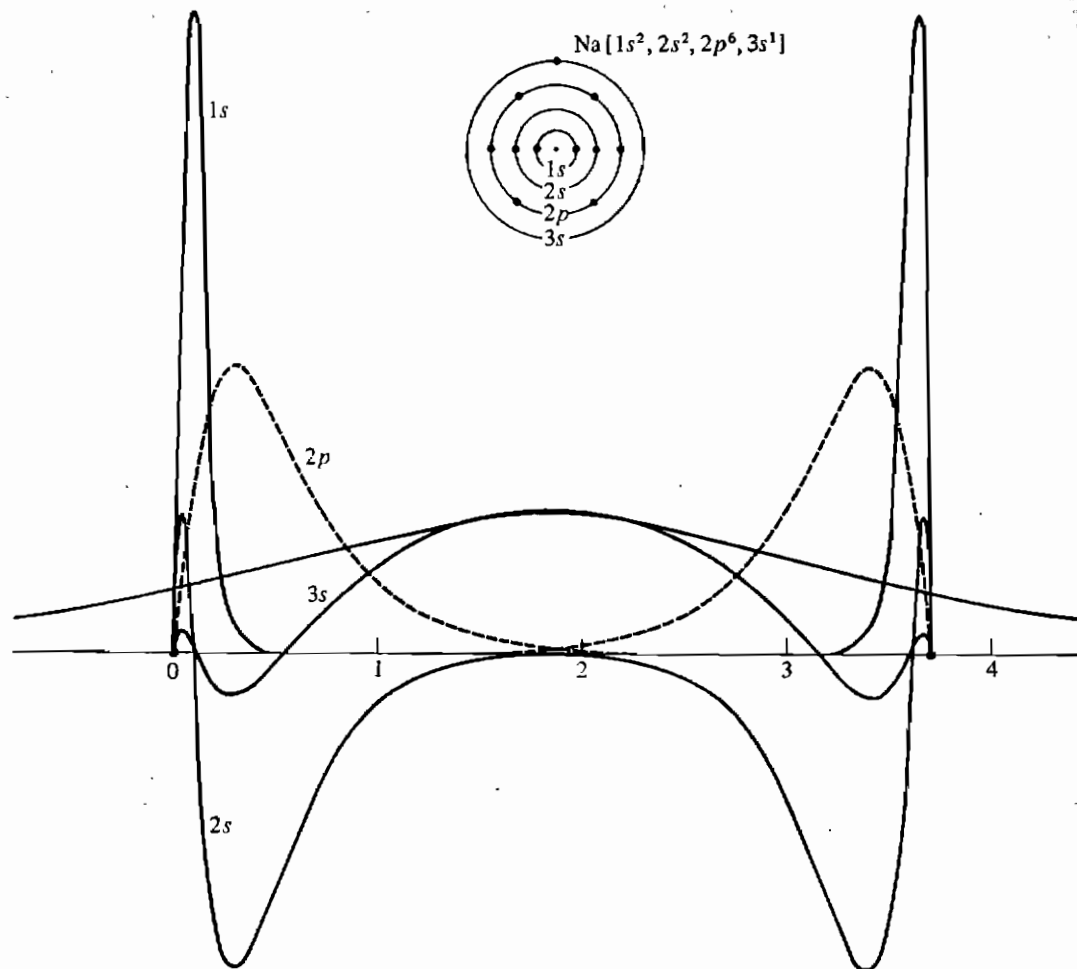


Figure 10.1

Calculated electron wave functions for the levels of atomic sodium, plotted about two nuclei separated by the nearest-neighbor distance in metallic sodium, 3.7 Å. The solid curves are $r\psi(r)$ for the 1s, 2s, and 3s levels. The dashed curve is r times the radial wave function for the 2p levels. Note how the 3s curves overlap extensively, the 2s and 2p curves overlap only a little, and the 1s curves have essentially no overlap. The curves are taken from calculations by D. R. Hartree and W. Hartree, *Proc. Roy. Soc.* **A193**, 299 (1948). The scale on the r -axis is in angstroms.

then we require that $\psi_n(\mathbf{r})$ be very small when r exceeds a distance of the order of the lattice constant, which we shall refer to as the “range” of ψ_n .

In the extreme case in which the crystal Hamiltonian begins to differ from H_{at} (for an atom whose lattice point we take as the origin) only at distances from $\mathbf{r} = \mathbf{0}$ that exceed the range of $\psi_n(\mathbf{r})$, the wave function $\psi_n(\mathbf{r})$ will be an excellent approximation to a stationary-state wave function for the full Hamiltonian, with eigenvalue E_n . So also will the wave functions $\psi_n(\mathbf{r} - \mathbf{R})$ for all \mathbf{R} in the Bravais lattice, since H has the periodicity of the lattice.

To calculate corrections to this extreme case, we write the crystal Hamiltonian H as

$$H = H_{at} + \Delta U(\mathbf{r}), \quad (10.2)$$

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Let $H_{at}(\vec{r})$ be the Hamiltonian of an isolated atom. For simplicity, consider a nondegenerate atomic orbital (i.e., an s-orbital) $\phi(\vec{r})$,

$$H_{at}(\vec{r}) \phi(\vec{r}) = E_{at} \phi(\vec{r}).$$

The Hamiltonian of a Bravais lattice of atoms can be written

$$H = \sum_{\vec{R} \in BL} H_{at}(\vec{r} - \vec{R}) + \Delta U(\vec{r}),$$

where $\Delta U(\vec{r} + \vec{R}) = \Delta U(\vec{r})$. We

seek solutions of H in the form of Bloch waves:

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \phi(\vec{r} - \vec{R}).$$

Here $\Delta U(\vec{r})$ represents the coupling between atoms, so we can take $H_{at}(\vec{r})\phi(\vec{r}-\vec{R}) = 0$.

The energy band $\epsilon(\vec{k})$ is determined by

$$H \Psi_{\vec{k}}(\vec{r}) = \epsilon(\vec{k}) \Psi_{\vec{k}}(\vec{r}).$$

$$\int d\vec{r} \phi^*(\vec{r}) H \Psi_{\vec{k}}(\vec{r}) = \epsilon(\vec{k}) \int d\vec{r} \phi^*(\vec{r}) \Psi_{\vec{k}}(\vec{r})$$

$$\begin{aligned} \int d\vec{r} \phi^*(\vec{r}) \left(\sum_{\vec{R}} H_{at}(\vec{r}-\vec{R}) + \Delta U(\vec{r}) \right) \Psi_{\vec{k}}(\vec{r}) \\ = \epsilon(\vec{k}) \int d\vec{r} \phi^*(\vec{r}) \Psi_{\vec{k}}(\vec{r}) \end{aligned}$$

Letting $H_{at}(\vec{r}-\vec{R})$ act to the left,

$$\text{we find } \phi^*(\vec{r}) H_{at}(\vec{r}-\vec{R}) = E_{at} \phi^*(\vec{r}) \delta_{\vec{R},0}.$$

$$\bullet (\varepsilon(\vec{k}) - E_{gt}) \int d\vec{r} \phi^*(\vec{r}) \chi_{\vec{k}}(\vec{r})$$

$$= \int d\vec{r} \phi^*(\vec{r}) \Delta U(\vec{r}) \chi_{\vec{k}}(\vec{r})$$

$$(\varepsilon(\vec{k}) - E_{gt}) \int d\vec{r} \phi^*(\vec{r}) \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \phi(\vec{r} - \vec{R})$$

$$= \int d\vec{r} \phi^*(\vec{r}) \Delta U(\vec{r}) \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \phi(\vec{r} - \vec{R})$$

$$\bullet (\varepsilon(\vec{k}) - E_{gt}) \left(1 + \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} \int d\vec{r} \phi^*(\vec{r}) \phi(\vec{r} - \vec{R}) \right)$$

$$= \int d\vec{r} \phi^*(\vec{r}) \Delta U(\vec{r}) \phi(\vec{r})$$

$$+ \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} \int d\vec{r} \phi^*(\vec{r}) \Delta U(\vec{r}) \phi(\vec{r} - \vec{R})$$

$$\bullet \varepsilon(\vec{k}) = E_{gt} + \frac{\beta + \sum_{\vec{R} \neq 0} \gamma(\vec{R}) e^{i\vec{k} \cdot \vec{R}}}{1 + \sum_{\vec{R} \neq 0} \alpha(\vec{R}) e^{i\vec{k} \cdot \vec{R}}}$$

where

$$\beta = \int d\vec{r} \phi^*(\vec{r}) \Delta U(\vec{r}) \phi(\vec{r}),$$

$$\alpha(\vec{R}) = \int d\vec{r} \phi^*(\vec{r}) \phi(\vec{r} - \vec{R}), \quad \text{and}$$

$$\gamma(\vec{R}) = \int d\vec{r} \phi^*(\vec{r}) \Delta U(\vec{r}) \phi(\vec{r} - \vec{R}).$$

β and $\gamma(\vec{R})$ are matrix elements

of $H - H_{at}$, and have units of energy, while $\alpha(\vec{R})$ is a wavefunction overlap integral, and is dimensionless.

If the atoms are well separated,

α , β , and γ are all small. β

is small because $\frac{\Delta U(\vec{r})}{E_{at}} \rightarrow 0$ as

the distance between atoms is

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increased. α and γ/E_{at} are small because the overlap of

$\phi^*(\vec{r})$ and $\phi(\vec{r}-\vec{R})$ is exponentially small if $|\vec{R}| >$ size of atom.

Thus we can restrict consideration to nearest neighbor coupling

only $\alpha(\vec{R}) = \begin{cases} \alpha, & \vec{R} = \text{nearest neighbor of origin} \\ 0, & \text{otherwise} \end{cases}$

$$\gamma(\vec{R}) = \begin{cases} \gamma, & \vec{R} = \text{n.n. of 0} \\ 0, & \text{otherwise} \end{cases}$$

$$\Sigma(\vec{k}) = E_{at} + \frac{\gamma \sum_{\text{n.n.}} e^{i\vec{k} \cdot \vec{R}}}{1 + \alpha \sum_{\text{n.n.}} e^{i\vec{k} \cdot \vec{R}}} + \beta$$

Since $\alpha \ll 1$, we can expand

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the denominator

$$\Sigma(\vec{k}) \approx E_{at} + \left(\beta + \gamma \sum_{nn.} e^{i\vec{k} \cdot \vec{R}} \right) \left(1 - \alpha \sum_{nn.} e^{i\vec{k} \cdot \vec{R}} \right)$$

$$\approx E_{at} + \beta + (\gamma - \beta\alpha) \sum_{nn.} e^{i\vec{k} \cdot \vec{R}}$$

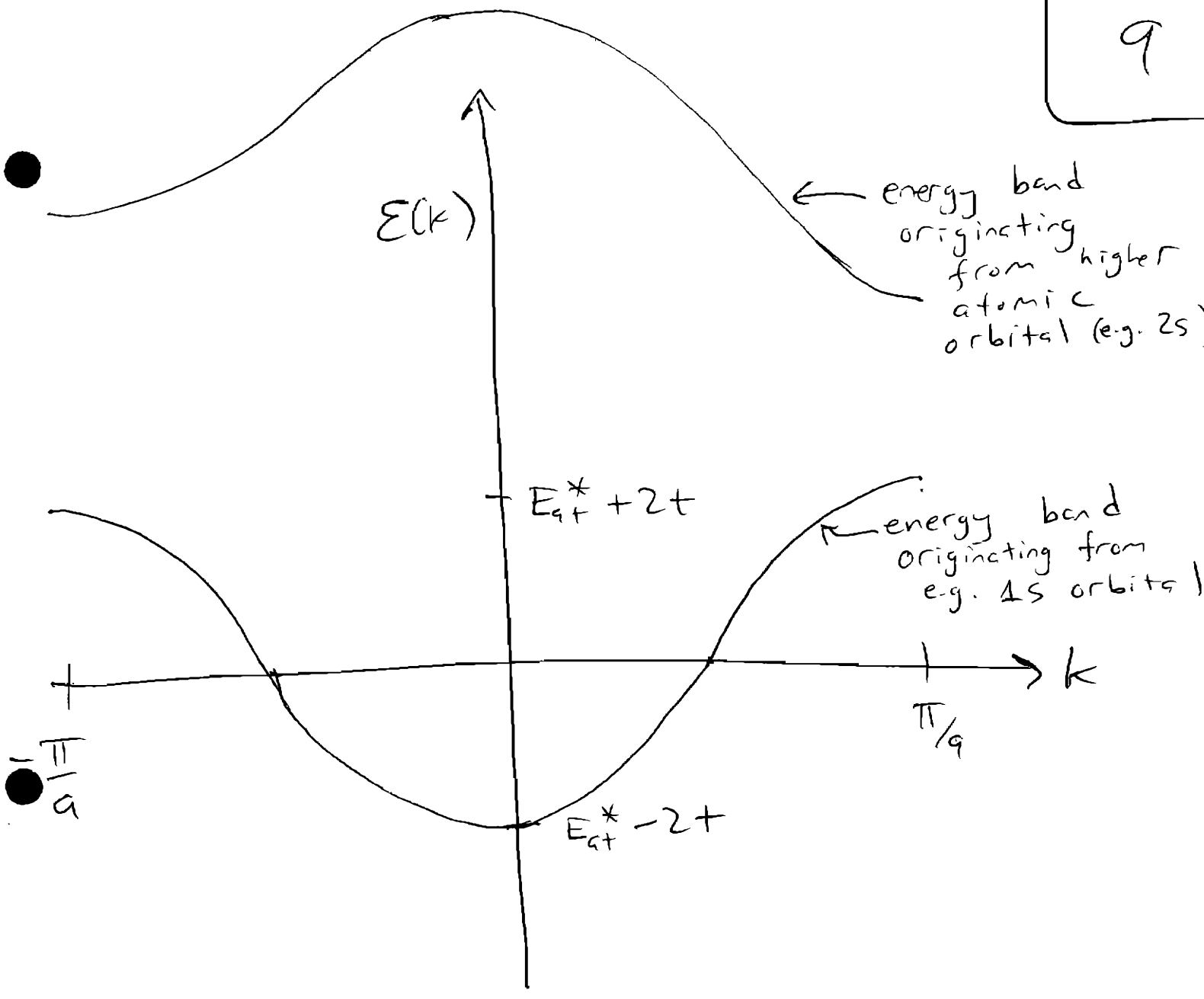
Let $E_{at}^* = E_{at} + \beta$

$$t = \beta\alpha - \gamma$$

$$\Sigma(\vec{k}) = E_{at}^* - t \sum_{nn.} e^{i\vec{k} \cdot \vec{R}}$$

For a 1D lattice with lattice constant a ,

$$\Sigma(k) = E_{at}^* - 2t \cos ka$$



Thus, starting from isolated atoms and considering the interatomic coupling as a perturbation, we also arrive at a picture of energy bands similar to that implied by the

nearly free electron model. (10)

- We see that each atomic orbital gives rise to an energy band, whose width is proportional to the matrix element t . Here the energy gaps are principally due to the gaps in the spectrum of a single atom. If $|t|$ becomes comparable to the difference in energies of various atomic orbitals, the tight-binding approximation is no longer good,
- and a nearly-free electron

model would be more appropriate.

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Back to our original question:
What happens as $t \rightarrow 0$?

Consider the 1D case. For $ka \ll 1$, we have

$$\begin{aligned} \epsilon(k) &\approx E_{qt} - 2t + t a^2 k^2 \\ &= \text{const.} + \frac{\hbar^2 k^2}{2m^*} \end{aligned}$$

$$\Rightarrow m^* = \frac{\hbar^2}{2ta^2}$$

As a is increased, t decreases

exponentially, and m^* grows (12)

exponentially. However, as long as t is finite, m^* is finite.

Our crystal has free charge carriers, provided the band is neither full nor empty, and

according to this model, the crystal of sodium atoms even with a lattice constant of 1 cm, would still be a "metal," although

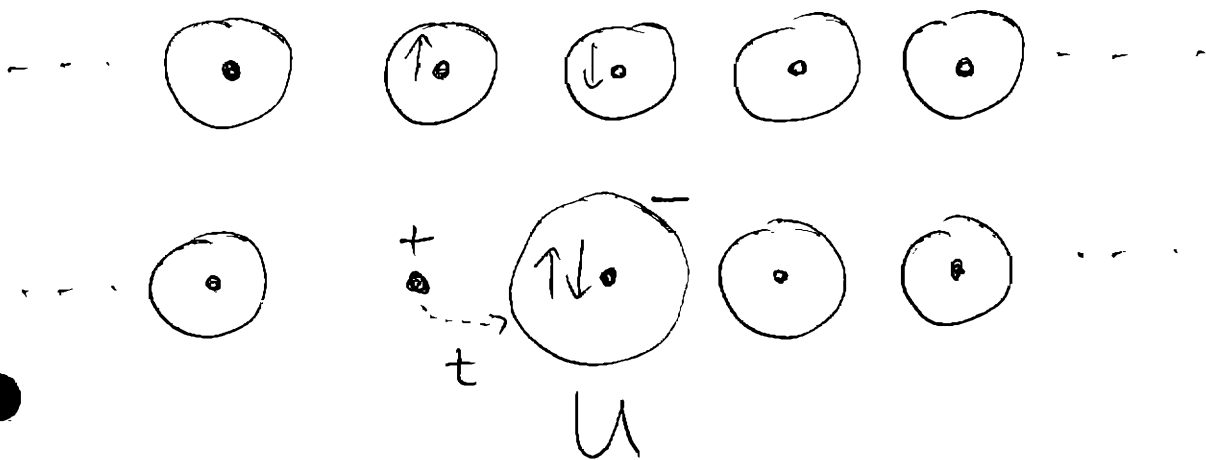
$\sigma = \frac{ne^2\tau}{m^*}$ would be small indeed.

What is wrong with this picture?

A: The assumption that electrons move independently!

Hubbard model

Consider a linear chain of atoms, each with one valence electron in an s -orbital:



If the electrons on two neighboring atoms have antiparallel spins, one electron can "hop" from its own atom onto its neighbor. The amplitude (matrix element) for this hop is t , calculated above. However, there is an energy cost to be paid,

$$U = E_+ + E_- - 2E_0 + t$$

where E_+ is the energy of the positive ion and E_- is

the energy of the negative ion. In general,

$U > 0$. Sir Neville Mott argued that band theory would break down, and the crystal would be an insulator, if

$$\frac{U}{t} > u_c \approx 1. \quad \text{Mott's}$$

idea was very controversial at the time, but eventually became accepted. Mott received the Nobel prize in 1977.

The Hamiltonian for this problem is known as the Hubbard model.

$$H = t \sum_{n, \sigma} (c_{n+1, \sigma}^\dagger c_{n \sigma} + \text{H.c.}) + U \sum_n c_{n \uparrow}^\dagger c_{n \uparrow} c_{n \downarrow}^\dagger c_{n \downarrow},$$

after an English physicist who wrote a series of papers in the 1960s in which he tried to use this model to explain ferromagnetism.

As far as I know, all these

papers by Hubbard used approximations which fail.

In fact, the Hubbard model is not a model of ferromagnetism, but of antiferromagnetism!

This just goes to show that you don't necessarily have to solve a model correctly to get it named after you!

Antiferromagnetism

Indeed, Hubbard was not even

the first person to introduce

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the Hubbard model. The model was first introduced by P.W. Anderson in 1958.

Anderson correctly deduced that the model exhibits antiferromagnetism. (By the way, Anderson shared the Nobel prize with Mott and van Vleck).

Anderson's argument used second order perturbation theory in t ,

assuming $\frac{U}{t} \gg 1$.

General remarks on perturbation (19)

● Theory

Let $H = H_0 + H_1$, with

$$H_0 |n\rangle = \epsilon_n^{(0)} |n\rangle.$$

One can calculate the eigenvalues of H as a power series in

● H_1 (see any quantum mechanics textbook for details). One finds

$$\epsilon_n = \epsilon_n^{(0)} + \langle n | H_1 | n \rangle + \sum_{m \neq n} \frac{|\langle n | H_1 | m \rangle|^2}{\epsilon_n^{(0)} - \epsilon_m^{(0)}} + \mathcal{O}(H_1^3).$$

Now consider just two atoms

● $|4\rangle = \begin{array}{c} \uparrow \\ \circ \end{array} \begin{array}{c} \downarrow \\ \circ \end{array} \quad \text{or} \quad \begin{array}{c} \uparrow \\ \circ \end{array} \begin{array}{c} \uparrow \\ \circ \end{array} .$

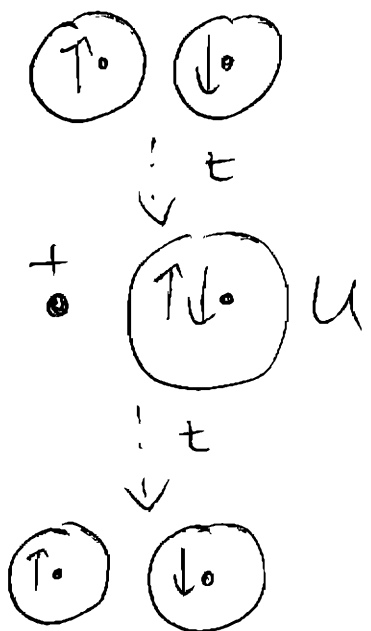
$$H_0 = U (n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow})$$

$$H_1 = t \sum_{\sigma=\uparrow}^{\downarrow} (c_{2\sigma}^\dagger c_{1\sigma} + c_{1\sigma}^\dagger c_{2\sigma})$$

For both cases $\epsilon^{(0)} = 0$,

and $\langle \psi | H_1 | \psi \rangle = 0$. However,

in second order, one finds



no hops possible due to Pauli principle

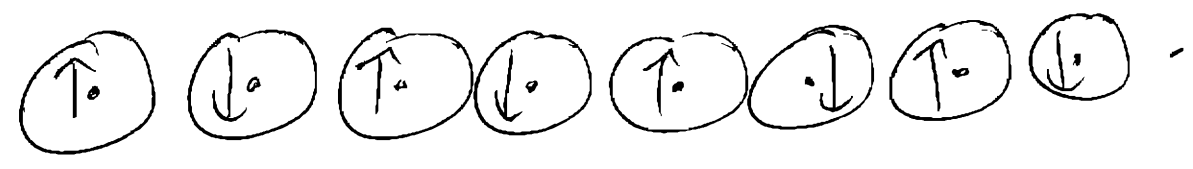
$$\epsilon = \frac{4t^2}{-U}$$

$$\epsilon = 0$$

The factor of 4 arises from the 4 different processes possible. Thus the energy of antiparallel spins (singlet state) is lower than the energy of parallel spins (triplet state) by an

amount $J = \frac{4t^2}{U}$. A

chain of atoms will thus tend to have a staggered magnetisation, called Néel order :



Most metal-oxide
compounds with one
valence electron per unit
cell are indeed antiferromag-
netic "Mott insulators."